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Some Peculiarities of Macrozwitterion Polymerization

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The authors dedicate the following article to Professor A. A. Berlin on the occasion of his 60th birthday.

ABSTRACT

Using elementary analysis, NMR on ^{31}P and ^{1}H nuclei, and electroconductivity methods, the acrylonitrile, methacrylonitrile, formaldehyde, and β-propiolactone anionic polymerization in the presence of triethylphosphine is shown to follow the macrozwitterion mechanism: quartary phosphonium being on one end of a polymer chain and the growing anion on the other. The number of covalent bonds through the whole polymer chain between charges forming the active center increases with the propagation reaction. The active centers stationary concentration in the system is low when connected with both the slow initiation reaction and with the fast active centers termination reaction. Thus the ion interaction of different growing polymer chains can be ignored. The active centers parts occurring in the form of ion pairs (the ends are near and form the "cyclic") and of free ions (the ends are separated) are determined by the monomolecular

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equilibrium, and its constant depends upon the macrozwitterion polymerization degree $K_d^{(n)} = K_d^{(I)} n^{3/2}$. Such constant dependence upon the chain length affords the macrozwitterion self-accelerated propagation with its length, as the free ion reactivity is more than that of ion pairs. The self-accelerated chain propagation effect shows up as an increase of polymerization initial rate order and polymer molecular weight in the monomer concentration. This effect can be avoided by the introduction of electrolyte into the system, which dissociates into ions and transforms all cyclic ion pairs into the linear form, the latter dissociating independently of chain length. The strict mathematical analysis of stationary and nonstationary polymerization kinetics made it possible to determine all the elementary constants separately: $K_i = 5.6 \times 10^{-4}$ liters/(mole)(min); $K_- = 2.5 \times 10^4$ liter/(mole)(min); $K_\pm =$ 2.0 liters/(mole)(min); $K_t = 0.84$/min; $K_t^1 = 4$/min; $K_d^{(I)} = 10^{-4}$; $K_3 = 0.07 \times 10^{-4}$ mole/liter.

The results of ionic polymerization studies in recent years have led to the concept that the active centers could be of different types: free ions, contact, and solvent-separated ion pairs. The existence of all these active centers was demonstrated and their reactivity was measured for the case of vinyl monomers polymerization, using "living" polymerization as an example. The reactivity changes as follows: Free ions > solvent-separated ion pairs ≫ contact ion pairs.

Active centers are in an equilibrium which depends upon the medium, counterion type and size, temperature, etc. but is independent of the polymer molecule [1]. Similar results were obtained for the anionic polymerization of episulfides [2, 3] and the cationic polymerization of heterocycles [4]. These regularities were referred to systems with ions, producing active centers, bonded only electrostatistically:

$$\sim\sim\sim M^{\pm}, X^{\mp} \rightleftharpoons \sim\sim\sim M^{\pm} \parallel X^{\mp} \rightleftharpoons \sim\sim\sim M^{\pm} + X^{\mp}$$

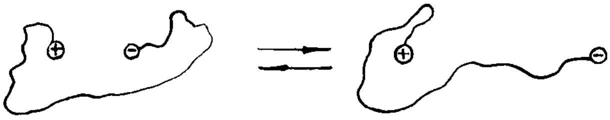
Polymerization by a macrozwitterion mechanism is a peculiar case which is accompanied by charge separation within one molecule, the opposite charges being interconnected not only electrostatically but also covalently. The propagation reaction results in an increase of the number of covalent bonds between charges.

The zwitterion mechanism was proposed for both cationic and anionic polymerizations initiated by uncharged Lewis acids and bases. The possibility of the realization of such a mechanism depends upon the monomer-catalyst bond energy, medium polarity, length and elasticity of monomer link, etc. Strict proof of the polymerization process performance by the zwitterion mechanism was obtained for acrylonitrile, methacrylonitrile, formaldehyde, and β-propiolactone in the presence of tertiary phosphines and amines [5-10]. At first the polymerization was shown to follow the anionic mechanism: representative inhibitors of radical polymerization such as diphenylpicrilhydrazine and hydroquinone do not influence polymerization, and water and carbon dioxide depress it. On the basis of elementary analysis data of polymers before and after reprecipitation, phosphorus was found in all samples. The content did not change after reprecipitation, which shows a phosphorus-polymer chain chemical binding. The phosphorus content depends only on the polymer molecular weight, with one phosphorus atom for each molecule. The valency state of phosphorus changes as a result of the initiation reaction: its three valency state changes to quaternary phosphonium in a compound that has been found by NMR to have ^{31}P and ^{1}H nuclei. An increase of electroconductivity with the polymerization reaction provides support for these results and also suggests that initiation is slow.

It might be well to point out the basic differences between the zwitterion mechanism and that of an entirely electrostatic interaction between charges which produces an active center:

1. The initiation reaction, which is an interaction of two neutral molecules—monomer and initiator—affords strong chemical binding between monomer and initiator. Charge separation occurs within one molecule. These conditions essentially restrict the number of possible monomer-initiator pairs capable of bipolar ion formation.
2. The propagation reaction may proceed on both ion pairs and free ions, yet the transfer of one type of active center into another in zwitterion polymerization depends on the degree of active center polymerization.

Let us now formulate the expression for the active centers equilibrium constant. To do this, the isolated polymer zwitterion in solution should be discussed:



A polymer molecule in solution is in the form of a twisted roll, and the distance between its ends is determined by the conventional Gaussian distribution. In this case the longer the polymer chain, the greater the distance between its ends. Electrostatic interaction between ions should draw the ends closer together and produce some kind of ion pair, which results, however, in a lower chain entropy. The probability of the existence of active centers in the form of ion pairs (when the ends are close together) and of free ions (when the distance between the ends of a polymer molecule is sufficiently great) is conditioned by the free energy change due to: 1) entropy change in passing from the normal Gaussian distance between the ends to the state when the ends are close enough to form a "cyclic," and 2) change in the Coulomb interaction energy in such a transition.

This probably depends upon the polymer chain length. The equilibrium monomolecular constant for ion pairs-free ions is defined in this case by

$$\ln K = -\frac{\Delta F_e + \Delta F_c}{kT} \tag{1}$$

where ΔF_e is the change in the electrostatic free energy, and ΔF_c is the change in the chain free energy when passing from an ion pair to free ions.

According to the statistics of a polymer chain in solution, the chain free energy change for such a transition is

$$\Delta F_c = kT \ln\left[\left(\frac{3}{2\pi n \ell^2}\right)^{3/2} \nu_s \right]$$

where ν_s is the effective volume of an ionic pair, and ℓ and r are the length and the number of segments in a polymer zwitterion, respectively [11].

From these equations the following expression for the constant of transition of polymer zwitterion with a degree of polymerization n from an ion pair to free ions was obtained:

$$K_d^{(n)} = K_d^{(1)} n^{3/2} \tag{2}$$

As seen from this equation, a probability of active centers occurring in the form of free ions increases with the polymer zwitterion length. For vinyl monomers the propagation rate constant on a free ion is greater than on an ion pair. Thus the propagation rate of a given polymer chain increases with the macromolecule length. This is the main specificity of zwitterion polymerization.

Slow initiation is a specific of acrylonitrile and methacrylonitrile polymerization in the presence of triethylphosphine in DMF, and the propagation and termination reactions are the fast ones. The stationary concentration of active centers in the system is low, thus at first one may ignore the interaction of ions of different growing polymer zwitterions, i.e., a free ion may produce an ion pair only with its "own" counterion. The free ion concentration (R_n) and the concentration of ion pairs (r_n) are related by

$$R_r = K_d^{(n)} r_n \tag{3}$$

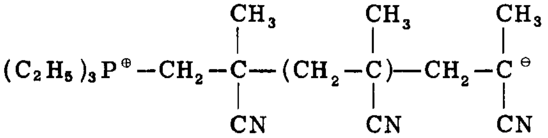
Kinetic regularities of acrylonitrile and methacrylonitrile polymerization in the presence of triethylphosphine, the molecular weight analysis of the forming polymers vs medium polarity, monomer and polymer concentrations, and electrolyte additions have shown the presence of two types of active centers of different reactivity in the system of free ions and ion pairs.

Starting from this, the kinetic scheme of polymerization by zwitterion mechanism can be written as

$$\begin{gathered}
C + M \xrightarrow{K_i} r_1 \\
r_1 + M \xrightarrow{K_\pm} r_2 \\
r_n + M \xrightarrow{K_\pm} r_{n+1} \\
r_n \xrightleftharpoons{K_d^{(n)}} R_n \\
R_n + M \xrightarrow{K_-} R_{n+1} \\
r_n \xrightarrow{K_t} P_n \\
R_n \xrightarrow{K_t'} P_n
\end{gathered} \tag{4}$$

where C, M, r_n, R_n, and P_n are the concentrations of a catalyst monomer, ion pairs, free ions, and dead polymer of n degree of polymerization, respectively; K is the corresponding rate constants; and $K_d^{(n)}$ is the monomolecular constant of ion pair transition into free ions for the active center of degree of polymerization n.

In the case of methacrylonitrile, the growing macrozwitterion has the structure



$$(C_2H_5)_3P^{\oplus}-CH_2-\underset{CN}{\overset{CH_3}{C}}-(CH_2-\underset{CN}{\overset{CH_3}{C}})-CH_2-\underset{CN}{\overset{CH_3}{C}}{}^{\ominus}$$

Ion pairs reactivity is much less than that of the free ions: additions of $Ph_3P^+MeI^-$ electrolyte dissociating to ions in solution, convert all cyclic ion pairs into the linear form, and depress the dissociation of these linear ion pairs. The free carbanion concentration decreases sharply and the polymerization reaction is depressed.

The expression for the polymerization rate vs monomer and initiator concentrations is then

$$-\,dM/dt = K_{\pm}M \sum r_n + K_{-}M \sum R_n \tag{5}$$

Ion pair and free ion concentrations can be obtained from the kinetic equations for the active center concentrations to a stationary approximation:

$$\frac{d(r_n + R_n)}{dt} = K_{\pm}Mr_{n-1} - K_{\pm}Mr_n + K_{-}MR_{n-1} - K_{-}MR_n - K_t r_n - K_t'R_n = 0$$

Assuming that the free ion and ion pair concentrations are related by Eq. (3), i.e., the rate of reaching equilibrium is much greater than the propagation rate, we obtain the following expression for r_n:

$$r_n = \frac{K_iCM}{K_{\pm}M + K_d^{(1)}n^{3/2}K_{-}M}\exp\left[-\sum_{x=1}^{n-1}\frac{K_t + K_t'K_d^{(1)}x^{3/2}}{K_{\pm}M + K_{-}MK_d^{(1)}x^{3/2}}\right] \tag{6}$$

Analysis of this equation was performed in an earlier paper [12]:

1. $K_t' \neq 0$, i.e., free ion termination cannot be ignored.

2. $K_-/K_t' > K_\pm/K_t$, i.e., the contribution of free ions to polymerization is greater than that of ion pairs.

3. When n is small, the ionic pairs concentration agrees with the normal exponential distribution $r_n \sim \exp(-n/P_\pm)$, and when n is big the free ion concentration R_n ($P_\pm = K_\pm M/K_t$; $P_- = K_- M/K_t'$) agrees with the $\exp(-n/P_-)$ distribution.

The total concentrations of ion pairs and free ions are then

$$\sum r_n = 2 \frac{K_i CM}{K_t' P_- K_d^{(1)}} \exp\left[- \frac{2K_t}{K_- K_d^{(1)} M}\right]$$

$$\sum R_n = \frac{K_i CM}{K_t'} \exp\left[- \frac{2K_t}{K_- K_d^{(1)} M}\right] \tag{7}$$

The final expression for the polymerization initial rate as a function of monomer and initiator concentration is

$$W_0 = \frac{K_i K_-}{K_t'} C_0 M_0^2 \exp\left[- \frac{2K_t}{K_- K_d^{(1)} M_0}\right] \tag{8}$$

It follows from Eq. (8) that the polymerization rate is proportional to the catalyst concentration. The formal rate order in the monomer can be greater than 2, and deviation from the second order increases with an increase in the ($K_t/K_- K_d^{(1)}$) parameter. Such a polymerization rate dependence upon the monomer concentration is explained by the fact that the propagation rate of a given polymer chain increases with its length, since a probability of the active center occurrence in the form of a more reactive free ion is greater.

Actually the polymerization rate is proportional to the initiator concentration (Fig. 1). Molecular weight is also seen to be independent of the catalyst concentration. The formal order of the polymerization rate in the monomer is equal to 2.5. The linearity of the initial rate in coordinates $\log (W_0/M_0^2)/(1/M_0)$ is shown in Fig. 2. This dependence is linear, and it enables the following constants ratios to be determined:

$$\frac{K_i K_-}{K_t'} = 3.5\ \text{liter}^2/(\text{mole}^2)(\text{min}); \qquad \frac{K_t}{K_- K_d^{(1)}} = 0.3\ \text{mole/liter}$$

The polymer molecular weight also increases more than first order with the monomer concentration and is proportional to the latter to the 1.7 power (Fig. 3). It is also connected with self-accelerated growth of the polymer chain.

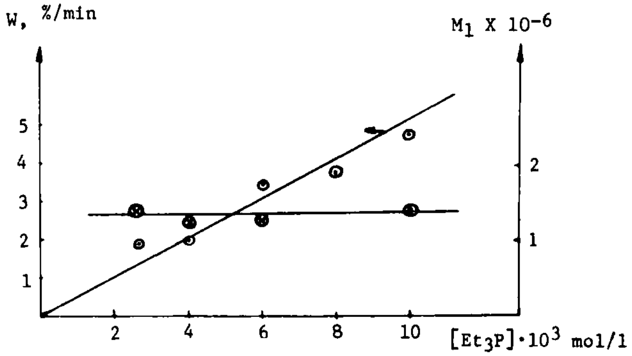


FIG. 1. Polymethacrylonitrile polymerization rate and molecular weight vs initiator concentration: [MAN] = 2.1 moles/liter, 40.8° C, DMF.

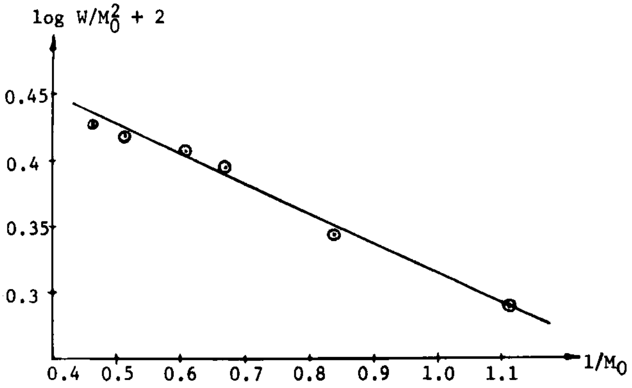


FIG. 2. Logarithmic anamorphosis of the initial rate vs monomer concentration: $[Et_3P] = 10^{-2}$ mole/liter, 40.8°C, DMF.

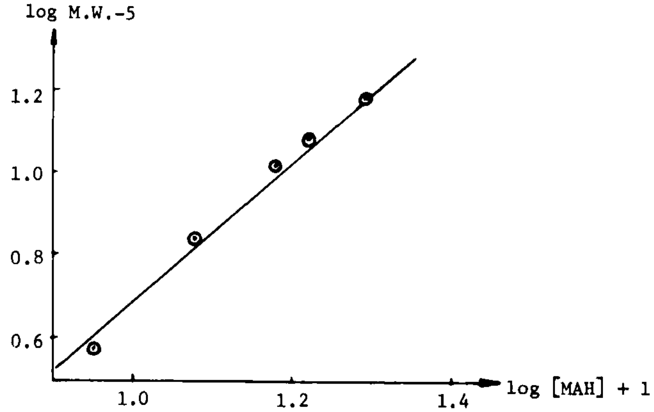


FIG. 3. Polymethacrylonitrile molecular weight vs monomer concentration: $[Et_3P] = 10^{-2}$ mole/liter conversion 26 to 28%.

A confirmation of self-acceleration in the polymer chain growth is the decrease of the polymerization initial rate order in the monomer from 2.5 to 2 in the presence of electrolyte. The latter transforms all "cyclic" ionic pairs  into the "linear" ones ∼∼∼∼∼ ⊖ ⊕ for which the dissociation constant is independent of the macromolecule length.

The polymerization rate and the polymer molecular weight as a function of electrolyte ($Ph_3MeP^+I^-$) concentration provided determination of the initiation rate constant $K_i = 5.6 \times 10^{-4}$ liter/(mole)(min) and of the relations

$$K_-/K_t' = 6.25 \times 10^3 \text{ mole/liter}; \qquad K_t/K_-K_3 = 4.8$$

where K_3 is the dissociation constant of "linear" ion pairs R_4P^+, ^-C ∼∼∼∼∼.

The above rate constant relationships are obtained from the dependencies of polymerization initial stationary rates. The condition of stationarity makes it impossible to determine the propagation and termination rate constants separately. Yet in the beginning of the process there is an induction period (Fig. 4) whose duration depends upon the monomer concentration and is independent of the catalyst concentration. If the induction period is connected with the "intrinsic" nonstationarity on active centers and not with the influence of the

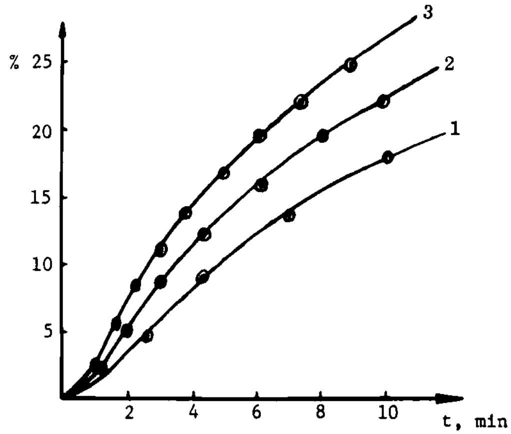


FIG. 4. Methacrylonitrile polymerization kinetic curves $[Et_3P] = 10^{-2}$ mole/liter, 40.8°C, DMF. [MAN] mole/liter: (1) 1.2; (2) 1.5; and (3) 1.95.

inhibitor introduced into the reaction medium with the solvent, monomer, or catalyst, then the mathematical analysis of the polymerization scheme with an allowance for the nonstationarity of the active center concentration should provide for the separate determination of some constants.

Let us discuss the possible reasons for the induction period and show that its nature is connected with the nonstationarity of the active center concentration.

One of the possible reasons for the induction period appearance is the presence in the system of inhibitor which is consumed during the induction period. Water can be such an inhibitor and is always in the system. However, water additions to the polymerization system do not cause any signficant change in the induction period. The stationary rate of polymerization and the molecular weight of polymethacrylonitrile decrease proportionally to the concentration of water added. Thus the presence of water traces (beyond the sensitivity limits of the Fisher method) cannot be the reason for the appearance of the induction period.

Let us consider the case when the system contains an insignificant amount of some effective inhibitor (I) of an unknown nature (solvent, monomer, and catalyst are chromatographically pure). Inhibitor consumption in the course of the induction period is according to the $K_i C_0 M_0 \tau = I_0$ condition. This inhibitor can be introduced into the system with monomer, solvent, and catalyst. The analysis of the polymerization scheme when initiation is slow and termination reaction is rapid leads, under stationary conditions, to the conclusion that in the case where the inhibitor is introduced into the system with the monomer, the induction period (τ) should be inversely proportional to the catalyst initial concentration ($\tau \sim 1/C_0$). In the case where the inhibitor is introduced with the solvent, the induction period should be inversely proportional to the monomer and catalyst initial concentrations ($\tau \sim 1/C_0M_0$). However, the value of the induction period is independent of the catalyst concentration. In case the inhibitor is present in the catalyst and is introduced into the reaction system together with the catalyst, the value of the induction period should be inversely proportional to the monomer concentration ($\tau \sim 1/M_0$). The induction period value vs the inverse initial concentration of the monomer is given in Fig. 5. Actually this dependence is linear, and it can be supposed that the inhibitor is introduced into the reaction medium together with the catalyst. Two reasons, however, make us doubt this: 1) the straight line in Fig. 5 does not proceed to zero when $1/M_0 \rightarrow 0$; and 2) the catalyst concentration under our conditions is not more than 10^{-2} mole/liter and this means that the most possible inhibitor concentration is not more than 10^{-6} mole/liter. In the case where one inhibitor molecule affords only one polymer chain termination, the concentration of dead polymer chains in the induction period cannot be more than 10^{-6} mole/liter. However, in the induction period the concentration of polymer chains exceeds 10^{-5} mole/liter, and the molecular weight of polymethacrylonitrile continues to increase further during the time equal to 2 to 3 induction periods. These results obviate the possibility of explaining induction periods by the presence of inhibitor in the system.

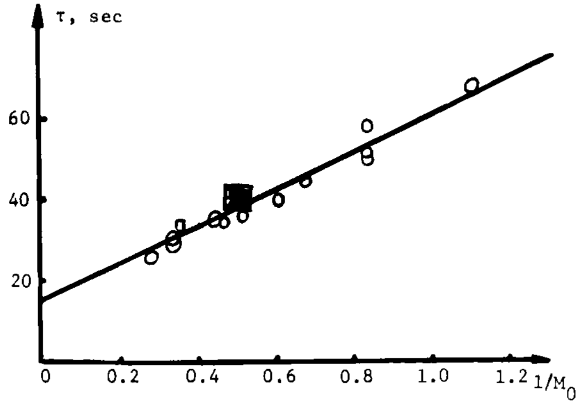


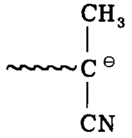
FIG. 5. Induction period vs $1/M_0$.

Strict mathematical analysis of the polymerization kinetic scheme including nonstationarity on the active centers and consideration of the dependence of the ion pair-free ion equilibrium constant upon the length of the growing polymer zwitterion provides the following expression for an induction period vs monomer concentration:

$$\tau = \frac{1}{K_t'} + \frac{2}{K_- K_d^{(1)}} \frac{1}{M_0} \tag{9}$$

This dependence is shown in Fig. 5. Using these data and the relations for the constants defined above, we obtain all the elementary constants:

$$\begin{aligned}
K_i &= 5.6 \times 10^{-4} \text{ liter/(mole)(min)} \\
K_- &= 2.5 \times 10^{4} \text{ liter/(mole)(min)} \\
K_{\pm} &= 2.0 \text{ liter/(mole)(min)} \\
K_t &= 0.84 \text{ min}^{-1} \\
K_d^{(1)} &= 10^{-4} \\
K_3 &= 0.07 \times 10^{-4} \text{ mole/liter} \\
K_t' &= 4 \text{ min}^{-1}
\end{aligned} \tag{10}$$

The free ion reactivity is much greater than that of an ion pair. The low value of the dissociation constant of "linear" ion pairs (K_3) of the R_4P^+, $^-C\sim\sim\sim\sim\sim$type seems surprising; it is three orders less than the dissociation constant of $Ph_3MeP^+I^-$ electrolyte. Unfortunately, we did not succeed in directly measuring the value of tetralkylphosphonium salt dissociation constant with the counterion  $\sim\sim\sim\sim\overset{CH_3}{\underset{CN}{C}}{}^{\ominus}$ because of the carbanion instability.

The calculated constant values (Eq. 10) make it possible to evaluate the concentration of active centers in the system. The concentration of stationary active centers is not more than 5×10^{-6} mole/liter. For such a low active center concentration the association effects of free ions from different macromolecules can be ignored. The free ions concentration is determined only by the monomolecular equilibrium of "cyclic" ion pairs; the summary concentrations of free ions and "cyclic" ion pairs are much the same.

In case there is no termination of polymer chains, the effective propagation rate constant of a separate polymer chain should increase with the degree of polymerization (n) according to

$$K_{eff} = \frac{K_{\pm} + K_d^{(n)} K_-}{1 + K_d^{(n)}} \tag{11}$$

(in which the accumulation of dead polymer ions is not considered). The theoretical dependence of the effective propagation rate constant vs the degree of polymerization is given in Fig. 6. The polymer chain propagation rate increases with the degree of polymerization—this is the main peculiarity of zwitterion polymerization.

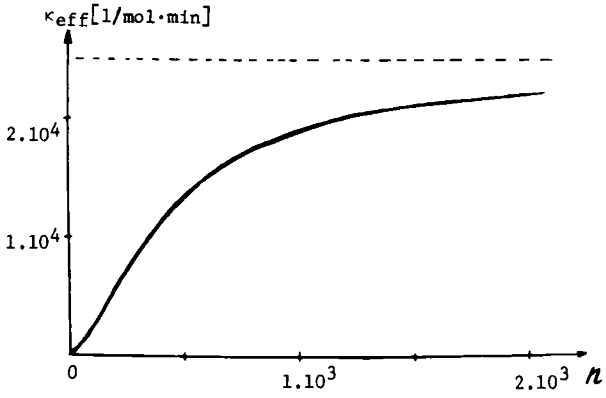


FIG. 6. Effective propagation rate constant vs degree of polymerization.

APPENDIX

When deriving the kinetic equations of the zwitterion polymerization (Eqs. 6-8), we suppose that the constant of the monomolecular transition ion pair-free ions depends upon the degree of polymer zwitterion polymerization [12]:

$$K_d^{(n)} = K_d^{(1)} n^{3/2}$$

This relation is obtained under the assumption that the mean square distance between the ends of polymer chain is according to the relation $(\overline{R}_0{}^2)^{1/2} \sim (n)^{1/2}$, which is rigorously met only in the θ-solvent. Polymer molecules are characterized in other solvents by the swelling coefficient $\alpha = (\overline{R}^2/R_0{}^2)^{1/2}$. The latter increases slowly with polymer molecular weight, and $\alpha \sim n^{0.1}$ when molecular weights are high (see, for example, Eq. 11). It should be noted that 0.1 is the maximum possible value of the exponent for the dependence of swelling coefficient upon the degree of polymerization. For finite chains this value is always less than 0.1. Thus the mean square distance between the ends of the real polymer chain is described by $(\overline{R}^2)^{1/2} \sim n^{0.5/0.6}$.

The chain free energy change when the distance between the ends goes from that of the ends being near and forming a "cycle" to the most likely distance is equal to

$$\Delta F_c = KT \ln[(\frac{3}{2\pi R^2})^{3/2} \nu_s]$$

where ν_s is the ion pair effective volume. The monomolecular constant of ion pair-free ion transition for the polymer zwitterion of n degree of polymerization is

$$K_d^{(n)} \sim e^{-\Delta F_c/KT} = K_d^{(1)} n^{1.5/1.8} \qquad \text{(A-1)}$$

Such a relationship is met for finite polymer chains in real solvents.

Equations for the initial polymerization rate (Eq. 8), active center concentration (Eq. 7), and the induction period (Eq. 9) are derived using Expression (2) for the monomolecular equilibrium constant instead of Expression (A-1). However, the use of Expression (A-1) for the monomolecular constant of the ion pair-free ions transition does not significantly change the relations obtained earlier, and only the absolute values of some of the above rate constants change. The change of the calculated rate constants absolute values (Eq. 10) will not be more than 30% in this case.

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