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 an Electric Field as a Relaxational Method for the Investigation of Kinetics. II. Determination of Some Kinetic Constants from Field Effects in Cationic Polymerization of 1,3-Dioxolane and Styrene

A. T. Ponomarenko[a]; V. G. Shevchenko[a]; N. S. Enikolopov[a]
[a] Institute of Chemical Physics Academy of Science of the USSR Moscow, USSR

To cite this Article Ponomarenko, A. T. , Shevchenko, V. G. and Enikolopov, N. S.(1977) 'Ionic Polymerization under an Electric Field as a Relaxational Method for the Investigation of Kinetics. II. Determination of Some Kinetic Constants from Field Effects in Cationic Polymerization of 1,3-Dioxolane and Styrene', Journal of Macromolecular Science, Part A, 11: 1, 195 — 223

To link to this Article: DOI: 10.1080/00222337708061261

URL: http://dx.doi.org/10.1080/00222337708061261

J. MACROMOL. SCI.–CHEM., A11(1), pp. 195-223 (1977)

Ionic Polymerization under an Electric Field as a Relaxational Method for the Investigation of Kinetics. II. Determination of Some Kinetic Constants from Field Effects in Cationic Polymerization of 1,3-Dioxolane and Styrene

A. T. PONOMARENKO, V. G. SHEVCHENKO, and N. S. ENIKOLOPOV

Institute of Chemical Physics
Academy of Science of the USSR
Moscow, USSR

ABSTRACT

The main results of the present study confirm the ideas previously proposed by us to explain electric field effects in ionic polymerization, namely, that they are mainly caused by space distribution of the ions present in the system at the moment of field application. Polymerization of 1,3-dioxolane by $SnCl_4$, $(C_2H_5)_2 \cdot OBF_3$, and $(C_6H_5)_3CSbF_6$ and also of styrene by $(C_6H_5)_3CSbF_6$ was studied. The ratios of the rate constants of free ions and ion pairs and approximate values of the constants were calculated. The possibility of secondary initiation in the system styrene–$(C_6H_5)_3CSbF_6$ was found, probably due to the discharge of SbF_6^- counterion at the anode. The data show that a transition to a new polymerization rate occurs in a definite time period dependent on the velocity of the space distribution of counterions or ions of both signs. This fact makes it possible to treat the proposed method of the analysis of electric field effects in polymerization kinetics as a relaxational one.

INTRODUCTION

In recent years, ideas on the nature of electric field effects in ionic polymerization have changed considerably. This is mainly due to the fact that some new effects have been found and to explain them new concepts have been developed.

As we discussed in detail in our previous paper [1], several interesting experimental facts were observed by Giusti et al. [2]. They found that under an electric field a progressive decoloration of the polymerizing solution takes place around the cathode and polymerization rate is greater near the anode [2, 3]. Of interest is the result of Giusti et al. that the field effect W_E/W_0 depends on the time interval of the field application and frequency of the change of its polarity. These observations led Giusti to the hypothesis that the rate increase of ionic polymerization under an electric field is due to electroinitiation processes [4]. The same idea was put forward by Funt et al. [5] in an analysis of the work of Ise et al. [6]. As follows from the concepts of Funt et al. [5], application of an electric field to anionic polymerization systems leads to the formation of new active centers due to electrolysis of macroions and counterions [7]. Depending on the reactivity of new active centers, the polymerization rate can become higher or lower, or remain the same. We believe that the question of electroinitiation in ionic polymerization under an electric field should not be excluded. Nevertheless, before we take into account the secondary initiation, the space distribution of the counterions and macroions must be considered.

The present work gives experimental results which confirm our viewpoint that the space redistribution of ions under an electric field is the main cause of electric field effects. We have also made an attempt to assess the role of electroinitiation phenomena in these effects.

The situation in the polymerizing system after the application of the field can be assumed to be as follows. At this moment an equilibrium exists between growing ion pairs and also growing macroions and counterions. After the field has been applied, the ions migrate to their respective electrodes. In unit time the number of counterions nearing their electrode is much greater than the number of macroions moving in the opposite direction, since the mobility of the latter is much lower and diminishes with the length of polymeric chain [8]. Then a space charge of the sign of the less mobile ions will build up in the system. For ionic polymerization systems in which the equilibrium

$$\text{ion pairs} \rightleftharpoons \text{free ions}$$

is labile enough, such redistribution will shift this above equilibrium to the right [1]. If the ions are more reactive, the polymerization rate should increase. At the same time, part of these macroions can discharge at the electrode, and if their loss is not compensated by a shift of the equilibrium, retardation of polymerization occurs.

In the previous paper [1] we showed that the ratio of polymerization rates W_E/W_0 depends on the ratio of mobilities of macroions and counterions (μ), the degree of dissociation of active centers (α), and the ratio of the rate constants of free ions and ion pairs ($\xi = k_p''/k_p'$). At that stage the possibility of electroinitiation, though not excluded, was not taken into account. To obtain a more general equation we suppose that the concentration of counterions diminishes under the action of the field according to the equation [1]:

$$n = n_0 \exp\{-t/\tau_n\}$$

Then the number of ions which have left the reaction volume is:

$$\begin{aligned}\Delta n &= n_0 - n \\ &= n_0 (1 - \exp\{-t/\tau_n\})\end{aligned}$$

If we suppose that part k of these ions discharges at their electrode, causing thus the formation of new active centers with the rate constant k_ψ, the polymerization rate can be written as follows:

$$W_E + W_\psi = (k_p'c_E + k_p''p_E + k_\psi k\Delta n)M \tag{1}$$

and

$$\frac{W_E + W_\psi}{W_0} = \frac{e^{-\mu x} + (\xi e^{-x} - e^{-\mu x})\alpha + \psi}{(\xi - 1)(1 - e^{-\mu x})\alpha^2 + (1 + \xi e^{-\mu x} - 2e^{-\mu x})\alpha + e^{-\mu x}} \qquad (2)$$

$$\psi = \xi k\alpha(1 - e^{-\mu x})[e^{-\mu x} + \alpha(1 - e^{-\mu x})]$$

where C_E is the concentration of ion pairs under the field; p_E is the concentration of macroions; M is the monomer concentration; and ψ describes the electro initiation process. $X = t/\tau_p$ is a parameter describing migration of macroions.

According to the previous analysis [1], we may suppose that electroinitiation will be the greatest when no positive field effect is expected, i.e., $W_E/W_0 = 1$, which happens at $\alpha \approx 1$. In this case we find:

$$(W_E + W_\psi)/W_0 \approx e^{-x} + k \qquad (3)$$

and

$$(W_E + W_\psi)/W_E \approx 1 + ke^{-x}\alpha \qquad (4)$$

Equation (4) holds for all α values.

Figure 1 presents the dependence of $(W_E + W_\psi)/W_E$ on the secondary initiation coefficient k. The greater α and k, the greater is the electroinitiation effect, though it does not exceed 2.

Later we shall return to the question of the role of the secondary initiation in the electric field effect on ionic polymerization in connection with our experimental results.

EXPERIMENTAL

Purification of Reagents

1,3-Dioxolane (DO), was dried over metallic sodium and distilled in a column over CaH_2 at atmospheric pressure (744 Torr). The fraction boiling at 72-75° C was selected, dried for several days over

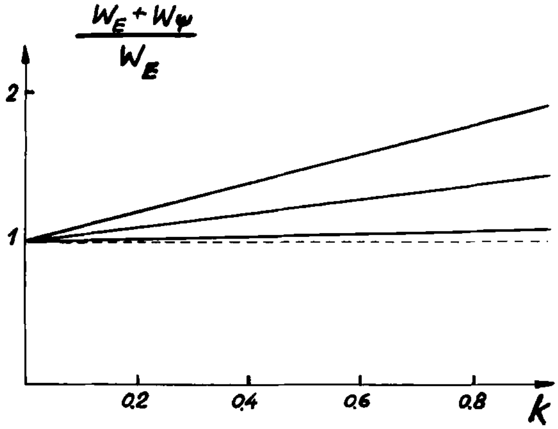

FIG. 1. Dependence of $(W_E + W_\psi)/W_E$ on k from Eq. (4): (1) $\alpha = 1$; (2) $\alpha = 0.5$; (3) $\alpha = 0.1$; $e^{-x} = 1$; $x = t/\tau_p = 0$.

Na-K alloy, redistilled into an ampoule and stored in vacuo. The purity of DO was assayed chromatographically.

Styrene (St) was washed twice with 10% alkali solution, then with distilled water until neutral. Afterwards styrene was dried over calcium chloride and distilled twice in vacuo. The fraction boiling at 41° C/16 Torr was selected and dried for several days under CaH_2 in vacuo.

α-methylstyrene was purified similarly to styrene (bp 52° C/10 Torr).

1,2-Dichloroethane (DCE) was washed with concentrated sulfuric acid and then 10% aqueous KOH, then washed with distilled water until neutral and dried over calcium chloride. Dried DCE was distilled over CaH_2, the fraction boiling at 81.5-81.7° C being selected. Distilled DCE was degassed and kept in vacuo over CaH_2.

Methylene chloride (MC) was purified similarly to DCE (bp 40° C).

Triphenylmethylhexafluoroantimony, $(C_6H_5)_3CSbF_6$, was synthesized by V. P. Volkov. Purity was followed by NMR.

Tin tetrachloride, $SnCl_4$, was boiled over P_2O_5 in a stream of argon, distilled at 113.5° C, and kept in sealed vessels. Before use $SnCl_4$ was redistilled in vacuo.

Boron trifluoride etherate, $(C_2H_5)_2 \cdot OBF_3$, was obtained by the saturation of absolute ether with boron trifluoride dried over P_2O_5, distilled at atmospheric pressure (bp 126-127° C), redistilled in vacuo, and stored in ampoules.

Commercially available methanol was used without purification.

Chlorobenzene was distilled at atmospheric pressure (the boiling point of the fraction used was 131-132 °C).

Benzene was washed first with H_2SO_4, then with water until neutral. Afterwards it was dried over KOH, metallic Na, and distilled over Na (the fraction used had bp 79.5-80° C).

Experimental Procedure

A schematic diagram of the apparatus is shown in Fig. 2. The cell (4) was placed in an oil thermostat (5), the temperature of which was kept stable within ±0.1° C by an ultrathermostat (7). Reagents were mixed by magnetic stirrer (6). A switch (11) connected the cell to a conductometer (2) developed at the Institute of Automation and Electrometry, Siberian Branch, Academy of Science of the USSR, [9], a high voltage source (1), or microammeter (3), which measured discharge currents. Polarization current was measured by milliammeter (8) and recorded by millivoltmeter (9) with variable measuring scale (10).

The general appearance of the cells is shown in Fig. 3. The cells are made of molybdenum glass. In the coaxial cell (Fig. 3a) the outer electrode is made of stainless steel and has a helicoid form

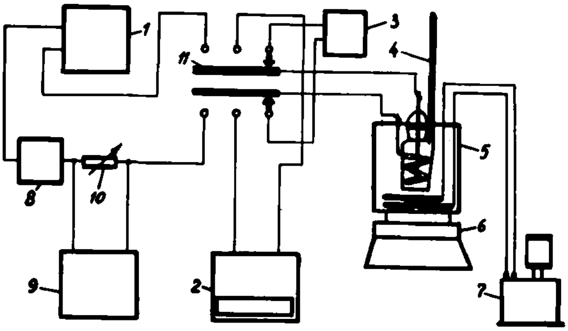

FIG. 2. Experimental apparatus: (1) high voltage generator; (2) conductometer; (3) microammeter; (4) electrolytical cell with dilatometer; (5) oil thermostat; (6) magnetic stirrer; (7) circulation pump thermostat; (8) milliammeter; (9) recording millivoltmeter; (10) variable resistor; (11) switch.

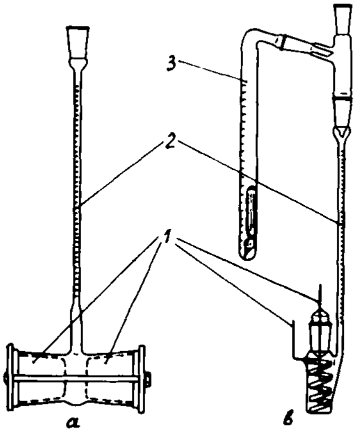

FIG. 3. Electrolytic cells with dilatometers: (a) plane-parallel electrodes; (b) coaxial electrodes: (1) electrodes; (2) graduated capillaries; (3) measuring tank; (4) ampoule with catalyst; (5) breaker.

and is closely adjoining inner wall of the glass cylinder which is closed with a lid having a sealed-in inner electrode of molybdenum wire (S_1 = 0.75 cm^2, S_2 = 6 cm^2). The design of the plane-parallel cell is clear from Fig. 3b (S_1 = S_2 = 6 cm^2). The electric field acted on the whole reaction volume, which did not exceed 10 ml. The experiments without the field were carried out in the same cell. In addition to the described cells, platinum electrode cells were used. No difference was observed in the kinetics of polymerization carried out in all kinds of the cells. The cells were filled in in vacuo. Dilatometry was used to follow the kinetics of polymerization. A voltage of 1 kV was applied after the rate of polymerization attained its maximum value. The calculated field strengths were 1 kV/cm in the plane-parallel cells and 0.4-7 kV/cm in coaxial cells. The polymerization was killed by addition of a cooled solution of methanolic ammonia. The intrinsic viscosity of polydioxolane was measured in chlorobenzene at 25° C.

The following parameters, which characterize the reaction systems, were controlled during the experiments: maximum rate of polymerization before and after the application of the field; intrinsic viscosity of the polymer in the whole volume of the cell and in its anode part; variation of the current with time after the application of the field (polarization current); variation of the current with time after the field was switched off (depolarization current); conductivity of the system before and after application of the field.

RESULTS AND DISCUSSION

Polymerization of 1,3-Dioxolane under an Electric Field

Now we consider the field effects in the polymerization of DO catalyzed by $SnCl_4$, $(C_2H_5)_2 \cdot OBF_3$ and $(C_6H_5)_3CSbF_6$. We tried to estimate the role of free ions and ion pairs in these systems and find some kinetic constants from the observed effects.

Of utmost interest to us was the connection between the usual polymerization and the polymerization under an electric field, in particular between the degree of dissociation of active centers (α) and the changes in polymerization rate and in the molecular weight of the polymer in various parts of the reaction volume. But in determining α some difficulties were encountered, so that values of α calculated from conductivity measurements and used later to calculate the kinetic constants from the observed field effects are valid as the illustration of our method of analysis only.

Figure 4 presents time dependencies of the relative conductivity x_τ/x_0 after small quantities of monomer have been added to the catalyst solution, and Fig. 5 is the change of 1/R during polymerization. If the catalyst is not ionogenic, i.e., $SnCl_4$ or $(C_2H_5)_2 \cdot OBF_3$, the conductivity increases after monomer has been introduced into the system. On the other hand, introduction of DO, styrene or α-methylstyrene to the solution of $(C_6H_5)_3CSbF_6$ leads to a decrease of the conductivity. Nevertheless, the change of x_τ/x_0 is not too great. Therefore, changes of the conductivity and changes of the rate of polymerization under the field complement each other and reflect the formation of some type of active centers in each particular system.

It is known that such catalysts as $Et_2O \cdot BF_3$ and $SnCl_4$ are not ionogenic in MC and DCE solutions. For example, the dissociation constant of Et_2OBF_3 in DCE at 10°C is $K = 1.6 \times 10^{-9}$ mole/liter and the equivalent conductance at concentrations about 10^{-3} mole/liter does not exceed 0.03 cm^2/ohm [10]. Since, according to Fig. 4, the conductivity of $Et_2O \cdot BF_3$ solution with small amounts of DO added (at concentrations lower than equilibrium ones [11, 12]) changes insignificantly, we may assume α to be around 5×10^{-4}. However,

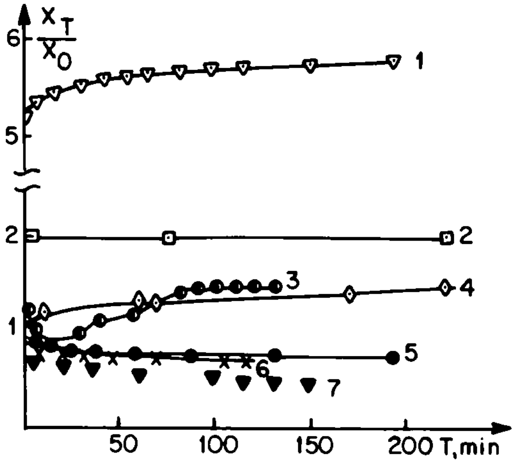

FIG. 4. Change of the relative conductivity x_T/x_0 of catalysts $SnCl_4$, $(C_2H_5)_2 \cdot OBF_3$ and $(C_6H_5)_3CSbF_6$ in presence of (1, 3, 6) DO, (4, 7), St and (2, 5) α-Me St: (1) $[SnCl_4] = 1.3 \times 10^{-2}$ mole/liter, [DO] = 0.5 mole/liter, 25° C; (2) $[(C_2H_5)_2OBF_3] = 6.9 \times 10^{-3}$ mole/liter, [α-Me St] = 0.27 mole/liter in DCE 25° C; (3) $[(C_2H_5)_2OBF_3] = 6.9 \times 10^{-3}$ mole/liter, [DO] = 0.4 mole/liter, in DCE, 25° C; (4) $[(C_2H_5)_2OBF_3] = 6.9 \times 10^{-3}$ mole/liter [St] = 0.45 mole/liter, in DCE, 25° C; (5) $[(C_6H_5)_3CSbF_6] = 5 \times 10^{-5}$ mole/liter, [α-Me St] = 0.14 mole/liter, in MC, 20° C; (6) $[(C_6H_5)_3CSbF_6] = 5 \times 10^{-5}$ mole/liter, [DO] = 0.39 mole/liter, in MC, 20° C; (7) $[(C_6H_5)_3CSbF_6] = 5 \times 10^{-5}$ mole/liter, [St] = 0.08 mole/liter, in MC, 20° C.

for $SnCl_4$ solutions conductivity increases sixfold. From the data of Pepper [13] and the present paper, α can be estimated to be around 2×10^{-2}.

The data on the conductivity of the $(C_6H_5)_3CSbF_6$–DO and $(C_6H_5)_3CSbF_6$–St systems apparently makes it possible to judge more precisely the state of the active centers. A slight decrease of conductivity (Fig. 4, curve 7, Fig. 5, curves 3-5) possibly indicates that the mobility of ions decreases due to viscosity increase. In collaboration with Companiets and Plechova we found for $(C_6H_5)_3CSbF_6$ in MC at 20° C $K = 1.7 \times 10^{-4}$ mole/liter, while Pepper et al. [14] give the value of 2.5×10^{-4} mole/liter at 25° C. Penczek [15] indicates that the active centers in such systems have a dissociation constant of the order of 10^{-5} mole/liter. On the basis of these results we may judge the degree of dissociation of the active centers to be $\alpha \approx 1$.

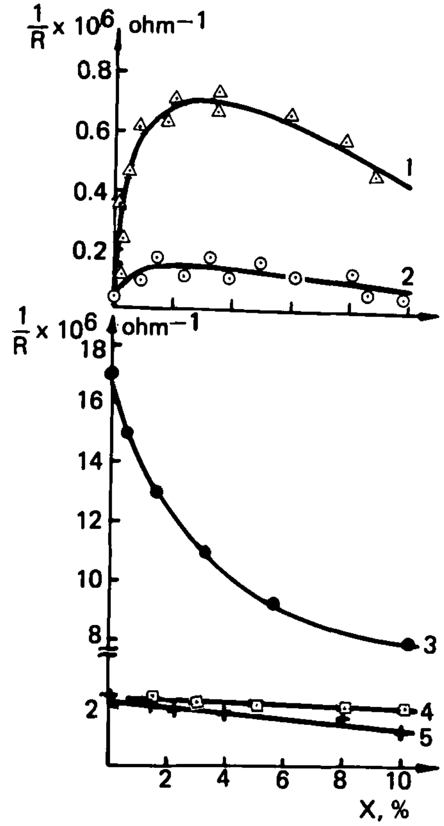

FIG. 5. Dependence of the conductivity on conversion, K_{cell} = 0.15/cm: (1) [$SnCl_4$] = 1.4×10^{-2} mole/liter, [DO] = 13.4 mole/liter, 40° C; (2) [$(C_2H_5)OBF_3$] = 7.3×10^{-3} mole/liter, [DO] = 13.4 mole/liter, 40° C; (3) [$(C_6H_5)_3CSbF_6$] = 1×10^{-5} mole/liter, [DO] = 5.08 mole/liter, in MC, 25° C; (4) [$(C_6H_5)_3CSbF_6$] = 1.2×10^{-5} mole/liter, [St] = 1.2 mole/liter, in DCE, 25° C; (5) [$(C_6H_5)_3CSbF_6$] = 2.8×10^{-6} mole/liter, [DO] = 6 mole/liter, in DCE, 25° C.

As follows from Fig. 6, polymerization of DO by $SnCl_4$ accelerates under a field with a clearly observed transient period, during which the polymerization rate gradually increases (the rate increase was observed in all kinds of cells). The length of this period is 3-6 min, which coincides with the time of the current decrease and is independent of the initial current value, as follows from Table 1. This fact

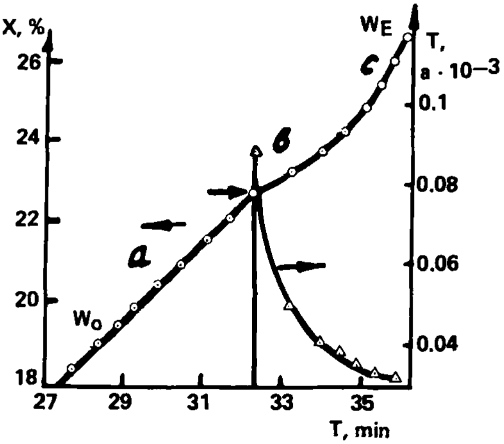

FIG. 6. Transient period after the application of the field. [$SnCl_4$] = 1.4 × 10^{-2} mole/liter, [DO] = 13.4 mole/liter, u = 1 kV, 40°C.

TABLE 1. Electric Field Effect on the Polymerization of DO[a]

Maximum polymerization rates (mole/liter-min)			
Without field W_0	In field W_E	$\frac{W_E}{W_0}$	Initial polarization current (mA)
0.094	0.154	1.64	0.5
0.088	0.160	1.81	0.32
0.083	0.131	1.58	0.4
0.095	0.145	1.52	0.2
0.137	0.172	1.25	0.2
0.127	0.184	1.45	0.15
0.092	0.149	1.62	0.17
0.120	0.189	1.56	0.08
0.122	0.236	1.93	0.09

[a] [DO] = 13.4 mole/liter; [$SnCl_4$] = 1.4 × 10^{-2} mole/liter; u = 1 kV, 40°C.

TABLE 2. Influence of the Polarity of the Applied Field on the Ratio of Polymerization Rates W_E/W_0[a]

Conditions	W_0 (mole/liter-min)	W_E (mole/liter-min)	W_E/W_0
Without field	0.14	–	–
Central electrode negative	0.12	0.19	1.6
Central electrode positive	0.13	0.28	2.1

[a] [DO] = 13.4 mole/liter, $[SnCl_4] = 1.4 \times 10^{-2}$ mole/liter, u = 1 kV, 40° C.

excludes Joule heating (which did not exceed 0.5° C) as a possible cause of the rate increase.

The change of the polarity of the applied voltage in coaxial cells leads to different field effects (see Table 2). The ratio W_E/W_0 is greater when the central electrode is positive. This is probably due to the quicker migration of counterions in the higher field around the central electrode. The above facts indicate the main part which counterions play in the change of polymerization kinetics of DO under the field. As will be shown later, an increase of the intrinsic viscosity of PDO in the anodic zone is also connected with the redistribution of counterions.

The field does not influence the rate of DO polymerization by Et_2OBF_3, though Fig. 7 shows the build-up of the space charge in this system which is evidenced by the depolarization current (curve 4). If the field is applied during the induction period, the polarization current increases with time (curve 3), which indicates the accumulation of ions in this system. However, conductivity data show that the equilibrium, free ions $\rightleftharpoons$ ion pairs, is shifted to the right, so that the redistribution of ions does not influence polymerization rate. This case will be analyzed later. Here we only point out that to shift this equilibrium significantly, far greater times than the time of polymerization are necessary, since $\alpha \ll 1$.

For the system DO–$(C_6H_5)_3CSbF_6$, the field effect depends on the polymerization rate at E = 0 (Fig. 8). At W_0 = 0.6 mole/liter-min, (Fig. 8, curves 1, 2), the field does not influence the rate of polymerization, though final conversion decreases slightly. When the rate is

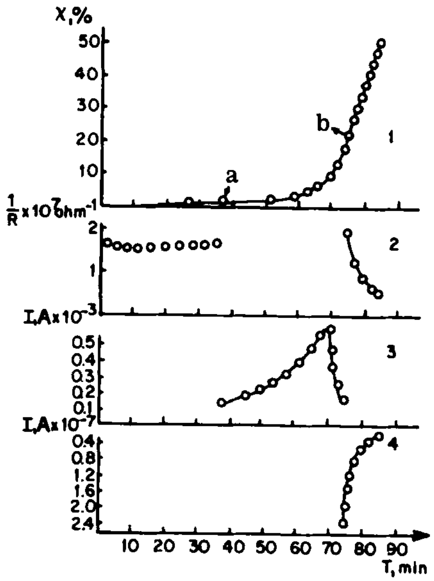

FIG. 7. Field effect on the polymerization of DO by $(C_2H_5)_2OBF_3$ with (a) voltage switched on, and (b) voltage switched off: (1) kinetics of DO polymerization; (2) conductivity; (3) polarization current; (4) depolarization current. $W_E = W_0 = 0.18$ mole/liter-min; [DO] = 13.4 mole/liter, $[Et_2O \cdot BF_3] = 7.3 \times 10^{-3}$ mole/liter, u = 1 kV, 40°C.

lower (about 0.25 mole/liter-min, curves 3-5) polymerization practically stops in 10-15 min after the application of the field.

The period in which the polymerization slows down is independent of the field's polarity, and the earlier the field has been applied, the shorter is this period (Figs. 9 and 10). At the same time polarization current in both cases decreases to a constant value in about 1 min. This decrease of the current is probably due to the migration of counterions, while macroions migrate much slower and their discharge at the electrode causes the polymerization to slow down. The above facts mean that we have the case when the degree of dissociation of active centers $\alpha > \alpha^*$, where α^* is the critical degree of dissociation at which the rate of polymerization decreases [1]. At high polymerization rates this does not happen, since the polymerization is complete before the ions redistribute under the field.

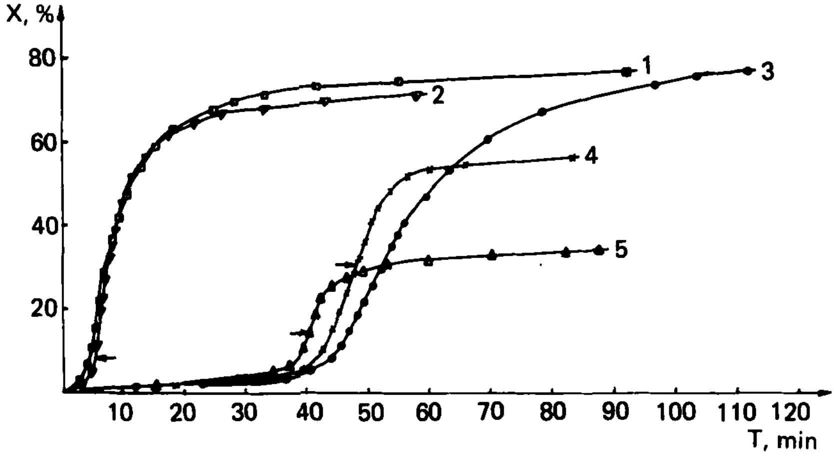

FIG. 8. Kinetics of DO polymerization in DCE at different catalyst concentrations (1, 3) without the field and (2, 4, 5) central electrode positive: (1, 2) [DO] = 5.08 mole/liter, [$(C_6H_5)_3CSbF_6$] = 1 × 10^{-5} mole/liter; (3, 4) [DO] = 6 mole/liter, [$(C_6H_5)_3CSbF_6$] = 2.8 × 10^{-6} mole/liter. u = 1 kV; 25° C.

When the field is applied at high conversion (Fig. 11) for 15 sec only, a space charge still forms, and, as in all other cases (Figs. 7 and 9), capacitance and conductivity of the system increase. If these changes were due to the movement of macroions which have low mobilities, far greater times would be needed for these effects to take place.

The observed difference of the intrinsic viscosities of the polymer in the anodic zone $[\eta]^+$ and in the remaining volume of the cell $[\eta]_0$ is also due to the space redistribution of ions (the polymer in the anodic zone was 8-10% of the whole volume). Figure 12 shows that $[\eta]_0$ remained practically the same under the field, but in the anodic zone, $[\eta]^+$ increases in systems in which the rate of the polymerization changes under the field. For example, in the system $SnCl_4$–DO the rate of the polymerization increases, and Table 3 shows that $[\eta]^+$ in this sytem is 1.4-1.5 times higher than $[\eta]_0$.

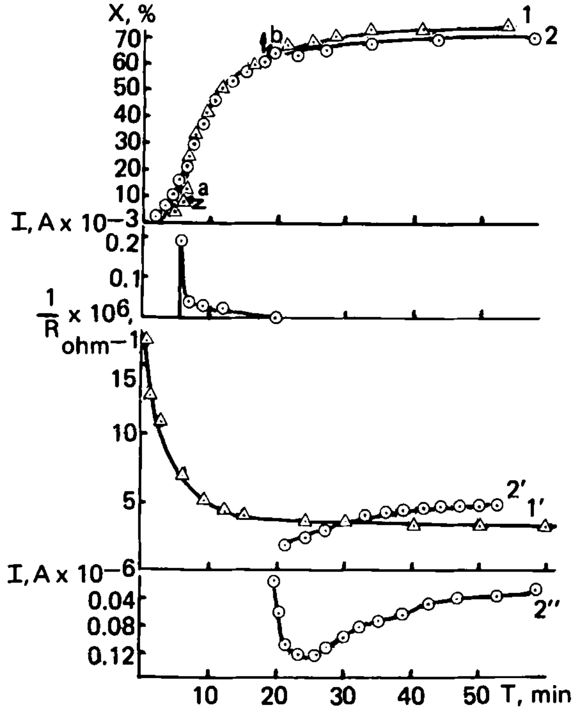

FIG. 9. Kinetics of DO polymerization in DCE and time dependencies of polarization and depolarization currents and conductivity: (1) without the field; (2) central electrode positive. (a) voltage switched on, (b) voltage switched off. [DO] = 5.1 mole/liter, $[(C_6H_5)_3CSbF_6] = 1 \times 10^{-5}$ mole/liter, u = 1 kV, 25°C.

For the system DO–Et_2OBF_3, the rate of the polymerization does not change in the electric field, so that no significant increase of $[\eta]^+$ is observed. Figure 13 shows that the ratio $[\eta]^+/[\eta]_0$ remains at a constant value of 1.1 in a range of conversions of 25-40%.

The influence of the electric field on the ratio $[\eta]^+/[\eta]_0$ is most distinctly observed in the system DO–$(C_6H_5)_3CSbF_6$. Thus, if the polymerization slows down, the ratio $[\eta]^+/[\eta]_0$ increases threefold, diminishing with conversion (Fig. 14).

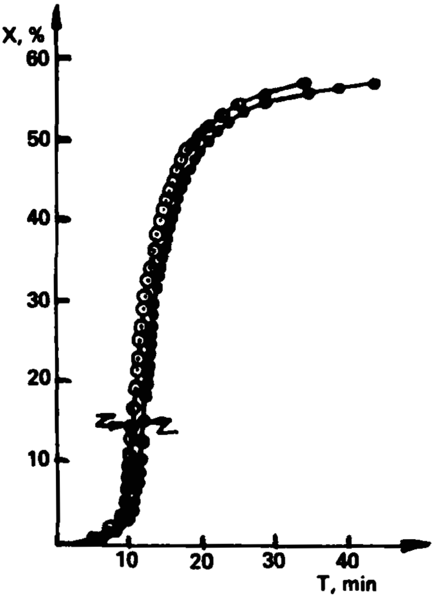

FIG. 10. Dependence or field effects on the polarity of the applied voltage: (1) central electrode negative; (2) central electrode positive. [DO] = 6 mole/liter, [$(C_6H_5)_3CSbF_6$] = 6 × 10^{-6} mole/liter, u = 1 kV, 25° C.

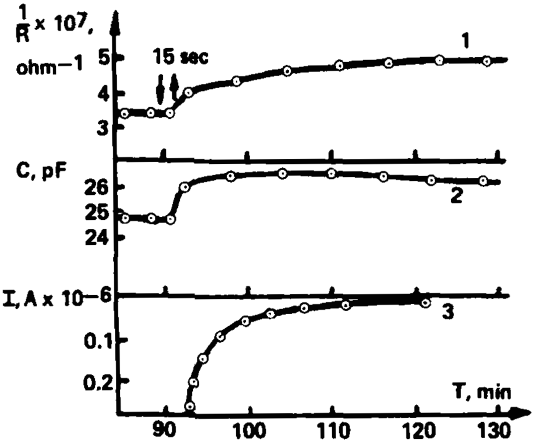

FIG. 11. Time dependence of (1) conductivity, (2) capacitance, and (3) depolarization current in the system DO–$(C_6H_5)_3CSbF_6$–DCE. (The field was applied at 76% conversion). [DO] = 6 mole/liter, [$(C_6H_5)_3CSbF_6$] = 6 × 10^{-6} mole/liter, u = 1 kV, 25° C.

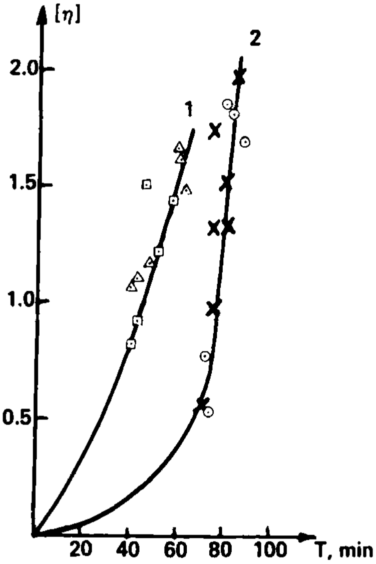

FIG. 12. Dependence of the intrinsic viscosity of PDO in the cell volume on the time of polymerization (▣ , ⊙) without the field and (▲ , ×) in the field: (1) [$SnCl_4$] = 1.4 × 10^{-2} mole/liter, [DO] = 13.4 mole/liter; (2) [$(C_2H_5)_2OBF_3$] = 7.3 × 10^{-3} mole/liter, [DO] = 13.4 mole/liter, u = 1 kV, 40° C.

TABLE 3. Intrinsic Viscosity of PDO in Anodic Zone and in the Remaining Volume[a]

No.	Conversion (%)	$[\eta]^+$	$[\eta]_0$	$[\eta]^+/[\eta]_0$
1	35.7	1.54	1.07	1.4
2	38.6	2.0	1.39	1.4
3	40.4	1.67	1.2	1.4
4	42.4	1.85	1.29	1.4
5	43	1.58	1.1	1.4
6	43.3	1.68	1.1	1.5

[a] [DO] = 13.4 mole/liter, [$SnCl_4$] = 1.4 × 10^{-2} mole/liter, u = 1 kV, 40° C.

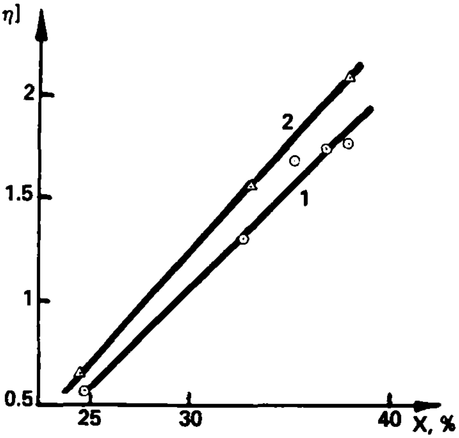

FIG. 13. Monomer conversion x and intrinsic viscosity [η] of the polymer (1) in the cell volume and (2) around the central electrode (anodic zone). [DO] = 13.4 mole/liter, [$(C_6H_5)_3CSbF_6$] = 2.8 × 10^{-6} mole/liter, u = 1 kV, 25° C.

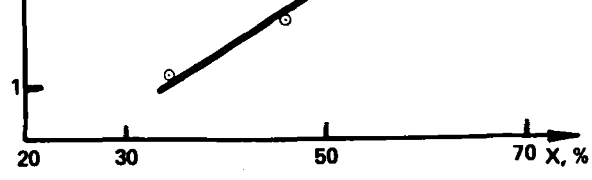

FIG. 14. Monomer conversion and the intrinsic viscosity of the polymer (1) in the cell volume and (2) around the central electrode, when $W_E < W_0$. Solvent, DCE; [DO] = 5.08 mole/liter; [$(C_6H_5)_3CSbF_6$] = 2.8 × 10^{-6} mole/liter.

TABLE 4. Intrinsic Viscosity of PDO in Anodic Zone $[\eta]^+$ and in the Remaining Volume $[\eta]_0$ when $W_E = W_0$

Conversion (%)	$[\eta]^+$	$[\eta]_0$	$[\eta]$ /$[\eta]_0$
32.2	1.58	2.25	0.7
36.6	2.77	3.57	0.8
50.7	3.25	3.5	0.9

[a]DO = 5.1 mole/liter, $[(C_6H_5)_3CSbF_6] = 1 \times 10^{-5}$ mole/liter, u = 1 kV, 25°C, solvent = DCE.

A rather definite principle is thus observed: the higher the degree of dissociation of active centers, the stronger the action of the field on the ratio of the intrinsic viscosities $[\eta]^+/[\eta]_0$. When the field does not influence the system as for DO–$(C_6H_5)_3CSbF_6$ (Fig. 8, curves 1, 2) a decrease of $[\eta]^+$ is observed (see Table 4).

To decrease $[\eta]^+$, SbF_6^- counterions should concentrate in the anodic zone, while macroions are not able to leave this zone because of the rapid increase in viscosity of the polymerizing system. As a result, this leads immediately after the application of the field to an increase of the rate of termination reactions, so that $[\eta]^+$ decreases. With further conversion this factor disappears, and the ratio $[\eta]^+/[\eta]_0$ tends to unity. For the case when the polymerization slows down in the field, we may assume that both counterions and macroions are able to leave the anodic zone so that $[\eta]^+$ increases according to the equation

$$\overline{M}_E \simeq M/C_E^*,$$

where $\overline{M}_E$ is the molecular weight of the polymer, M is the monomer concentration, and C_E^* is the concentration of active centers.

Polymerization of Styrene and the Formation of New Active Centers under an Electric Field

Polymerization of styrene was in most cases carried out in DCE with $(C_6H_5)_3CSbF_6$ as a catalyst.

Figure 15 presents the field effect on this system. The rate of

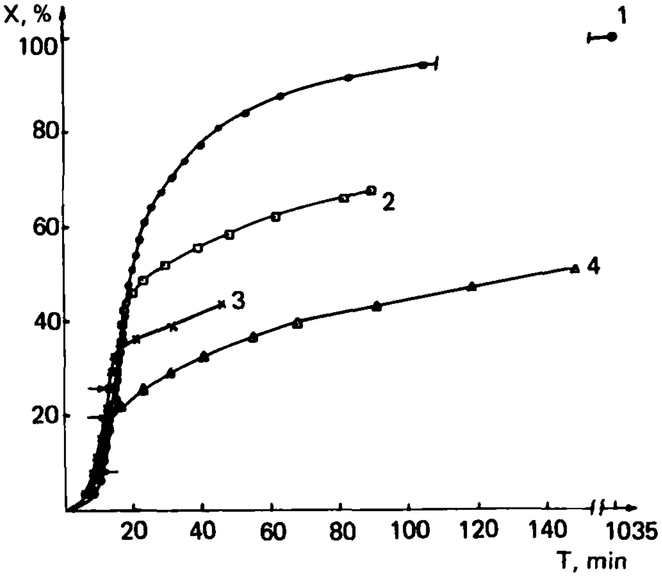

FIG. 15. Kinetics of styrene polymerization in DCE: (1) without the field; (2) central electrode negative; (3, 4) central electrode positive. [St] = 1.2 mole/liter, $[(C_6H_5)_3CSbF_6] = 1.2 \times 10^{-5}$ mole/liter, u = 1 kV, 25° C.

the process is 4×10^{-2} mole/liter-min at.E = 0, markedly decreasing in the field. Polarization current decreased from its initial value of 0.9-1 mA to 0.1 mA in 2.5-3 min. An interesting peculiarity of this system has been observed: the polymer precipitates from the solution shortly after the field has been applied. The polymer obtained under the field was only partly soluble in benzene and toluene at elevated temperatures, which made it impossible to determine the molecular weight of this polymer. The IR spectra of this and the usual polystyrene were identical.

The action of the field on the polymerizations of DO and styrene was different. While polymerization of DO stops completely (Fig. 8), polymerization of styrene proceeds at a constant rate, though much smaller than that prior to application of the field (Fig. 15). The effect depends significantly on the extent of the reaction at the time the field is applied and the polarity of the electrodes in the coaxial cell. The later the field is applied, the less is the rate of polymerization. Furthermore, when the central electrode is negative, the

TABLE 5. Kinetics of the Polymerization of Styrene in Benzene[a]

Time (min)	Conversion (%)
51	3.38
1330	22.0
1700	25.4
4650	33.0
5900	34.0

[a] [St] = 1.2 mole/liter, [$(C_6H_5)_3CSbF_6$] = 1.12×10^{-3} mole/liter, 25° C; polymerization rate W = 2×10^{-4} mole/liter-min.

period in which the polymerization slows down is greater than when it is positive. These facts led us to the conclusion that electroinitiation takes place in the styrene–$(C_6H_5)_3CSbF_6$ system; while macroions discharge at the cathode, new active centers form at the anode. This assumption was verified in two ways. First of all, replacement of one solvent (DCE) for another (benzene) led to a very low rate of polymerization (Table 5), and no influence of the field on this system has been observed. It is usually assumed that the initiation of vinyl polymerizations by the catalysts similar to $(C_6H_5)_3CSbF_6$ proceeds through the addition of $(C_6H_5)_3C^+$ to the double bond [16].

Accordingly, when a nonpolar solvent is used, polymerization is limited by initiation reactions because of the low degree of dissociation of the catalyst (we estimated K for $(C_6H_5)_3CSbF_6$ in benzene to be $\sim 10^{-8}$ mole/liter at 25° C). This means that the equilibrium, free ions $\rightleftharpoons$ ion pairs, is shifted to the right (for both catalyst and the active centers) and is not responsive to the field, since the space distribution of ions does not change and the field is too weak to cause the direct dissociation of ion pairs. Practically speaking, this is the reason why no secondary active centers form in this system.

The possibility of the formation of new active centers is indicated by special experiments with tetrabutylammoniumhexafluoroantimony, $(C_4H_9)_4NSbF_6$, which caused DO, styrene, and α-methylstyrene to polymerize under the field in DCE. An interesting fact is that after the anode became coated with polymer, the polymerization stopped, which made it necessary to change the polarity of the electrodes (maximum current values were ~1 mA diminishing to 0.1-0.2 mA in 1-2 min).

The reactions expected to take place at the anode are summarized in Eqs. (5)-(8).

$$SbF_6^- + e \longrightarrow SbF_5 + F \tag{5}$$

$$2F + RH \longrightarrow RF + HF \tag{6}$$

$$HF + SbF_5 \longrightarrow HSbF_6 + M \longrightarrow \text{secondary active centers} \tag{7}$$

$$SbF_5 + M \longrightarrow \text{secondary active centers} \tag{8}$$

Figure 16 indicates that the rate of the polymerization decreases with conversion, so that each subsequent application of the field causes a smaller amount of the monomer to polymerize.

One can calculate what part of SbF_6^- counterions in the system $(C_6H_5)_3CSbF_6$–styrene–DCE turns into secondary active centers. If we assume that "old" active centers are deactivated completely and

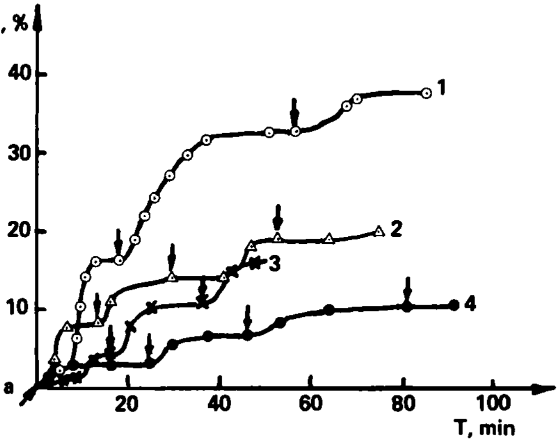

FIG. 16. Electroinitiated polymerization of (1) α-methylstyrene, (2, 3) styrene, and (4) DO in DCE. $[(C_4H_9)_4NSbF_6] = 5 \times 10^{-6}$ mole/liter, [α-MeSt] = 1.9 mole/liter, [St] = 1.2 mole/liter, [DO] = 4 mole/liter, u = 1 kV, 25°C. Arrows indicate the reversals of the field polarity.

TABLE 6. Polarity of the Electrodes and the Coefficient of Secondary Initiation of Styrene in DCE[a]

Electrode polarity	$W_\psi \times 10^3$ (mole/liter-min)	k (%)
$S_2^+ > S_1^-$	5.4	9.2
$S_2^- > S_1^+$	4.6	7.8

[a] $[St] = 1.2$ mole/liter, $[(C_6H_5)_3CSbF_6] = 1.2 \times 10^{-5}$ mole/liter, $u = 1$ kV, 25°C; inner electrode surface $S_1 = 0.75\ cm^2$, outer electrode surface $S_2 = 6\ cm^2$.

the constant rate of polymerization in the field is provided by "new" active centers, the equation for the polymerization rate can be written in the form:

$$W_\psi = kk_\psi M[C^-]$$

where $[C^-]$ denotes the concentration of counterions. The calculation for Fig. 15 gives the values of W_ψ and k (we assumed k_ψ to be equal to k_p'' for this system), which are presented in Table 6.

Thus, we see that for styrene polymerization under an electric field, $(W_E + W_\psi)/W_0 < 1$ when $\alpha \approx 1$, and the role of the secondary initiation becomes observable only after the ratio W_E/W_0 decreases sufficiently.

Some Kinetic Constants for DO and Styrene Polymerizations

At first we discuss the question why no field effect is observed in some systems. One of the reasons for this is too high a polymerization rate, which leads to a rapid increase of the viscosity of the system, preventing redistribution of the ions (Fig. 8, curves 1, 2). The second reason is a low degree of dissociation of active centers, so that polymerization is complete before the redistribution of ions shifts the equilibrium, free ions $\rightleftharpoons$ ion pairs, to the left. The third is that the ratio of the rate constants k_p''/k_p' is several units, the latter are almost as reactive as the former and the rate of polymerization remains the same.

Our experiments show that no rate change is observed in two systems: $(C_6H_5)_3CSbF_6$–DO–DCE at high catalyst concentrations and $Et_2 \cdot OBF_3$–DO. While in the former the effect is absent because of the high rate of polymerization, in the latter it is due to low degree of dissociation of active centers. Indeed, the factor determining the field effect is

$$(1/\alpha) \exp \{-t/\tau_n\} = 2 \times 10^3 \exp \{-t/\tau_n\}$$

since $\alpha = 5 \times 10^{-4}$ [1]. From this we see that the time required to change significantly the rate of the process is about $8\tau_n$, which is 40-50 min, and in this time the polymerization is completed so that no influence of the field is observed. However, in anionic systems the rate increase is observed at such degrees of dissociation, which is explained by the high value of the ratio $k_p''/k_p' \sim 10^3$. Rozenberg [17] found k_p for this system to be 6.8×10^{-2} liter/mole-sec. Our own results and the low value of k_p permit the conclusion that the polymerization in the system $Et_2 \cdot OBF_3$–DO proceeds mostly by ion pairs.

The system DO–$(C_6H_5)_3$ with low catalyst concentration is described by Eqs. (10) and (11) of the previous paper [1]. The value of k_p'' was calculated in two ways. First, by means of Eq. (10) the value of $k_t + (1/\tau_n)$ was determined from the time dependence of W_E. Then, k_t was found from Eq. (9):

$$K_t = \left(k_t + \frac{1}{\tau_n}\right) \frac{\ln (M_0/M_\infty)_E}{\ln (M_0/M_\infty)_0} \tag{9}$$

where M is the monomer concentration less the equilibrium value, which is 1 mole/liter at 20° C [11] and 2 mole/liter at 40° C [12]. Then the values of τ_p and k_p'' are easily determined:

$$k_p'' = (k_t/[C]) \ln (M_0/M_\infty)_0 \tag{10}$$

where [C] is catalyst concentration (initiation effectiveness is assumed to be 1). From τ_p and the cell's known dimensions, the mobility of the macroions is calculated. The following values were obtained:

$$k_t = 8.2 \times 10^{-4}/\text{sec}$$

$$k_p'' = 330 \pm 50 \text{ liter/mole-sec}$$

$$\mu^+ = 3 \times 10^{-6} \text{ cm}^2/\text{V-sec}$$

The other way to determine these constants is as follows. Taking logarithm of Eq. (11) of the previous paper [1], we have

$$\ln (W_E/M) = \ln (k_p''[C]) - [k_t + (1/\tau_p)]t$$

Then from the time dependence of $\ln (W_E/M)$, $\ln (k_p''[C])$ and $k_t + 1/\tau_p$ are determined (Fig. 17). The value of k_p'' determined by this method is $k_p'' = 560 \pm 50$ liter/mole-sec.

For the system styrene–$(C_6H_5)_3CSbF_6$ the constants were determined by the same method (Fig. 17). Linearity of the $\ln (W_E/M)$–t dependence justifies the chosen method.

$$k_t = 1.5 \times 10^{-3}/\text{sec}$$

$$k_p'' = 230 \pm 40 \text{ liter/mole-sec}$$

$$\mu^+ = 2.8 \times 10^{-6} \text{ cm}^2/\text{V-sec}$$

The values of k_p'' are close to those found by other workers. Penczek, gives in one of his early papers [18], $k_p = 50$ liter/mole-sec for the system DO–$(C_6H_5)_3CSbF_6$, while later [15] he found $k_p = 140 \pm 25$ liter/mole-sec. Komarov and one of the authors of the present paper studied the polymerization of DO in detail and found [19] that k_p varies from 80 to 300 liter/mole-sec for different

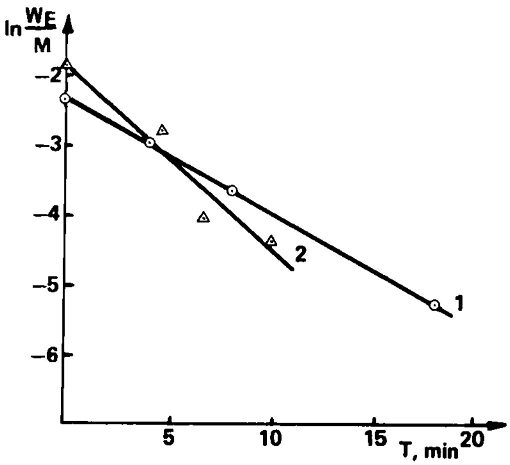

FIG. 17. Time dependence of ln (W_E/M) after the application of the field: (1) [DO] = 6 mole/liter, [$(C_6H_5)_3CSbF_6$] = 2.8 × 10^{-6} mole/liter; (2) [St] = 1.2 mole/liter, [$(C_6H_5)_3CSbF_6$] = 1.2 × 10^{-5} mole/liter; in DCE, u = 1 kV, 25°C.

TABLE 7. Polymerization Constants and Cation Mobilities from the Experiments under an Electric Field

System	K_p'' (liter/mole-sec)	K_p' (liter/mole-sec)	K_p''/K_p'	μ^+ (cm^2/V-sec)
DO–$(C_6H_5)_3CSbF_6$[a]	330 ± 50 (560 ± 50)	–	–	3 × 10^{-6}
DO–$SnCl_4$	0.12[b]	9.7 × 10^{-3}	12	–
St–$(C_6H_5)_3CSbF_6$[a]	230 ± 40	–	–	2.8 × 10^{-6}

[a] In DCE.

[b] Approximate to the value of the initiation effectiveness.

dielectric constants of the media. For the case when the solvent was MC, $k_p = 300$ liter/mole-sec [20]. For the system styrene–$(C_6H_5)_3CSbF_6$ in MC, Pepper [14] gives $k_p = 175$ liter/mole-sec, which is close to the value found by us.

For the system DO–$SnCl_4$ the values of k_p'' and k_p' were found from Eq. (6) of the previous paper [1] which simplifies greatly at $\alpha \ll 1$:

$$\frac{k_p''}{k_p'} = \frac{\lambda - \exp\{-t/\tau_n\}}{\alpha(1 - \lambda)}$$

where

$$\lambda = (W_E/W_0)(\alpha + \exp\{-t/\tau_n\})$$

The value of $\tau_n = 2$ min was found from the mobility μ_n, which was determined from the time dependence of the polarization current. The mean time of the transient period was estimated to be $t_0 = 3$ min, and $W_E/W_0 = 1.6$. From these data the ratio of the rate constants is easily found (Table 7): $k_p''/k_p' = 12$.

The value of k_p' is determined from Eq. (11):

$$k_p' = W_0/[C]M[1 + (k_p''/k_p')\alpha] \qquad (11)$$

and thus $k_p' = 9.7 \times 10^{-3}$ liter/mole-sec and $k_p'' = 0.12$ liter/mole-sec. It is necessary to point out that the ratio of the constants seems to be determined more precisely than the constants themselves.

CONCLUSION

The main peculiarity of ionic polymerization under an electric field is that the chain growth and the migration of charged particles, namely, counterions and macroions, takes place simultaneously. This leads to space redistribution of these ions which determines the change of the polymerization rate and the molecular weight of the polymer in various parts of the reaction volume. From the above facts the need of experimental verification of some details of the proposed method arises. This is related to the development of rapid methods to record the relaxation processes in the system after the application of the field: the change of the polymerization rate, the molecular weight of the polymer in various parts of the reaction volume and also the molecular weight distribution, as pointed out by Funt [5], mobilities of ions in model systems, polarization and, especially, depolarization currents. These methods would deepen our knowledge of the field effect on ionic polymerization processes as well as the mechanism of the process without the field.

ACKNOWLEDGEMENTS

The authors are very grateful to M. A. Akhmametiev, K. M. Sobolevskyi, and Yu. Ya. Shagalov from IAE, Siberian Branch of the Academy of Sciences of the USSR who placed at our disposal an IKP-1M conductometer and took part in conductivity measurements.

The authors are also grateful to V. P. Volkov for the synthesis of $(C_6H_5)_3CSbF_6$ for the present experiments.

REFERENCES

[1] A. T. Ponomarenko, V. G. Shevchenko, and N. S. Enikolopov, J. Macromol. Sci.–Chem., A9, 1195 (1975).
[2] P. Giusti, P. Cerrai, M. Tricoli, P. L. Magagnini, F. Andruzzi, Makromol. Chem., 133, 299 (1970).
[3] P. Cerrai, P. Giusti, G. Guerra, M. Tricoli, Eur. Polym. J., 10, 1141 (1974).
[4] P. Giusti, Makromol. Chem., 175, 1157 (1974).
[5] J. Tanner, V. Hornof, and B. L. Funt, Makromol. Chem., 157, 227 (1972).
[6] N. Ise, H. Hirohara, T. Makino, K. Takaya, and M. Nakayama, J. Phys. Chem., 74, 606 (1970).
[7] N. Ise, K. Takaya, and H. Hirohara, Makromol. Chem., 157, 235 (1972).
[8] B. I. Saszin and V. P. Shuvayev, Vysokomol. Soedin., A10, 730 (1968).
[9] M. A. Akhmametyev, K. M. Sobolevskyi, and Yu. Ya. Shagalov, Measurements of Complex Conductivites in Physical Chemistry, Novosibirsk, 1972, p. 14.

[10] R. Velichkova and I. Panayotov, Makromol. Chem., 138, 171 (1970).
[11] E. B. Ludvig, E. L. Berman, Z. N. Nysenko, V. A. Ponomarenko, and S. S. Medvedev, Vysokomol. Soedin., A8, 1375 (1971).
[12] L. A. Haritonova, G. V. Rakova, A. A. Shaginyan, and N. S. Enikolopyan, Vysokomol. Soedin., A9, 2586 (1967).
[13] D. C. Pepper, Trans. Faraday Soc., 45, 397 (1949).
[14] F. W. Burns, B. McCarthy, R. M. O'Connor, and D. C. Pepper, paper presented at IUPAC Symposium on Macromolecules, Helsinki 1972; Preprints, 1, p. 30.
[15] S. Penczek, Makromol. Chem., 175, 1217 (1974).
[16] T. Higashimura, T. Fukushima, and S. Okamura, J. Macromol. Sci.-Chem., A1, 683 (1967).
[17] B. A. Rozenberg, Thesis, Moscow, 1971.
[18] A. Stolarczyk, P. Kubisa, and S. Penczek, paper presented at 1st International Microsymposium on Advances in Ionic Polymerization, Jablonna, Poland, 1972, B4.
[19] B. A. Komarov, A. T. Ponomarenko, V. P. Volkov, B. A. Rozenberg, and N. S. Enikolopov, Vysokomol. Soedin., A16, 2464 (1974).
[20] O. A. Plechova, V. V. Ivanov, T. I. Prokofyeva, E. F. Oleynik, N. S. Enikolopyan, Vysokomol. Soedin., A15, 14 (1973).

Accepted by editor March 23, 1975
Received for publication May 5, 1976