Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Ionic Polymerization under Electric Field.* V. Cationic Polymerization of Styrene Catalyzed by Boron Trifluoride Etherate

Ichiro Sakurada[a]; Norio Ise[a]; Yuzuru Hayashi[a]
[a] DEPARTMENT OF POLYMER, CHEMISTRY KYOTO UNIVERSITY, KYOTO, JAPAN

To cite this Article Sakurada, Ichiro , Ise, Norio and Hayashi, Yuzuru(1967) 'Ionic Polymerization under Electric Field.* V. Cationic Polymerization of Styrene Catalyzed by Boron Trifluoride Etherate', Journal of Macromolecular Science, Part A, 1: 6, 1039 — 1058

To link to this Article: DOI: 10.1080/10601326708053756

URL: http://dx.doi.org/10.1080/10601326708053756

J. MACROMOL. SCI.—CHEM., A1(6), pp. 1039–1058, Oct., 1967

Ionic Polymerization under Electric Field.* V. Cationic Polymerization of Styrene Catalyzed by Boron Trifluoride Etherate

ICHIRO SAKURADA, NORIO ISE, and YUZURU HAYASHI
DEPARTMENT OF POLYMER CHEMISTRY
KYOTO UNIVERSITY
KYOTO, JAPAN

Summary

The cationic polymerizations of styrene under an electric field have been investigated by using boron trifluoride etherate as a catalyst and binary mixtures of toluene, 1,2-dichloroethane, and nitrobenzene of various compositions as the solvent. The polymerization rate of styrene in dichloroethane was tripled in the presence of a rather low-intensity electric field of 0.25 kV/cm. The field-accelerating effects were found to be nil in pure toluene, increasing with increasing dielectric constant of the mixed solvents and, through the maximum value in pure dichloroethane, decreased with further increase in the dielectric constant. This observation might indicate that the ion pair of the growing chain ends is too "firm" to show the field effects in toluene, whereas the degree of dissociation of ion pairs in nitrobenzene is large to such an extent that the application of the electric field can no longer increase the population of free ions. This interpretation is in qualitative agreement with the prediction of the kinetic scheme presented previously. On the other hand, the degrees of polymerization were not influenced by the electric field.

In a series of recent work, various types of polymerization of vinyl monomers were carried out under an electric field and the field influences on the rate of polymerization and the degree of polymerization (*1*–*5*) were studied. These studies, which have been conducted mostly in 1,2-dichloroethane (DCE), have revealed that

---

[*] Presented in part at the International Symposium on Macromolecular Chemistry, Tokyo-Kyoto, 1966.

the electric field increased the rates of polymerization of some cationic polymerizations, and the magnitude of the field effect is in order of the polymerizability of the monomer. The kinetic interpretation given previously (*4*) shows that the field effect increases with the dissociation of the ion pairs at growing chain ends. Therefore, it is interesting to investigate the field effect in various solvents. More polar solvent would give rise to larger populations of free ions in the absence of specific ion-solvent interaction (*6*). This paper concerns an experimental study on the cationic polymerization of styrene catalyzed by boron trifluoride etherate (BF_3OEt_2) in nitrobenzene, DCE and toluene, and in their mixtures.

EXPERIMENTAL

Materials

Commercial styrene and DCE were carefully purified as reported previously (*4*). Commercially available nitrobenzene was washed with an aqueous solution of sodium hydroxide, dried with Drierite for 4 weeks, and fractionally distilled. Commercial toluene was washed with sulfuric acid and then with water, dried with Drierite for 1 to 4 weeks, heated over calcium hydride under reflux for 2 or 3 days, and fractionally distilled. As in the previous work, our major concern has been in removal of ionic impurities, which may cause undesirable effects (such as the Joule heat effect or the electrolytic initiation of polymerization). The purity was checked by electric conductivity which was measured by applying a (d-c) high voltage before polymerization. The highest specific conductivities were 10^{-11} mho/cm and 10^{-7} mho/cm for DCE and nitrobenzene, respectively. Those of toluene and styrene were too small to be measured by our method. A commercial sample of boron trifluoride etherate was distilled at atmospheric pressure under nitrogen.

Polymerizations

The polymerizations were carried out in a glass vessel with a pair of parallel-plate platinum electrodes (area 2 cm^2, electrode distance 3.7 cm, cell constant 1.0 cm^{-1}) and a thermometer. The polymerization procedures were previously described (*4*).

Miscellaneous

The degrees of polymerization were determined viscometrically in benzene solution at 30°C, using the following equation (7) unless otherwise specified:

$$[\eta] = 1.0 \times 10^{-4} \times M_w^{0.72}$$

The electric conductivity was measured at 1000 cycles/sec using a Wheatstone bridge, unless otherwise specified.

RESULTS

1,2-Dichloroethane

Initial Rate of Polymerization. In Fig. 1, the logarithm of the ratio of initial monomer concentration, $[M]_0$, and the concentration of unconsumed monomer, $[M]_t$, $[=(1-c)[M]_0$, c, conversion$]$ was plotted against the polymerization time t. The filled and blank circles denote the values obtained in the presence and absence of an electric field (0.25 kV/cm), respectively. At low conversions $\log[M]_0/[M]_t$ is a linear function of t, which indicates the stationary state of the concentration of active chain ends. The initial rate of polymerization R_p was obtained from the slope of the linear part of the curve.

It should be noted that the initial rate of polymerization obtained under the electric field, R_{pE}, is corrected for temperature rise due

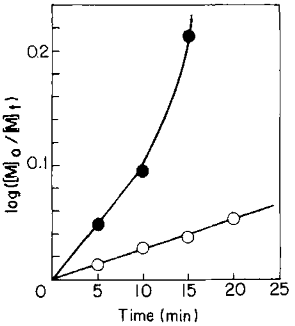

FIG. 1. Time change of the concentration of monomer unconsumed. $[M]_0 = 1.72$ moles/liter, $[BF_3OEt_2]_0 = 2.0 \times 10^{-3}$ mole/liter, 0°C. ●, 0.25 kV/cm; ○, 0 kV/cm.

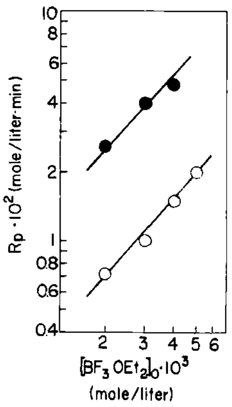

FIG. 2. Initial rate of polymerization and catalyst concentration: styrene-BF_3OEt_2-DCE. $[M]_0 = 1.72$ moles/liter, 0°C. ●, 0.25 kV/cm; ○, 0 kV/cm.

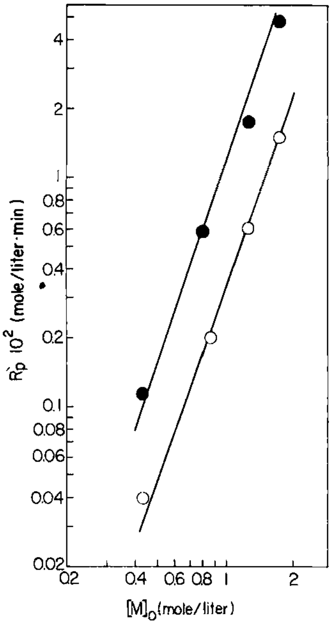

FIG. 3. Initial rate of polymerization and monomer concentration: styrene-BF_3OEt_2-DCE. $[BF_3OEt_2]_0 = 4.0 \times 10^{-3}$ mole/liter, 0°C. ●, 0.25 kV/cm; ○, 0 kV/cm.

to the Joule heat. The method of this correction was described earlier (2).

Figure 2 shows R_p values as a function of initial catalyst concentration. Evidently the rate of polymerization is enhanced by application of an electric field (0.25 kV/cm). Furthermore, the field effect is independent of initial catalyst concentration and the rate is proportional to the first power of the concentration.

Figure 3 shows the monomer concentration dependence of R_p. It is seen that R_{pE} is larger than R_{p0} and the R_p values are proportional to the third power of monomer concentration both in the presence and absence of the electric field. In other words, the field effect is independent of monomer concentration. Changes in the dielectric constant of the solution due to the variation of monomer concentration were compensated by keeping the sum of volume fractions of monomer and toluene (substitute for styrene) constant.

Thus, from Figs. 2 and 3,

$$\mathrm{R}_{pE} = k_E[\mathrm{BF_3OEt_2}]_0[\mathrm{M}]_0^3 \qquad \text{for } E = 0.25 \text{ kV/cm} \tag{1}$$

$$R_{p0} = k_0[\mathrm{BF_3OEt_2}]_0[\mathrm{M}]_0^3 \qquad \text{for } E = 0 \tag{2}$$

where

$$k_E = 2.1 \text{ and } k_0 = 0.85 \text{ mole}^{-3}\text{-liter}^3\text{/min.}$$

The ratio of R_{pE} and R_{p0} was found to increase with increasing field strength E, as is shown in Fig. 4. It is seen that the field effect amounts to 4 at 1.0 kV/cm. This is the largest field effect hitherto obtained in our laboratory. This value should be compared with 1.4 found for *p*-methoxystyrene (2) and isobutyl vinyl ether (5) catalyzed by iodine in DCE.

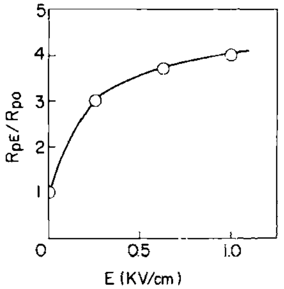

FIG. 4. Field effect and field strength: styrene–BF_3OEt_2–DCE.

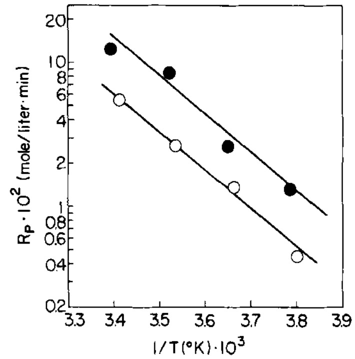

FIG. 5. Temperature dependence of initial rate of polymerization: styrene–BF_3OEt_2–DCE. $[M]_0 = 1.72$ moles/liter, $[BF_3OEt_2]_0 = 2.0 \times 10^{-3}$ mole/liter. ●, 0.25 kV/cm; ○, 0 kV/cm.

Figure 5 gives the temperature dependence of R_{pE} and R_{p0}. The apparent overall activation energy is 12.4 kcal/mole both in the presence and absence of the electric field.

Degree of Polymerization. Figure 6 shows the degree of polymerization of polystyrene produced under an electric field of 0.25 kV/cm and without the field as a function of catalyst concentration. The degree of polymerization is found to be independent of the concentration and the field.

Figure 7 presents the degree of polymerization ($\bar{P}$) as a function of initial monomer concentration. The degree of polymerization is not affected by the presence of the electric field and a linear relation holds between $1/\bar{P}$ and $1/[M]_0$. The intercept is zero and the slope is 2.1×10^{-3}.

Figure 8 gives the degree of polymerization at various temperatures. The degree of polymerization decreases with rising tempera-

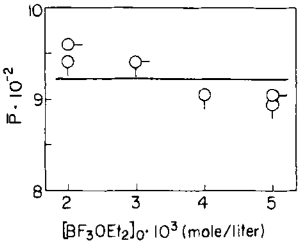

FIG. 6. Degree of polymerization and catalyst concentration: styrene–BF_3OEt_2–DCE. $[M]_0 = 1.72$ moles/liter, 0°C. ○-, 0.25 kV/cm; ⚲, 0 kV/cm.

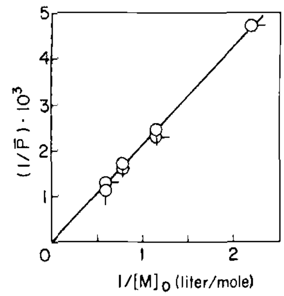

FIG. 7. Degree of polymerization and monomer concentration: styrene-BF_3OEt_2-DCE. $[BF_3OEt_2]_0 = 4.0 \times 10^{-3}$ mole/liter. ○-, 0.25 kV/cm; ♀, 0 kV/cm.

ture, and the apparent activation energy for the degree of polymerization E_p is -4.6 kcal/mole, both in the presence and absence of the electric field.

The field strength dependence of the degree of polymerization is shown in Fig. 9. No field effect is observable up to 1 kV/cm.

Electric Conductivity. The equivalent conductivity Λ of our catalyst solution (in the absence of monomer) is shown as a function of catalyst concentration in Fig. 10. The conductivity decreases with increasing catalyst concentration and decreasing temperature. The slope of the $\Lambda - c$ relation below $[BF_3OEt_2] = 10^{-2}$ is between -0.36 and -0.16, which indicates a rather small contribution of triple ions (in addition to ion pairs) according to the Fuoss-Kraus theory of ion association (*8*).

Figure 11 shows the specific conductivity (κ) of a polymerizing solution as a function of time. The κ value is independent of time. It is noteworthy that the specific conductivity of the polymerizing

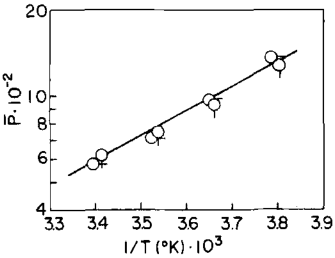

FIG. 8. Degree of polymerization and temperature. $[M]_0 = 1.72$ moles/liter, $[BF_3OEt_2]_0 = 2.0 \times 10^{-3}$ mole/liter. ○-, 0.25 kV/cm; ♀, 0 kV/cm.

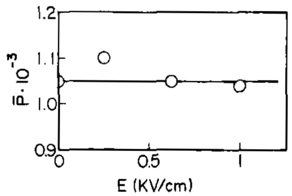

FIG. 9. Degree of polymerization and field strength: styrene-BF_3OEt_2-DCE.

solution (5×10^{-7} mho/cm) is smaller than that of corresponding catalyst solution, which is 1.5×10^{-6} mho/cm at $[BF_3OEt_2]_0 = 6.0 \times 10^{-3}$ mole/liter. This is probably due to the fact that in the catalyst solution the dielectric constant is higher and the viscosity lower than in the polymerizing solution, because of polymer coating over the electrode surface.

Table 1 shows that the specific conductivity of the polymerizing solution increases with increasing temperature and catalyst concentration.

Nitrobenzene

Initial Rate of Polymerization. These experiments were carried out at 10°C. The initial rate of polymerization (R_p) was determined from the initial slope of the time-conversion curve. The effects of catalyst and monomer concentrations on R_p are given in Figs. 12 and 13, respectively. The dielectric constant of the solutions was adjusted as in the case of DCE. In the concentration range covered, no field effects were observable. Furthermore, as is shown in Fig. 14, no

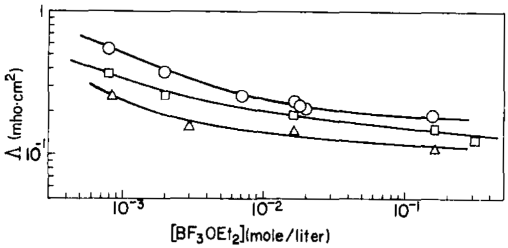

FIG. 10. Electric conductivity of catalyst solution and catalyst concentration: BF_3OEt_2-DCE. ○, 30°C; □, 0°C; △, −30°C.

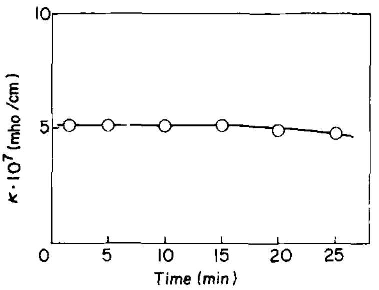

FIG. 11. Time change of specific conductivity of polymerizing solution. $[M]_0 = 1.72$ moles/liter, $[BF_3OEt_2]_0 = 6.0 \times 10^{-3}$ mole/liter, 0°C.

field effects were detected up to 0.7 kV/cm. Figures 12, 13, and 14 lead us to the relation

$$R_{p0} = R_{pE} = k[BF_3OEt_2]_0[M]_0^3 \quad (3)$$

with $k = 5.9$ mole^{-3}-liter^3/min.

The R_p value was found to increase with rising temperature, as is shown in Fig. 15, from which the apparent overall activation energy is 10.7 kcal/mole.

Degree of Polymerization. The degree of polymerization ($\bar{P}$) against catalyst concentrations is shown in Fig. 16. Clearly, $\bar{P}$ is independent of catalyst concentration and field strength. $1/\bar{P}$ is plotted against $1/[M]_0$ in Fig. 17.

Toluene

Initial Rate of Polymerization. These experiments were carried out at 30°C. Figure 18 gives the time-conversion curves of styrene

TABLE 1

Specific Conductivity of Polymerizing Solution[a]

T, °C	$[BF_3OEt_2]_0$, moles/liter	κ, mho/cm
30	1.58×10^{-3}	3.69×10^{-7}
	1.58×10^{-2}	1.66×10^{-6}
0	1.58×10^{-3}	3.18×10^{-7}
	1.98×10^{-1}	1.06×10^{-5}
−30	1.58×10^{-3}	2.04×10^{-7}

[a] $[M]_0 = 1.72$ moles/liter: styrene–BF_3OEt_2–DCE.

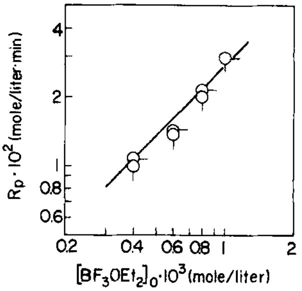

FIG. 12. Initial rate of polymerization and catalyst concentration: styrene–BF_3OEt_2–nitrobenzene. $[M]_0 = 1.72$ moles/liter, 10°C. ○-, 0.25 kV/cm; ♀, 0 kV/cm.

catalyzed by BF_3OEt_2 in toluene at 30°C. No field effects were observed. The initial rate of polymerization R_p (determined from the initial slope of the time-conversion curve) is given as a function of monomer concentration in Fig. 19. The catalyst-concentration dependence of R_p is given in Fig. 20. From Figs. 18, 19, and 20 it is

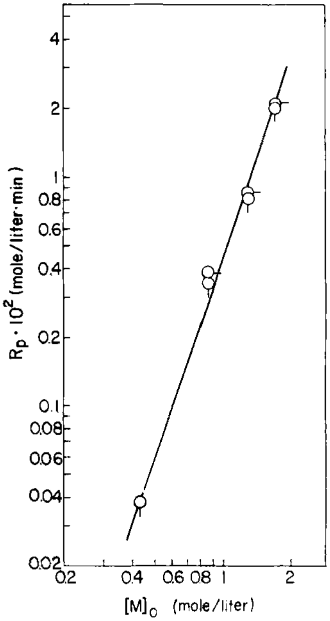

FIG. 13. Initial rate of polymerization and monomer concentration: styrene–BF_3OEt_2–nitrobenzene. $[BF_3OEt_2]_0 = 0.8 \times 10^{-3}$ mole/liter, 10°C. ○-, 0.25 kV/cm; ♀, 0 kV/cm.

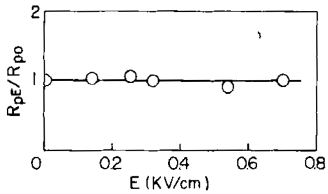

FIG. 14. Field effect and field strength: styrene-BF_3OEt_2-nitrobenzene.

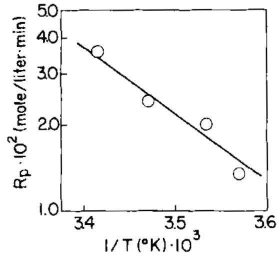

FIG. 15. Temperature dependence of initial rate of polymerization: styrene-BF_3OEt_2-nitrobenzene. $[M]_0 = 1.72$ moles/liter, $[BF_3OEt_2]_0 = 0.8 \times 10^{-3}$ mole/liter.

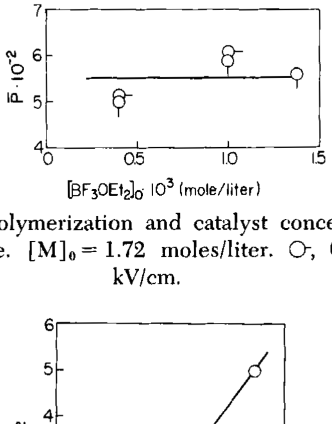

FIG. 16. Degree of polymerization and catalyst concentration: styrene-BF_3OEt_2-nitrobenzene. $[M]_0 = 1.72$ moles/liter. O-, 0.25 kV/cm; ♀, 0 kV/cm.

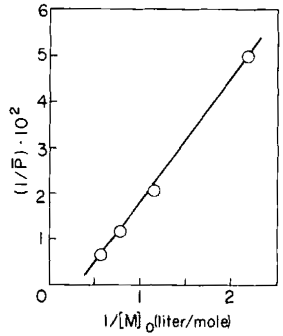

FIG. 17. Degree of polymerization and monomer concentration: styrene-BF_3OEt_2-nitrobenzene. $[BF_3OEt_2]_0 = 1.3 \times 10^{-3}$ mole/liter.

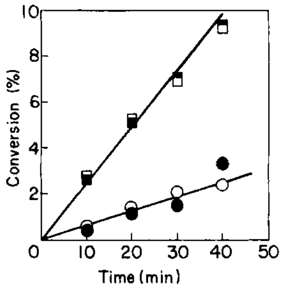

FIG. 18. Time-conversion curves: styrene-BF_3OEt_2-toluene. $[M]_0 = 1.72$ moles/liter. $[BF_3OEt_2]_0$: circle, 1.2×10^{-1} mole/liter; square, 1.2×10^{-2} mole/liter. ●, ■, 1 kV/cm; ○, □, 0 kV/cm.

found that the electric field has no effects on the rate of polymerization, and R_p can be written

$$R_{p0} = R_{pE} = k[BF_3OEt_2]_0[M]_0^3 \qquad (4)$$

with $k = 7.2 \times 10^{-2}$ mole^{-3}-liter^3/min. at catalyst concentration lower than about 2×10^{-2} mole/liter. Above this R_p decreases with increasing catalyst concentration.

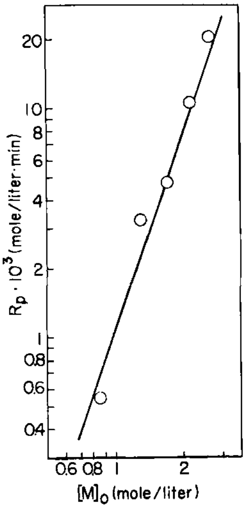

FIG. 19. Initial rate of polymerization and monomer concentration: styrene-BF_3OEt_2-toluene. $[BF_3OEt_2]_0 = 1.5 \times 10^{-2}$ mole/liter, 30°C.

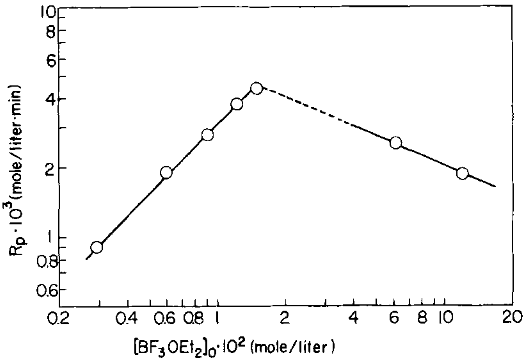

FIG. 20. Initial rate of polymerization and catalyst concentration: styrene–BF_3OEt_2–toluene. $[M]_0 = 1.72$ moles/liter, 30°C.

Mixed Solvents

Initial Rate of Polymerization. Figure 21 shows the field effect on the rate of polymerization as a function of solvent composition. The abscissa gives the composition of the mixed solvent and the dielectric constant at 25°C. The electric field was 0.25 kV/cm. The results clearly show that R_{pE}/R_{p0} increases with increasing dielectric constant (DC) and decreases to 1 for DC = 35 (pure nitrobenzene), after passing through a maximum at DC = 10 (pure DCE).

Electric Conductivity. The specific conductivity of the polymerizing solutions was obtained from the values of applied field strength and current. The conductivity thus determined should be distin-

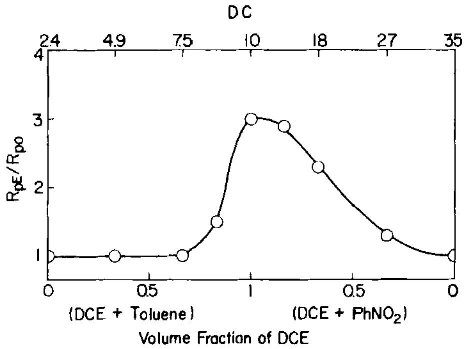

FIG. 21. Field effects and solvent composition: styrene–BF_3OEt_2. $E = 0.25$ kV/cm.

TABLE 2

Specific Conductivity of Polymerizing Solutions and Solvent Composition[a]

DCE + nitrobenzene ($[BF_3OEt_2]_0 = 1.3 \times 10^{-3}$ mole/liter)

Nitrobenzene content, vol.%	T, °C	κ_E,[b] mho/cm
17	0	2.4×10^{-7}
33	0	2.8×10^{-7}
67	0	4.5×10^{-7}

DCE + toluene ($[BF_3OEt_2]_0 = 4.0 \times 10^{-3}$ mole/liter)

DCE content, vol.%	T, °C	κ_E,[b] mho/cm
33	30	1×10^{-8}
67	30	1×10^{-7}
83	0	2×10^{-7}
100	0	8×10^{-7}

[a] $[M]_0 = 1.72$ moles/liter.

[b] κ_E, calculated from the current value after 2 min of polymerization initiation.

guished from that measured by the Wheatstone bridge and will be denoted by κ_E. Table 2 gives κ_E values of polymerizing solution of various compositions. Clearly the κ_E value becomes larger as the fraction of polar solvent (and hence the dielectric constant) increases.

DISCUSSION

Evidently the electric field increases the rate of the polymerization of styrene catalyzed by boron trifluoride etherate in DCE, mixtures of DCE and toluene, and mixtures of DCE and nitrobenzene. As in the previous work (*1*–*5*), the effects can easily be shown not to be due to the Joule heat.

Electroinitiation can also be ruled out. As shown in Table 2, the specific conductivity κ_E of the polymerizing solution increased with the increasing dielectric constant. If electroinitiation was responsible for the observed field effects, the field effect should increase with increasing quantity of electricity passed, and hence conductivity and dielectric constant. This is in disagreement with the experimental results observed in the mixture of DCE and nitrobenzene (see Fig. 21).

Thus we ascribe the field effects to the dissociation of ion pairs of the growing chain ends in the presence of a high electric field, and to the enhanced contribution of free-ion propagations.

Discussion appears to be desirable on the monomer-concentration dependence of the rate of polymerization R_p. The present study shows that R_p can be expressed

$$R_p = k[\mathrm{BF_3OEt_2}]_0[\mathrm{M}]_0^3 \tag{5}$$

in toluene, in DCE, and also in nitrobenzene, when the catalyst concentration is below 2×10^{-2} mole/liter. Mizote et al. reported, however, that the R_p was proportional to the second power of monomer concentration in DCE (9). The discrepancy appears to be due to our having maintained the dielectric constant of the solutions constant. Aoki also reported a square relation for styrene–BF_3OEt_2 systems in benzene, carbon tetrachloride, nitrobenzene, and nitroethane (*10*). This author kept the dielectric constant of the solutions constant by adding benzene. In our experiments toluene was used. The discrepancy between Aoki's data and ours appears to be due to this difference. In this respect, Higashimura and Okamura (*11*) reported that the initial rate of polymerization of styrene by $SnCl_4$ and the degree of polymerization increased more sharply with monomer concentration in toluene solvent than in benzene. This was explained by the chain transfer to or termination by toluene. It appears that this explanation may also apply to the discrepancy mentioned above.

To explain Eq. (5), the following elementary processes are proposed. Following Williams (*12*), we assume that the initiation is the formation of a complex (CM) from catalyst (C) and monomer (M) and the subsequent reaction of CM with M to form a dimeric ion pair $M_2^{\pm}$. Thus we have for initiation,

$$\mathrm{C} + \mathrm{M} \overset{k_i}{\rightleftharpoons} \mathrm{CM} \tag{6}$$

$$\mathrm{CM} + \mathrm{M} \xrightarrow{k_i} \mathrm{M}_2^{\pm} \tag{7}$$

where K_i is the equilibrium constant of the reaction of complex formation and k_i is the rate constant. Then the rate of initiation

$$R_i = k_i[\mathrm{CM}][\mathrm{M}] = k_iK_i[\mathrm{C}][\mathrm{M}]^2 \tag{8}$$

We further assume that a portion of the ion pairs (α) dissociates into free ions M_2^+ and A^- immediately after the ion pairs are formed and that a dissociation equilibrium can be set up with a dissociation constant K. K can be written

$$K = [M^+][A^-]/[M^\pm] \tag{9}$$

where M^+ and $M^\pm$ are free ion and ion pairs of any chain length, respectively, and the brackets denote concentration.

As in the previous treatments (2,5) it is assumed that propagation, chain transfer, and termination proceed both through ion-pair and free-ion mechanisms, and that the dissociation equilibrium can be characterized by the constant K. Hence

propagation:

$$M_2^\pm + M \xrightarrow{k'_p} M_n^\pm \tag{10}$$

$$M_2^+ + M \xrightarrow{k''_p} M_n^+ \tag{11}$$

transfer:

$$M_n^\pm + X \xrightarrow{k'_{tx}} P_n + X^\pm \tag{12}$$

$$M_n^+ + X \xrightarrow{k''_{tx}} P_n + X^+ \tag{13}$$

termination:

$$M_n^\pm \xrightarrow{k'_t} P_n \tag{14}$$

$$M_n^+ + A^- \xrightarrow{k''_t} P_n \tag{15}$$

where X denotes chain transfer agents; P_n the n-meric dead polymer molecule; k the rate constant of the reaction indicated by the suffix; the suffixes p, tx, and t represent propagation, transfer, and termination, respectively; and the primes ′ and ″ the rate constants corresponding to ion-pair and free-ion mechanisms. The rate of propagation R_p can then be given as

$$\begin{aligned} R_p &= k'_p[M^\pm][M] + k''_p[M^+][M] \\ &= [k'_p(1-\alpha) + k''_p\alpha][M^*][M] \end{aligned} \tag{16}$$

where $[M^*]$ is the total concentration of active chain ends, including both free-ion and ion-pair ends. The rate of chain transfer R_{tx} is

$$R_{tx} = \sum_x [k'_{tx}(1-\alpha) + k''_{tx}\alpha][M^*][X] \tag{17}$$

where the summation covers all chain transfer agents. The rate of termination R_t may be written

$$\begin{aligned} R_t &= k_t'[\mathrm{M}^{\pm}] + k_t''[\mathrm{M}^+][\mathrm{A}^-] \\ &= k_t'(1-\alpha)[\mathrm{M}^*] + k_t''\alpha^2[\mathrm{M}^*]^2 \\ &= k_t'(1-\alpha)[\mathrm{M}^*] + k_t''(1-\alpha)\mathrm{K}[\mathrm{M}^*] \\ &= (1-\alpha)(k_t' + k_t''K)[\mathrm{M}^*] \end{aligned} \tag{18}$$

We assume here the stationary state of $[\mathrm{M}^*]$. Since $R_i = R_t$, Eqs. (8) and (18) give

$$[\mathrm{M}^*] = \frac{k_i K_i [\mathrm{C}][\mathrm{M}]^2}{(1-\alpha)(k_t' + k_t''K)} \tag{19}$$

Therefore, Eq. (16) can be written

$$R_p = \frac{k_i K_i}{k_t' + k_t''K}\left(k_p' + \frac{\alpha}{1-\alpha}k_p''\right)[\mathrm{C}][\mathrm{M}]^3 = k[\mathrm{C}][\mathrm{M}]^3 \tag{20}$$

which is in agreement with Eq. (5) found experimentally, if the rate of polymerization is assumed to be equal to the rate of propagation.

If K_i and k_i are assumed to be independent of the electric field, as was shown in the previous paper (*4*), the field effect on the rate of polymerization can be approximated from Eq. (20) by

$$\frac{R_{pE}}{R_{p0}} = \frac{k_p' + k_p''(\alpha_E/1-\alpha_E)}{k_p' + k_p''(\alpha_0/1-\alpha_0)}\,\frac{K_0 k_t'' + k_t'}{K_E k_t'' + k_t'} \approx \frac{k_p' + k_p''(\alpha_E/1-\alpha_E)}{k_p' + k_p''(\alpha_0/1-\alpha_0)} \tag{21}$$

where α_E and α_0 designate the degrees of dissociation in the presence and absence of the electric field. Since α_E is larger than α_0 by the Wien effect, we obtain $R_{pE}/R_{p0} > 1$, which is substantiated by experimental results.

Now our discussion will be extended to the degree of polymerization. First it would be interesting to obtain the rate-constant ratios from the degree of polymerization. For the ternary system solvent–toluene–monomer, it was shown (*13,14*) that the degree of polymerization $\bar{P}$ can be written as a function of conversion as

$$\frac{1}{\bar{P}} = \frac{k_{tm}}{k_p} + \frac{k_{t''}}{k_p}\,\frac{\ln[\mathrm{M}]_0/[\mathrm{M}]_t}{[\mathrm{M}]_0 - [\mathrm{M}]_t} \tag{22}$$

where $k_{t''} = k_t + k_{tt}[\mathrm{T}] + k_{ts}[\mathrm{S}] = k_{t'} + k_{tt}[\mathrm{T}]$ (distinguish between $k_{t''}$ and k_t'', and $k_{t'}$ and k_t'), k_t denotes the overall rate constant of termination $[=(1-\alpha)(k_t' + Kk_t'')]$, k_{tt} and k_{ts} designate the overall rate constants of chain transfer to toluene and solvent, respectively, and [S] and [T] give the concentrations of solvent and toluene, respectively. For styrene–toluene–BF_3OEt_2–DCE, from the degree of polymerization (*15*) and conversion, we obtained $k_{tm}/k_p = 0.32 \times 10^{-2}$, $k_{t'}/k_p = 0.18 \times 10^{-2}$, and $k_{tt}/k_p = 0.30 \times 10^{-2}$ at 0°C, [M] + [T] = 20 vol.%, and [M] = 1.72 moles/liter for [T] = 0. From these data we obtain $k_{t'}/k_{tm} = 0.56$ at 0°C. This ratio was earlier reported to be 2.0 at 30°C (*7*). From the comparison of these two values, it is understood that termination is slower at lower temperatures.

It is easily shown that by using Eqs. (16), (17), and (18), the degree of polymerization can be written

$$\begin{aligned}\frac{1}{\bar{P}} &= \sum_x \left\{\frac{(1-\alpha)k'_{tx} + \alpha k''_{tx}}{(1-\alpha)k'_p + \alpha k''_p}\frac{[\mathrm{X}]}{[\mathrm{M}]}\right\} + \frac{(1-\alpha)(k'_t + k''_t K)}{(1-\alpha)k'_p + \alpha k''_p}\frac{1}{[\mathrm{M}]} \\ &\equiv a[\mathrm{X}]/[\mathrm{M}] + b/[\mathrm{M}] \qquad (23)\end{aligned}$$

Equation (23) shows that $1/\bar{P}$ is a linear function of 1/[M] and $\bar{P}$ does not depend on the catalyst concentration. This agrees with the experimental results.

As was mentioned above, no field effect was observed on the degree of polymerization even though the rate of polymerization was accelerated in the case of styrene–DCE systems. From the data shown in Fig. 21, R_{pE}/R_{p0} is nearly 3 at 0.25 kV/cm. From the comparison of Eqs. (21) and (23), it will be seen that b on the right side of Eq. (23) was reduced to one third by the electric field. The observed insensitivity of the degree of polymerization toward the electric field requires, therefore, that a on the right side of Eq. (23) be sufficiently larger than b. The latter, $(1-\alpha)(k'_t + k''_t K)/[(1-\alpha)k'_p + \alpha k''_p]$, can be written $(1-\alpha)k'_t/k_p$ by using an assumption, $Kk''_t < k'_t$, which was mentioned in the previous paper (*4*), and the definition of k_p, and can approximately be written k_t/k_p, since $k_t = (1-\alpha)(k'_t + k''_t K) \approx (1-\alpha)k'_t$. Since the solvent transfer reaction is negligible in the case of DCE (*16*), furthermore, k_t/k_p is approximately equal to $k_{t'}/k_p$, which was found to be 0.18×10^{-2} in the absence of the electric field as was mentioned above. Thus the value b, or k_t/k_p, should become 0.06×10^{-2} in the presence of an electric field. On the other hand, the factor a is $k_{tt}/k_p + k_{tm}/k_p$, since the solvent transfer is negligible. These two factors were found to be about 0.3×10^{-2} in the preceding sections. Thus, as far as k_{tt}/k_p and k_{tm}/k_p do not decrease by the application of the electric field, our kinetic scheme can explain the observed fact that the degree of polymerization is not influenced by the field.

Next, the information presented in Fig. 21 will be discussed briefly. As mentioned in the previous paper (*4*), Eq. (21), which gives the field effect on the rate of polymerization, predicts no field effect for sufficiently small and large values of the degree of dissociation α. In the range of intermediate values of α, Eq. (21) shows $R_{pE}/R_{p0} > 1$. Evidently, the degree of dissociation would be small or large according as the dielectric constant is low or high. Thus our interpretation embodied by Eq. (21) can also qualitatively account for the observed variation of the field effect with dielectric constant. It is interesting to note that, as seen from Table 2, the electric conductivity of polymerizing solution increased with the content of polar solvent in the mixtures. One of the simplest interpretations of these conductivity data is that the population of free ions becomes higher as the dielectric constant increases.

REFERENCES

1. I. Sakurada, N. Ise, and T. Ashida, *Makromol. Chem.*, **82**, 284 (1965).

2. I. Sakurada, N. Ise, and T. Ashida, *Makromol. Chem.*, **95**, 1 (1966).

3. I. Sakurada, N. Ise, and S. Kawabata, *Makromol. Chem.*, **97**, 17 (1966).

4. I. Sakurada, N. Ise, Y. Tanaka, and Y. Hayashi, *J. Polymer Sci.*, **A4**, 2801 (1966).

5. I. Sakurada, N. Ise, and S. Hori, *Kobunshi Kagaku*, **24**, 145 (1967).

6. See, for example, chapters by E. R. Nightingale and J. E. Prue, *Chemical Physics of Ionic Solutions* (B. E. Conway and R. G. Barradas, eds.), Wiley, New York, 1966.

7. T. Higashimura, S. Imanishi, T. Fukushima, Y. Imanishi, and S. Okamura, *Kobunshi Kagaku*, **22**, 205 (1965).

8. R. M. Fuoss and F. Accascina, *Electrolytic Conductance*, Wiley (Interscience), New York, 1959, Chap. 18.

9. A. Mizote, T. Tanaka, and T. Higashimura, *Kobunshi Kagaku*, **22**, 78 (1966).

10. S. Aoki, *Kobunshi Kagaku*, **20**, 726 (1963).

11. T. Higashimura and S. Okamura, *Kobunshi Kagaku*, **13**, 397 (1956).

12. G. Williams, *J. Chem. Soc.*, **1940**, 775.

13. S. Okamura and T. Higashimura, *Kobunshi Kagaku*, **13**, 262 (1956).

14. S. Okamura, T. Higashimura, and Y. Sakurada, *Kogyo Kagaku Zasshi*, **61**, 1640 (1958).

15. The degree of polymerization was determined here by $[\eta] = 4.37 \times 10^{-4} \times M_n^{0.66}$ at 25°C in benzene, which was proposed by D. C. Pepper [*J. Polymer Sci.*, **7**, 347 (1951)] to make comparison with data of Higashimura et al., who also used the above equation, possible.

16. T. Tanaka, A. Mizote, T. Higashimura, and S. Okamura, *J. Polymer Sci.*, **A3**, 2567 (1965).

Zusammenfassung

Die unter dem Einfluss von elektrischen Feldern vorsichgehenden Polymerisationen von Styrol wurden untersucht, wobei Bortrifluorid-Ätherat als Katalysator und binäre Mischungen aus Toluol, 1,2-Dichloräthan und Nitrobenzol in verschiedenen Mischungsgraden als Lösungmittel verwendet wurden. Die Polymerisationsgeschwindigkeit von Styrol in Dichloräthan verdreifachte sich bei Gegenwart eines relativ schwachen elektrischen Feldes von 0.25 kV/cm. Feldbeschleunigende Effekte wurden bei reinem Toluol nicht gefunden, sie stiegen aber mit steigender Dielektrizitätskonstanten des Mischlösungsmittels an um einen Maximalwert bei reinem Dichloräthan zu erreichen und dann aber mit steigender Dielektrizitätskonstanten wieder abzufallen. Diese Beobachtungen dürften darauf hinweisen, dass das Ionenpaar der wachsenden Kettenenden zu stabil ist, um in Toluol die Feldeffekte zu zeigen. Dagegen ist der Dissoziationsgrad des Ionenpaars in Nitrobenzol gross genug, sodass die Anwendung eines elektrischen Feldes die Anzahl der freien Ionen nicht mehr erhöhen kann. Diese Interpretation ist in qualitativer Übereinstimmung mit der Voraussage der früher mitgeteilten kinetischen Schemas. Andererseits wurde der Polymerisationsgrad durch das elektrische Feld nicht beeinflusst.

Résumé

On a etudié la polymérisation cationique du styrène sous un champs électrique, avec, l'éthèrate du trifluorure de bore comme catalyseur et les mélanges binaires toluene, dichloro-1,2-éthane, et nitrobenzene de compositions variées comme solvant. La vitesse de polymérisation du styrène en dichloroethane était triplée en présence d'un champs électrique d'une intensité plutôt basse de 0.25 kV/cm. Les effets accélerateurs du champs etaient nuls dans le toluène pur, s'élèvant avec l'accroissement de la constante diélectrique de solvants mixtes, et passant par une valeur maxumum dans le dichloroéthane pur, diminuent avec l'augmentation continue de la constante diélectrique. Cet observation indique peut-être que la paire d'ions des bouts de chaîne croissante est trop "firme" pour montrer les effets du champs dans le toluène, tandis que le degré de dissociation des paires d'ions dans le nitrobenzène est si large, que l'application d'un champs électrique ne peut plus augmenter la population dé ions libres. Cette interprétation est en accord qualitative avec les prédictions du schemat cinétique presenté antèrieurement. D'un autre côté le champs électrique était sans influence sur les degrés de polymérisation.

Received by editor March 7, 1967
Submitted for publication August 22, 1967