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Ionic Polymerization under an Electric Field as a Relaxational Method for the Investigation of Kinetics. I. On Results of the Change in Space Distribution of Ions

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ABSTRACT

Investigations were made which show that the change in the dynamics of polymerization and in molecular weight of the polymer under an electric field is connected with the redistribution of the ions growing macromolecules and counterions. Analysis of the equations obtained showed that the field can either increase or decrease the rate of the process. The effect's trend and magnitude depend on the ratio of the mobilities of macroions and counterions, degree of dissociation of active centers, and the ratio of rate constants of free ions and ion pairs. An analysis of literature data relevant to polymerization under an electric field was made.

INTRODUCTION

In many ways ionic polymerization systems resemble nonaqueous electrolyte solutions with the difference that ion-pairs and also cations or anions grow. Chain growth at present is believed to proceed on polarized molecules, contact, or solvent-separated ion-pairs. A change in the type of active centers may take place with a change in the initial characteristics of reaction systems: its dielectric constant, solvation action of the solvent, and ionic strength of the solution. In many cases the role of each particular species in the polymerization process is determined by kinetic methods based upon equilibrium transitions and the different reactivity of ions and ion-pairs. It proved to be possible, for example, to determine the nature of active centers, especially in anionic polymerization, by the change in reaction kinetics after the introduction of strong electrolytes into the reaction system. In this case, according to the mass law, the free ions $\rightleftharpoons$ ion-pairs equilibrium shifts to the right. Since the ratio of rate constants for anionic systems is $\sim 10^3$ and ~ 10 for cationic, such a shift of the equilibrium leads to a change in the polymerization rate. At the same time, such electrolytes can influence not only the propagation process but also initiation reactions, for example, through changing the effectiveness of this process. This recently stimulated the development of a new method to determine the nature of active centers in ionic polymerization through perturbations caused by an external electric field. A great deal of research on this method has been done by Ise et al. The development of the method introduced in the present paper was also greatly stimulated by the very interesting observations of Giusti et al.

Ionic polymerizations in an external electric field have been studied for 10 years, and a considerable amount of experimental data has been obtained. A marked change of polymerization dynamics is observed for many anionic and cationic systems. In several cases the molecular weight of polymers increased either in the whole volume or in parts of it. The present paper deals with the determination of the cause of the observed phenomena and their quantitative description.

An analysis of previous hypotheses on electric field effects has been made. Experimental data show that the polymerization rate increase can be explained through either the direct or indirect influence of the field on the state of active centers present in the system.

As a result of direct influence, we can conceive the dissociation of active centers—ion-pairs—as it happens in electrolytes at field strengths of the order of 20 to 100 kV/cm. Calculations have shown that the generally used field strengths of 0.1 to 1 kV/cm, which lead to a threefold increase in polymerization rate, are too small to cause direct dissociation of ion-pairs. At the same time, and taking into account the fact that ions move in the electric field, a rate increase can be observed due to desolvation of the ions as proposed by Ise et al. But at least three assumptions must be made for this to be the case: 1) the polymerization rate is limited by the solvation of active centers; 2) the velocity of the macroion must be high enough for the ion to travel a distance of several radii during the relaxation time of the solvent atmosphere which is of the order of 10^{-6} to 10^{-9} sec; and 3) there is no space charge distribution in the reaction volume. This means that, similar to direct dissociation of ion-pairs, desolvation of ions will take place at field strengths much higher than those used in experiments. If we assume that ions of both signs take part in redistribution, then the decrease in the average concentration of macroions should lead to a decrease in the polymerization rate. On the other hand, since the mobility of growing macroions is a priori less than that of counterions, the latter will redistribute much faster. This will lead, according to the mass law, to a relative increase in the concentration of propagation species in the form of macroions. The concept described makes it possible to predict the dependence of the electric field effect's trend and magnitude on the degree of dissociation of active centers and the ratio of rate constants of free ions and ion-pairs. Such an analysis is presented in this paper with several equations for determining the elementary polymerization constants in some cases. The investigations have shown that the change in the space distribution of counterions and growing macroions plays the main part in the change of polymerization dynamics. Thus ionic polymerization perturbed by an external electric field can be treated as a relaxational method to investigate polymerization kinetics which can also be applied in studying other ion-molecular reactions in solutions.

DISCUSSION OF THE MAIN RESULTS OF ELECTRIC FIELD EFFECTS ON IONIC POLYMERIZATION

The concept of the nature of electric field effects took shape as experimental data accumulated. First, special experiments ruled out such possibilities as temperature rise due to Joule heating [1] and electrochemical initiation [10] (as was shown later, electrochemical initiation may take place in some cases).

The first experiments showed that a considerable rate increase of cationic polymerization is observed at rather low field strengths. For the polymerization of p-methoxystyrene initiated by iodine, the rate increase was 3.5 at E = 2 kV/cm [1]. Similar results were obtained for other vinyl monomers: α-methylstyrene [2-5], isobutyl vinyl ether [6], and styrene [11] in various catalytic systems [7-15], and radiation-induced polymerization [16].

We regret that these papers have no data on the dynamics of rate change and time dependencies of the current, for this prevents an analysis of these systems from the standpoint of ion redistribution. The main result of the investigations was to show that the higher the relative reactivity of a monomer, the greater the rate increase. At first it was proposed that the rate increase was due to an increased degree of dissociation of active centers as happens in weak electrolyte solutions at field strengths of 20 to 100 kV/cm.

But, as it turned out later, the field effect increased with an increase of the dielectric constant of the medium. For the styrene-trifluoride boron etherate-dichloroethane-toluene system [5], the change of the dielectric constant (ϵ) from 6.6 to 8.8 led to a field effect increase from 1 to 3, diminishing with the further increase of ϵ. Such a dependence is explained by Ise et al. as follows: for low ϵ values and consequently low degrees of dissociation α, the product $k_p''\alpha \ll k_p'$ and is independent of α (k_p'' and k_p' are the rate constants of free ions and ion-pairs, respectively). Then, with the increase of ϵ as α reaches 1, it is assumed that a slight increase of the degree of dissociation caused by the external field has a negligible influence on the product $k_p''\alpha$.

As will be shown in the theoretical part of this paper, an increase in the degree of dissociation of active centers above a certain critical value leads to a decrease in the polymerization rate. The decrease of the ratio W_E/W_0 with the increase of ϵ [5] is due, we think, to a kind of compensation effect, i.e., an increase in the degree of dissociation of active centers due to the redistribution of ions is comparable to the decrease in the concentration of active centers due to their discharge at the electrodes.

The change in experimental methods gained new insight into the nature of the field effect. In particular, the field effect proved to depend on the time interval during which the field is applied. And if the polarity of the field is reversed every 60 sec (with switching off for 15 sec), the polymerization rate remains constant in the anethol-iodine system [17]. Moreover, the inhomogeneity observed in the reaction volume disappeared with the reversal of the field's polarity. Similar results were obtained for polymerizations of styrene, acenaphthylene, and anethole in the presence of $(C_2H_5)_2OBF_3$ [17]. In the same paper, through the use of sensitive methods, the rate of polymerization in the anode compartment was found to be higher than in the cathode counterpart.

At the same time, it was found for the polymerization of trioxane in nitrobenzene that the field effect is different in coaxial and plane-parallel cells [18]. In the former the rate decreased, while in the latter it increased twofold. A considerable increase in the intrinsic viscosity of the polymer was observed in coaxial cells at the same time.

The experiments differed from the previous ones in that the field was applied at the maximum rate of polymerization. Such a difference in the behavior of coaxial and plane-parallel cells led the authors to discuss the role of electrokinetic phenomena in electric field effects in ionic polymerization, particularly migration and redistribution of macroions and counterions. The concept that the change in polymerization kinetics is due to redistribution of ions became evident after finding that the molecular weight of polydioxolane in the anode zone of the cell was 2 to 2.5 times higher than in the rest of the volume [19].

Before analyzing anionic polymerization under an electric field, it is necessary to point out the following. The use of a living, low molecular weight polymer as an initiator excludes the uncertainty of the initiation stage and also termination of active centers. In living anionic systems, stable active centers are formed which thus posess high reactivity. This circumstance could help obtain information on the nature of active centers in the anionic polymerization of styrene and other monomers which may be treated as model systems to study the influence of an electric field on ionic polymerization.

It must be noted that the investigation of the electric field effect on anionic polymerization led to ambiguous conclusions regarding its mechanism.

An analysis of these investigations has also been made of works on cationic polymerization and was based upon the assumptions of direct dissociation of ion-pairs or desolvation of macroions while moving in the external field. These works differed in that the rate constants of free ions and ion-pairs and not overall polymerization rates were compared.

The monomer used was usually styrene and its derivatives; the initiators were alkali metal salts of living polystyrene.

According to Szwarc, for two-stage polymerization the observed rate constant can be written in the form

$$k_p = k_p' + \frac{k_p''\sqrt{K}}{\sqrt{[C]}}$$

where K is the dissociation constant of ion-pairs and [C] is the concentration of active centers.

In the case of styrene polymerization with Li^+ as the counterion, the product $k_p''\sqrt{K}$ was found to increase in the field while k_p' remained constant [23]. Similar to cationic polymerization, this system followed the same principle in respect to the dielectric constant of the reaction media: at low α values, k_p did not change, but it did increase at high ϵ values.

The reasons for the rate increase are now going to be discussed. If we ascribe the rate increase to direct dissociation of ion-pairs due to the Wien effect [24-26], we have

$$\frac{k''_{p,E}}{k''_{p,0}} \left(\frac{K_E}{K_0}\right)^{1/2} = \left(\frac{K_E}{K_0}\right)^{1/2}$$

where, according to Onsager [34],

$$\left(\frac{K_E}{K_0}\right)^{1/2} = 1 + \frac{b}{2} + \frac{b^2}{4} + \cdots$$

where $b = 9.636E/\epsilon T^2$ for the 1:1 type electrolyte, E is the field intensity in kV/cm, and ϵ is the dielectric constant. Thus we can calculate the values of $(K_E/K_0)^{1/2}$ and compare them to experimental data.

It follows from Table 1—which comes from Ref. 23—that the experimental values of $(K_E/K_0)^{1/2}$ are much greater than those calculated. These results are of interest in connection with the possibilities of changing the degree of dissociation of active centers due to space redistribution of ions discussed in this paper. One may certainly doubt the applicability of the metal sphere model of ions used by Onsager in deriving the above equation. Nevertheless, the difference is too great to be explained by the roughness of the approximation.

Thus neither of the above concepts adequately explains the observed field effect on ionic polymerization, which led to the concept of direct field influence on k_p'' [23].

A model which proposes desolvation of macroions under the influence of the field has it that, since THF is a weak solvating agent, [28, 29], anionic active centers are easily desolvated while moving in the field. The rate increase is then due to greater accessibility of the monomer to the active surface of the growing macroion. For example, at a THF content 60 vol%, $k''_{p,E}$ becomes independent of the field,

TABLE 1. Electric Field Effect on Anionic Polymerization of Styrene in Benzene-THF Mixtures

THF content (vol%)	E(kV/cm)	$\frac{k''_{p,E}}{k''_{p,0}}\left(\frac{K_E}{K_0}\right)^{1/2}$	$\left(\frac{K_E}{K_0}\right)^{1/2}$ after Onsager's equation
40	0	1	1
	1.8	1.20	1.027
	4.0	1.80	1.056
	5.0	2.20	1.070
50	0	1	1
	1.0	1.09	1.012
	3.0	1.47	1.037
	5.0	1.82	1.061
	7.6	3.00	1.093
60	0	1	1
	0.5	1.09	1.006
	1.0	1.46	1.011
	2.0	1.83	1.022
	3.0	2.10	1.033
	5.0	2.16	1.055

beginning at 3 kV/cm. This limiting value of $k_p'' = 10^5$ liter/(mole)(sec) is ascribed by Ise et al. to a completely desolvated active center. For lower THF contents this limiting value is not observed, and this can be ascribed to increased solvating power and accordingly to the increased field intensity necessary to strip the ion free of the surrounding solvent.

The above assumptions have been proved in several experiments. When THF was replaced by dimethoxyethane, which has a greater solvating power [30, 31], no field effect was observed [42]. This result rejects the Wien effect as being responsible for the field effect since a greater number of solvent-separated ion-pairs, which have a larger dissociation constant than contact pairs, is present in DME [31, 32]. If we assume that the limiting value $k_{p,E}'' = 10^5$ liter/(mole)(sec) can be ascribed to a desolvated active center, then this limiting rate constant must be independent of the counterion in the given solvent. This assumption has been proved for the polymerization of styrene in tetrahydropyrane (THP) [27]. Alkali metal salts (counterions–Li^+, Na^+, K^+, Cs^+) of living polystyrene were used as initiators. It turned out that, for Na- and K-salts, $k_{p,E}''$ reached the limiting value of 1.2×10^5 liter/(mole)(sec) for E = 3 kV/cm, while for Li-salt, $k_{p,E}''$ continued to increase. No field effect has been observed for Cs-salt, which the authors ascribe to a low dissociation constant of this salt.

Of particular interest are the works by Giusti et al. [17] and the reply by Ise et al. [45]. The Italian group has shown that uninterrupted and interrupted every 60 sec for 15 sec application of the field led to different field effects, while the periodic reversal of the field's polarity completely cancelled the field effect. This result, as was indicated above, denies direct dissociation of ion-pairs and desolvation of ions, and along with other works [18-22] speaks in favor of the change in space distribution of ions after applying the field. In the case of anionic polymerization of styrene in THP (initiator—Na-salt of living α-methylstyrene), the reversal of the field's polarity every 30 sec (E = 3 kV/cm) did not alter the field effect. This result can be explained as follows: there are reference data that anions have a mobility of about 10^{-4} cm^2/(V)(sec) [33], so that they cover the distance of ~1 cm between the electrodes in 3 to 4 sec. Thus, to alter the field effect, the periodic reversal of the field should be made more frequent.

The material reviewed above leads to several conclusions. It must be noted once more that the generally used field strengths of 1 to 10 kV/cm lead to $(K_E/K_0)^{1/2} = 1.01$ to 1.09, and the expected rate increase is much lower than observed experimentally. Moreover, if direct dissociation really takes place, it should increase with the decrease of ϵ, which is contrary to the experimental facts. It follows from the experiments by Giusti et al. [17] that the field effect is greatest when the field is applied continuously. This leads us to the conclusion that direct dissociation of active centers under the field strengths used does not take place. The same conclusion was reached by Ise et al. [23].

Desolvation of growing macroions, as mentioned earlier, is contrary to the experimental data obtained by the Italian group. Actually, if desolvation really takes place, the value of the rate increase should be independent of the interval of voltage application or its polarity. Apart from this, desolvation of a growing macroion may be conceived if the time τ_r in which it travels the distance of a radius of solvent atmosphere r is less than the relaxation time of the atmosphere τ_{rel}, i.e., $\tau_r = r/\mu E < \tau_{rel}$: Taking r = 5 Å, $\mu = 10^{-6}$

$cm^2/(V)(sec)$, and $E = 5 \times 10^3$ V/cm, we obtain $\tau_r = 10^{-5}$ sec. The usual values of τ_{rel} are 2 to 3 decades lower, and thus desolvation seems to be improbable at such field strengths, though there were attempts to prove the possibility of such phenomena [44]. Thus we come to the conclusion that no matter how we treat electric field effects, space redistribution of ions must be taken into account. A number of recently published papers confirm this point of view [20-22].

ON THE CONSEQUENCES OF A CHANGE IN THE SPACE DISTRIBUTION OF IONS IN AN EXTERNAL ELECTRIC FIELD

We assume that the change in the degree of dissociation of active centers in the form of ion pairs is due to the pulling out of the more mobile counterions in the systems where a rate increase is observed. However, to explain the retardation of the polymerization rate observed in our experiments [19, 21], we must take the redistribution of growing macroions into account. In the general case, one has to treat the redistribution of ions of both signs.

The same problem was treated by Talrose et al. while treating the radiolysis of gases in an external electric field [35]. It turned out that the radiation yield can be either increased or decreased depending on experimental conditions. Along with this, the composition of radiolysis products changed. The authors explain the radiolysis mechanism in detail and assume that pulling out electrons and ions to the electrodes decreases the probability of their homogeneous recombination which turns out to be heterogeneous on the electrode surface. Apart from this, ions spend less time in the radiolysis volume, which changes the probability of ion-molecular reactions. If, for example, the characteristic time of reaction τ_M is greater than the time τ_E that an ion spends in the cell, $\tau_M > \tau_E = \ell^2/2\mu U$ (ℓ is the distance between the electrodes, μ is the ion's mobility, and U is the applied voltage), the reaction would be depressed. Radiolysis of gases in electric fields has been widely employed to study its mechanism.

To analyze the influence of an electric field on ionic polymerization, known solutions with similar problems can be used, but with some restrictions. Let us assume that at the moment of voltage application an equilibrium exists in the system

$$AB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + B \tag{1}$$

where AB is an ion-pair, A is a macroion, and B is a counterion, the polymeric chain being propagated by the AB and A reactive species. Then one can obtain a set of equations describing the change of their concentration with time for plane-parallel cells [37]:

$$\frac{\partial p}{\partial t} = k_1 C - k_{-1} pn + D_p \frac{\partial^2 p}{\partial x^2} - \mu_p \frac{\partial (Ep)}{\partial x}$$

$$\frac{\partial n}{\partial t} = k_1 C - k_{-1} pn + D_n \frac{\partial^2 n}{\partial x^2} + \mu_n \frac{\partial (En)}{\partial x}$$

$$\frac{\partial C}{\partial t} = -k_1 C + k_{-1} pn + D_C \frac{\partial^2 C}{\partial x^2}$$

$$\frac{\partial E}{\partial x} = \frac{4\pi e}{\epsilon}(p - n)$$

where $[AB] = C$; $[A] = p$; $[B] = n$ concentrations; D and μ are diffusion coefficient and mobility, respectively; ϵ is the dielectric constant; e is the electron charge; and E is the field intensity.

An approximate solution of this system was given by Thomson [38], who found that, in the central part of the cell, the field is uniform, while near the electrodes there are voltage gradients in zones of thickness $\mu_n/(\mu_n + \mu_p)f\ell$ (near the cathode) and $\mu_p/(\mu_n + \mu_p)f$ (near the anode). Here ℓ is the distance between the electrodes, $f = j/j_s$ is the current saturation, and j is the current density ($j_s = k_1 Ce\ell$).

With the use of the above concepts, a solution of the problem of the hypothetical cationic polymerization in the gaseous phase has been obtained when the mobility of the positive ions is much less than that of negative ones ($\mu_p \ll \mu_n$). The solution was in the form of the dependence of the ratio p_E/p_0 on f [39, 41]. It turned out that for $\mu_n = 0.5$ cm^2/(V)(sec), $\mu_p = 3.3 \times 10^{-3}$ cm^2/(V)(sec), and $k_{-1} = 10^{-6}$ cm^3/sec, the ratio $p_E/p_0 \approx 6$ when $f = 0.6$. This result shows that the concentration of less mobile ions can be increased under the influence of the field. But in a liquid phase it is impossible to reach so great a current saturation, since for this to be the case, field strengths near breakdown are necessary, whereas f = 0.01 to 0.1 in commonly used fields. In case of ionic polymerization, even for f = 0.01 to 0.1 in the reaction volume there is a slowly disappearing positive or negative space charge (for cationic and anionic systems, respectively), which prevents stationary conditions to be reached by the redistribution of macroions. Thus, when considering the field effect on ionic polymerization, two difficulties arise: nonstationarity of the problem (a purely mathematical difficulty) and the absence of data on the mobility of macroions in polymeric solutions, especially its dependence on the degree of polymerization. Thus, to describe field effects, we have made the following assumptions which make a solution fairly easy.

1. The decrease of the volume-average concentration of n-ions is described by the equation $dn/dt = -n/\tau_n$, where $\tau_n = \ell^2/\mu_n U$ for plane-parallel electrodes, or $\tau_n = (r_2{}^2 \ln r_2/r_1)/2\mu_n U$ for coaxial electrodes (when $r_2 \gg r_1$). The adoption of this condition means that the electric field is uniform and no space charge is present. This approximation is true for $t \leq to = \min(\tau_n)$, i.e., until the most mobile ions reach the electrode and the space charge appears, thus preventing the ions from reaching the electrodes.

2. The concentrations C, p, and n are equilibrious at any time, i.e., the relation $pn/C = K = k_1/k_{-1}$ holds. Indeed, since p reaches equilibrium,

$$p = p_0 + x_1 x_2 \frac{1 - e^{-\beta t}}{x_1 - x_2 e^{-\beta t}}$$

where x_1 and x_2 are the roots of the equation:

$$x^2 + (K + p_0 + n_0)x + p_0 n_0 - KC_0 = 0$$

and

$$\beta = k_{-1} \sqrt{(K + p_0 + n_0)^2 - 4(p_0 n_0 - KC_0)}$$

It can be seen from these expressions that the equilibrium is reached during the time $t_p = 1/\beta$. Taking $K = 10^{-8}$ mole/liter,

$C_0 \approx 10^{-4}$ mole/liter, $k_{-1} = (4\pi e/\epsilon)(\mu_n + \mu_p)$ (which is true for nonpolar media [40 j]), and the initial concentrations differing from equilibria by 1%, we obtain $t_p \approx 10^{-3}$ to 10^{-4} sec.

At the same time, the characteristic time of ions redistribution is $\tau_n = \ell^2/\mu_n U \approx 10^2$ sec if $\ell = 1$ cm, $\mu_n \approx 10^{-5}$ cm²/(V)(sec), and $U = 10^3$ V. And so, $t_p \ll \tau_n$, i.e., equilibrium is reached before ions are redistributed.

3. k_p'' and k_p', the rate constants of free ions and ion-pairs, respectively, and also K do not depend on the length of polymeric chains. The statement is rather difficult to prove, though we can assume that is holds for rather long chains (~10 monomeric units) when the influence of the "tail" on the growing end is negligible. For very long chains the conformation of the macromolecule must be taken into account since the growing end can be either inside or outside the ball. It is evident that in the former case k_p would decrease with the length of the chain due to diffusion hindrance.

4. The polymerization rate must be low enough or otherwise polymerization may take place before the redistribution of ions. The field effect may be low or completely absent in this case. Analytically, it can be written in the form $\Delta M = Wt_p \ll M_0$, where M_0 is the monomer concentration at the moment the field is applied. If this is so, we have the right to ignore the details of the process during the distribution of the ions, which means that such reactions as chain transfer can be excluded. But these reactions must be taken into account when considering the field effect on the degree of polymerization, which will be done later.

Considering these points, we may write the following system of equations which describes the field effect on ionic polymerizations:

$$\begin{aligned} \frac{dC}{dt} &= -k_1 C + k_{-1} pn \\ \frac{dn}{dt} &= -k_{-1} pn + k_1 C - \frac{n}{\tau_n} \\ \frac{dp}{dt} &= -k_{-1} pn + k_1 C - \frac{p}{\tau_p} \end{aligned} \tag{2}$$

Now the system is easy to solve and the solution is

$$n = n_0 \exp(-t/\tau_n) \tag{3}$$

$$C = \frac{C_0 \frac{1-\alpha}{\alpha} \exp(-t/\tau_n)}{1 + \frac{1-\alpha}{\alpha} \exp(-t/\tau_n)} \tag{4}$$

$$p = \frac{C_0 \exp(-t/\tau_p)}{1 + \frac{1-\alpha}{\alpha} \exp(-t/\tau_n)} \tag{5}$$

From the above equations, the ratio of the polymerization rates with and without the field can be obtained:

$$\frac{W_E}{W_0} = \frac{\exp(-t/\tau_n) + \left[\frac{k_p''}{k_p'} \exp(-t/\tau_p) - \exp(-t/\tau_n)\right] \alpha}{\left(\frac{k_p''}{k_p'} - 1\right)[1 - \exp(-t/\tau_n)]\alpha^2 + [1 + \frac{k_p''}{k_p'} \exp(-t/\tau_n) - 2\exp(-t/\tau_n)]\alpha + \exp(-t/\tau_n)} \tag{6}$$

To simplify the equations we introduce the following relations:

$$\frac{t}{\tau_p} = x; \quad \frac{\tau_p}{\tau_n} = \frac{\mu_n}{\mu_p} = \mu; \quad \xi = \frac{k_p''}{k_p'}$$

And so Eq. (6) takes the form:

$$\frac{W_E}{W_0} = \frac{e^{-\mu x} + (\xi e^{-x} - e^{-\mu x})\alpha}{(\xi - 1)(1 - e^{-\mu x})\alpha^2 + (1 + \xi e^{-\mu x} - 2e^{-\mu x})\alpha + e^{-\mu x}} \tag{7}$$

These expressions are valid for $t \leq t_0$, where t_0 is the polarization time. But, since there is no analytical dependence of t_0 on the system's parameters, the value of t_0 must be determined experimentally. In particular, we found that the time during which the rate of the polymerization changes coincides with the time of the current decrease, which opens possibilities for determining t_0.

The voltage application time aiming at the determination of kinetic parameters with the aid of the proposed method should be discussed. In principle, the influence of the field can be studied at any stage of the process—in the beginning, in the middle, or when the process is over—it all depends on the parameters of the polymerizing system. In our experiments the field was applied after the system reached the maximum rate of polymerization, for we considered the initiation to be over by this time. This very case is analyzed later.

Let us return to Eq. (6) and try to find conditions for increasing the rate of polymerization. The solution of inequality $W_E/W_0 > 1$ leads to

$$\alpha < \alpha^* = \frac{e^{-\mu x} + \xi(e^{-x} - e^{-\mu x})}{(\xi - 1)(1 - e^{-\mu x})} \tag{8}$$

where α^* is a critical degree of dissociation of active centers. Thus it can be seen that there are combinations of parameters α, μ, and ξ when a rate increase is impossible, Figures 1 and 2 present the dependence of α^* on ξ and μ, respectively. Strong dependence is observed for low values of ξ and μ. It is believed that for actual systems $\mu > 10$, so that experiments are carried out in the region of weak dependence of α^* on μ. The situation is different with respect to ξ. For living anionic systems, $\xi \approx 10^3$ and $\alpha \ll 1$, so

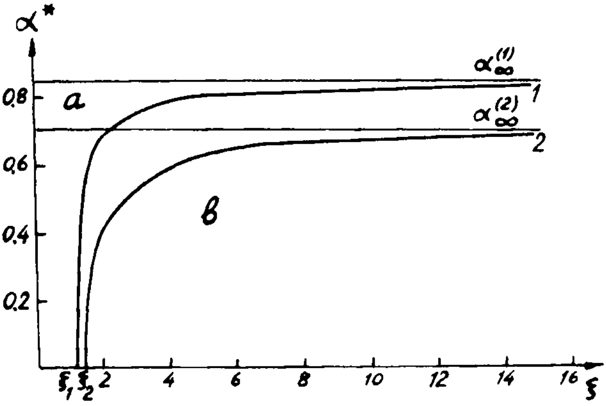

FIG. 1. Regions of the rate increase in the plane α^*- ξ. α is the maximum degree of dissociation when the rate increase can be observed. $\xi = k_p''/k_p'$, (1) $\mu = 10$, $t/\tau_n = 1$; (2) $\mu = 4$, $t/\tau_n = 0.4$; $x = t/\tau_p = 0.1$, a = rate decrease, and b = rate increase.

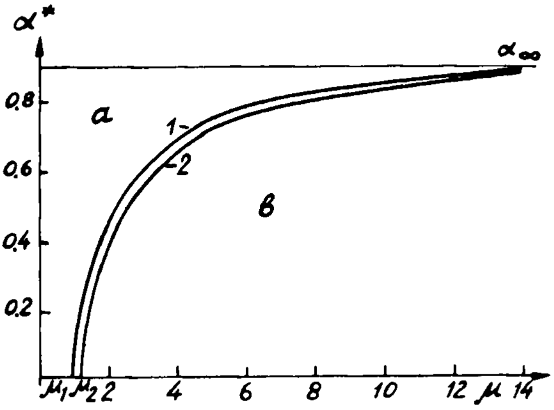

FIG. 2. Regions of the rate increase in the plane α^*-μ. $\xi = k_p''/k_p'$, $\mu = (\mu_p/\mu_n)$, the ratio of the mobilities; (1) $\xi = 10^2$, (2) - $\xi = 10$, $x = t/\tau_p = 0.1$, a = rate decrease; and b = rate increase.

we are sure to be in the region of the rate increase. For cationic systems, $\xi \approx 2$ to 10 and α may vary from 0 to 1, so either an increase or decrease of the polymerization rate can be observed. In particular, we can conclude that by changing α (which can be done by changing the dielectric constant of solvent), we can move from the region of rate increase to the region of rate decrease. Moving vertically in the plane α^* -ξ, it is possible to find the border between the two regions, which will give us the kinetic parameters of the system, for example, ξ.

Figures 3 and 4 represent the calculated dependencies of W_E/W_0 on ξ and α, respectively. A general principle is observed: the greater α and ξ, the greater is the rate increase. On the other hand, at low values of α and ξ (see Fig. 4 curves 1, 1', and 4 of Fig. 3) the polymerization rate can remain constant.

Here we must point out that living anionic systems should be treated separately due to special features of their analysis. In this case, the rate of polymerization is written in the form

$$W = k_p'CM + k_p''pM = \left(k_p' + \frac{k_p''\sqrt{K}}{\sqrt{C}}\right)CM = k_pCM \qquad (9)$$

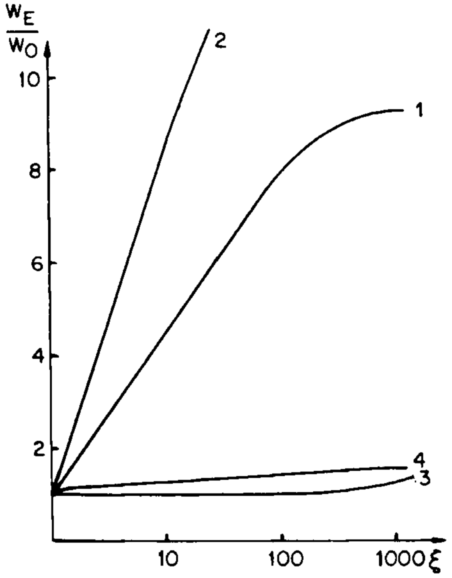

FIG. 3. Dependence of the rate increase W_E/W_0 on the ratio of the rate constants $\xi = k_p''/k_p'$. (1) $\mu = 100$, $\alpha = 0.1$; (2) $\mu = 100$, $\alpha = 10^{-3}$; (3) $\mu = 10$, $\alpha = 10^{-3}$; (4) $\mu = 10$, $\alpha = 0.1$; $x = t/\tau_p = 0.05$; (1, 2) $t/\tau_n = 5$; (3, 4) $t/\tau_n = 0.5$; $\mu = (\mu_p/\mu_n)$, the ratio of the mobilities; and α is the degree of dissociation of active centers.

since $\alpha \ll 1$. The values of C and M are generally known from spectroscopic measurements, so that linear dependence of k_p on $1/\sqrt{C}$ gives the values of k_p' and k_p''.

As noted earlier, Ise et al., while studying the electric field effect on living anionic polymerization, found that the electric field increased the slope while leaving the intercept constant [23]. The value of K remains the same in low electric fields, and spectroscopic measurements showed no change in the concentration of living ends. These facts led them to the conclusion that the field increased k_p'', the rate constant of free ions, and this supported the concept of ion desolvation in the external field.

But, as we found, the same result can be explained by assuming

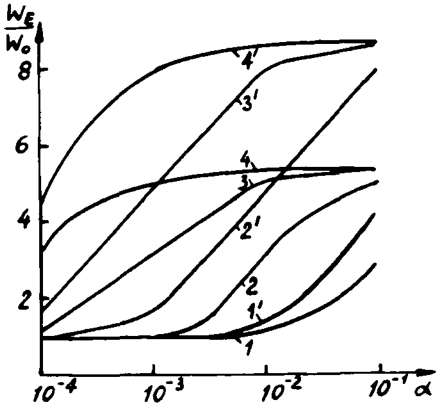

FIG. 4. Dependence of the rate increase W_E/E_0 on the degree of dissociation of active centers (α). (1, 1') $\xi = 10$; (2, 2') $\xi = 10^2$; (3, 3') $\xi = 10^3$; (4, 4') $\xi = 10^4$; (1-4) $t/\tau_n = 1.5$; (1'-4') $t/\tau_n = 2$; $x = t/\tau_p = 0.02$.

that the field shifts the equilibrium between ion-pairs and free ions. By substituting the values of p and C into Eq. (9) and taking $\alpha \approx 10^{-3} \ll 1$, we obtain

$$k_p = k_p' + k_p'' \frac{\sqrt{K}}{\sqrt{C}} \exp(t/\tau_p) = k_p' + \frac{1}{\sqrt{C}} \tan \varphi_E$$

Taking the logarithm of the ratio of slopes with and without the field (in Ise's notations, $k_{p,E}''/k_{p,0}''$,) which is equal to $\exp(t/\tau_p)$, we have

$$\ln \frac{k_{p,E}''}{k_{p,0}''} = \frac{t}{\tau_p} = \frac{\mu_p t}{\ell} E = \ln \frac{\tan \varphi_E}{\tan \varphi_0}$$

It is clear that the logarithm depends linearly on the electric field E. Figures 5 and 6 show that this is really so, though not for every system, which may be due to their individual properties. In particular, as follows from Fig. 7, the field effect $k_{p,E}/k_{p,0}$

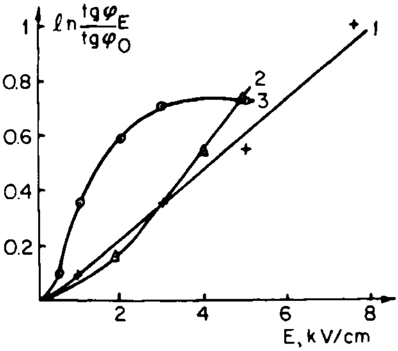

FIG. 5. Field effect on the living polymerization of styrene in binary mixtures of benzene-THF. Initiator: Li-salt of living polystyrene. THF content (vol%): (1) 40; (2) 50; and (3) 60 [23].

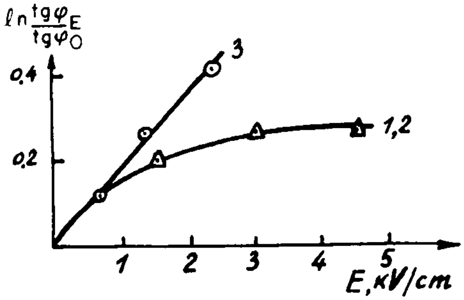

FIG. 6. Field effect on the polymerization of o-methylstyrene in MTHF. Initiators: alkali metal salts of living polystyrene. Counterions: (1) Na^+; (2) K^+; and (3) Li^+ [34].

depends strongly on the degree of dissociation of active centers. Comparing Figs. 5 and 7, we see that both $k_{p,E}/k_{p,0}$ and $\tan\varphi_E/\tan\varphi_0$ increase with an increase of the dielectric constant of the system. Thus the above experimental facts are in agreement with the theoretical results displayed by Fig. 3. Finally, we note that the relative change in the living ends concentration $\Delta C/C \approx \alpha(e^{t/\tau} - 1) \approx \alpha \ll 1$ and apparently lies beyond the sensitivity

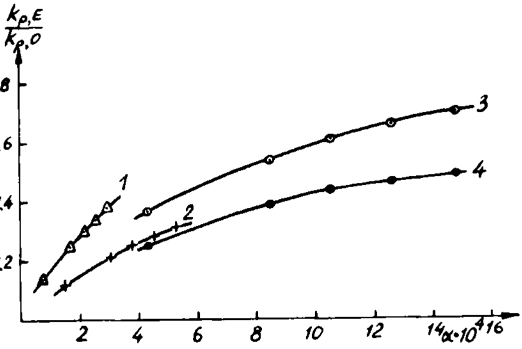

FIG. 7. Field effect $k_{p,E}/k_{p,0}$ and the degree of dissociation α for the polymerization of styrene in binary mixtures of THF-benzene. Initiator: Li-salt of living polystyrene [23]. THF content (vol%):

Curve 1 (40): $\xi = 1580$ } E = 5 kV/cm
Curve 2 (50): $\xi = 1130$ }
Curve 3 (60): $\xi = 1040$; E = 5 kV/cm
Curve 4 (60): $\xi = 1040$; E = 2 kV/cm

limits of spectroscopic measurements and so cannot be observed experimentally.

When $\alpha \approx 1$, the case needs separate consideration. A new effect can be expected, since Equilibrium (1) is completely shifted to the right. This means that not only the redistribution of counterions, but also that of growing macroions should be taken into account. To simplify the analysis, let us assume that voltage is applied after initiation has been completed, i.e., the concentration of active centers depends mostly on termination reactions $p_n \xrightarrow{k_t} P_n$, where P_n is the polymer of length n, and k_t is the termination rate constant, which includes all possible termination processes.

After the electric field has been applied, active centers move to the electrodes, which increases the termination rate constant. Thus we have without field:

$$\frac{dp}{dt} = -k_t p$$

and in the field:

$$\frac{dp}{dt} = -k_t p - \frac{p}{\tau_p} = -\left(k_t + \frac{1}{\tau_p}\right) p$$

Their solutions are:

$$p = p_0 \exp(-k_t p)$$

$$p = p_0 \exp\left\{-\left(k_t + \frac{1}{\tau_p}\right) t\right\}$$

For the rate of polymerization, we have

$$W_0 = -\frac{dM}{dt} = k_p''Mp_0 \exp(-k_t t)$$

$$W_E = -\frac{dM}{dt} = k_p''Mp_0 \exp\left\{-(k_t + 1/\tau_p)t\right\} \tag{10}$$

Integrating these equations from t = 0 to t = ∞, we obtain, without field:

$$\ln \frac{M_0}{M_\infty} = \frac{k_p''p_0}{k_t}$$

and in the field:

$$\ln \frac{M_0}{M_\infty} = \frac{k_p p_0''}{k_t + \frac{1}{1/\tau_p}}$$

Thus we see that the final degree of conversion is lower in the field, i.e., M_∞ is higher. And so, by comparing M_∞ in the field and without it, we may find k_t from the relation

$$\frac{\left(\ln \frac{M_0}{M_\infty}\right)_0}{\left(\ln \frac{M_0}{M_\infty}\right)_E} = 1 + \frac{1}{k_t \tau_p} \tag{11}$$

if τ_p is known.

Now we shall see the effect of the external electric field on the degree of polymerization.

For this we assume the following polymerization scheme:

$$\left.\begin{aligned} & C_n + M \xrightarrow{k_p'} C_{n+1} \\ & P_n + M \xrightarrow{k_p''} P_{n+1} \end{aligned}\right\} \text{chain propagation}$$

$$\left.\begin{aligned} & C_n + M \xrightarrow{k_{tm}'} P_n + C_1 \\ & P_n + M \xrightarrow{k_{tm}''} P_n + p_1 \end{aligned}\right\} \text{chain transfer}$$

$$\left.\begin{aligned} & C_n \xrightarrow{k_t'} P_n \\ & P_n + n \xrightarrow{k_t''} P_n \end{aligned}\right\} \text{chain termination}$$

The rates of the respective elementary polymerization reactions are

$$\begin{aligned} W_p &= k_p'CM + k_p''pM \\ W_{tm} &= k_{tm}'CM + k_{tm}''pM \qquad (12) \\ W_t &= k_t'C + k_t''p \end{aligned}$$

We now obtain the expression for the average degree of polymerization in an electric field:

$$\frac{1}{\overline{P}} = \frac{W_{tm} + W_t}{W_p}$$

$$= \frac{k_{tm}' + k_{tm}'' \frac{\alpha}{1-\alpha} \exp(-t/\tau_n)}{k_p' + k_p'' \frac{\alpha}{1-\alpha} \exp(-t/\tau_n)} + \frac{k_t' + k_t'' K}{k_p' + k_p'' \frac{\alpha}{1-\alpha} \exp(-t/\tau_n)} \frac{1}{M}$$

$$= a_E + b_E \frac{1}{M}$$

The expression for $\overline{P}$ without the field is the same when the factor $\exp(-t/\tau_n)$ is omitted. That means that $b_E < b_0$ always, while $a_E < a_0$ only if $k_p''/k_p' > k_{tm}''/k_{tm}'$. This has been experimentally observed for polymerizations of styrene, α-methoxystyrene, and isobutyl vinyl ether [43].

Thus we see that the degree of polymerization increases under an electric field.

(When this paper was being prepared for print, a paper by Giusti et al. [36] came to our attention in which the rate increase of cationic polymerization under an electric field was ascribed to electroinitiation, i.e., the generation of new active centers due to the discharge of counterions at the electrodes. We agree with these assumptions as regards the rate increase and, moreover, we have experimentally proved it. This question will be discussed in detail in a future paper.)

CONCLUSION

The expressions obtained describe changes in the kinetic characteristics of ionic polymerization systems. They may be applied to analyze published experimental data. As noted above, the absence of data on currents and original kinetic curves make quantitative analysis difficult.

REFERENCES

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

[2] I. Sakurada, N. Ise, Y. Tanaka, and I. Hayashi, J. Polym. Sci., A-1, 4, 2801 (1966).

[3] I. Sakurada, N. Ise, and I. Hayashi, J. Macromol. Sci., A1, 1039 (1967).

[4] I. Sakurada, N. Ise, and Y. Tanaka, Polymer, 8, 625 (1967).

[5] I. Sakurada, Y. Tanaka, and N. Ise, J. Polym. Sci., A-1, 6, 1463 (1968).
[6] I. Sakurada, N. Ise, and S. Hori, Kobunshi Kagaku, 24, 145 (1967).
[7] I. Sakurada, N. Ise, T. Hayashi, and M. Nakao, Ibid., 25, 41 (1968).
[8] I. Sakurada, N. Ise, I. Hayashi, and M. Nakao, Macromolecules, 1, 265 (1968).
[9] N. Ise, I. Hayaski, S. Shen, and I. Sakurada, Makromol. Chem., 117, 180 (1968).
[10] Y. Tanaka, N. Ise, and I. Sakurada, Macromolecules, 2, 215 (1969).
[11] N. Ise, Advan. Polym. Sci., 6, 347 (1969).
[12] P. Cerrai, F. Andruzzi, and P. Guisti, Makromol. Chem., 117, 128 (1968).
[13] P. Cerrai, F. Andruzzi, and P. Giusti, Chim. Ind., 51, 687 (1969).
[14] F. Andruzzi, P. Cerrai, M. di Maina, and P. Giusti, Ibid., 52, 146 (1970).
[15] P. Giusti, P. Cerrai, F. Andruzzi, and P. Magagnini, Eur. Polym. J., 7, 165 (1971).
[16] I. Sakurada, N. Ise, and S. Kawabata, Makromol. Chem., 97, 17 (1966).
[17] P. Giusti, P. Cerrai, M. Tricoli, P. Magagnini, and F. Andruzzi, Ibid., 133, 299 (1970).
[18] A. T. Ponomarenko, L. A. Tkachenko, and N. S. Enikolopyan, Vysokomol. Soedin., B, 14, 155 (1972).
[19] A. T. Ponomarenko, L. A. Tkachenko, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, 196, 393 (1971).
[20] A. T. Ponomarenko, L. S. Zarkhin, V. G. Shevchenko, L. A. Tkachenko, and N. S. Enikolopyan, Reports of the International Symposium on Advances in Ionic Polymerization, Jablonna, Poland, 1972, B13.
[21] A. T. Ponomarenko, V. G. Shevchenko, and N. V. Koslova, Reports of the XVIIIth Conference on Polymers, Nauka, Moscow, 1973, p. 54.
[22] A. T. Ponomarenko, V. G. Shevchenko, and N. S. Enikolopyan, Reports of the Vth Conference on Physicochemical Analysis of Liquid Systems, Kaunas, 1973, p. 26.
[23] N. Ise, H. Hirohara, T. Makino, and I. Sakurada, J. Phys. Chem., 72, 4543 (1968).
[24] M. Wien, Ann. Phys., 83, 327, 795 (1927).
[25] M. Wien, Phys. Z., 28, 751, 834 (1927).
[26] H. Eckstrom and C. Shmelzer, Chem. Rev., 24, 367 (1939).

[27] H. Hirohara, M. Nakayama, K. Takaya, and N. Ise, Trans. Faraday Soc., 66, 1165 (1970).
[28] D. Bhattacharyya, C. Lec, J. Smid, and M. Szwarc, J. Phys. Chem., 69, 612 (1965).
[29] T. Shimomura, K. Tolle, J. Smid, and M. Szwarc, J. Amer. Chem. Soc., 89, 796 (1967).
[30] F. Cafasso and B. Sundheim, J. Chem. Phys., 31, 809 (1959).
[31] T. Hogen-Esch and J. Smid, J. Amer. Chem. Soc., 88, 307 (1966).
[32] T. Shimomura, J. Smid, and M. Szwarc, Ibid., 89, 5743 (1967).
[33] H. Hirohara, K. Takaya, M. Nakayama, and N. Ise, Trans. Faraday Soc., 66, 3163 (1970).
[34] L. Onsager, J. Chem. Phys., 2, 599 (1934).
[35] V. L. Talrose, "Radiolysis in Electric and Magnetic Fields," Paper Presented at the Gordon Conference, 6/VIII, 1966.
[36] P. Giusti, Makromol. Chem., 175(4), 1157 (1974).
[37] G. Jaffe, Ann. Phys., 16, 217 (1933).
[38] J. J. Thomson, Conduction of Electricity Through Gases, London, 1929.
[39] G. V. Karachevtsev, I. K. Larin, and V. L. Talrose, Khim. Vys. Energ., 2, 524 (1968).
[40] P. Debye, Trans. Electrochem. Soc., 82, 265 (1942).
[41] G. V. Karachevtsev, A. M. Kogan, I. K. Larin, E. M. Mostovaya, and V. L. Talrose, Khim. Vys. Energ., 4, 277 (1970).
[42] N. Ise, H. Hirohara, T. Makino, K. Takaya, and M. Nakayama, J. Phys. Chem., 74, 606 (1970).
[43] T. Higashimura and N. Kanoh, Kobunshi Kagaku, 23, 114 (1966).
[44] J. Tanaka, Thesis, University of Kyoto, Japan.
[45] K. Takaya, H. Hirohara, and N. Ise, Makromol. Chem., 139, 277 (1970).

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