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Effect of the polarity of reaction medium and electric field on zwitter-ion polymerization of methacrylonitrile

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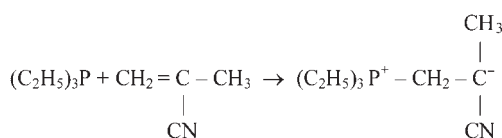
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Abstract

The mechanism of polymerization of methacrylonitrile initiated by triethylphosphine in dimethylformamide and tetrahydrofuran was investigated. The elemental analysis has shown that phosphorus is chemically bound to the polymeric molecules. Analysis by NMR spectroscopy, as well as conductivity measurements, prove that the zwitter-ion structure is formed in the initiation process



Monomer addition to the carbanion leads to macrozwitter-ion. The initiation reaction is slow and it is the rate determining step. Spontaneous monomolecular termination reaction is inherent to the system. During its life-time, the active centres can exist as either ion pairs or free ions. In the propagation step the free ion is by far the more reactive of the two species. In dimethylformamide the ion pairs play virtually no part in the propagation step and the polymer is formed through the propagation of free ions. The ion pairs-free ions intramolecular equilibrium constant depends on the length of the macrozwitter-ion. Consequently, the polymerization rate depends on the length of the growing chains. The paper presents experimental evidence for this and reports elementary constants for the macrozwitter-ion polymerization.

It could have been expected that the zwitter-ion polymerization is strongly influenced by the polarity of the reaction medium. Therefore, we investigated the polymerization of methacrylonitrile initiated by triethylphosphine in tetrahydrofuran, as well as the influence of an external electric field on this system.

In tetrahydrofuran polymerization is very slow and only oligomers are formed. Addition of dimethylformamide to tetrahydrofuran – monomer mixture, i.e. an increase in the dielectric constant of the reaction medium, increases the rate of polymerization and molecular weight of the polymer. In tetrahydrofuran, the presence of an external electric field was found to lead to a strong increase in both polymerization rate and molecular weight. These results suggest that an increase of dielectric constant of the reaction

medium as well as the application of external electric field both enable the dissociation of low reactivity ion pairs into the highly reactive free ions.

KEY WORDS:

dielectric constant
dimethylformamide
effect of external electric field
equilibrium ion pair-free ion
methacrylonitrile
tetrahydrofuran
triethylphosphine
zwitter-ion polymerisation

KLJUČNE RIJEČI:

dielektrična konstanta
dimetilformamid
hibridna ionska polimerizacija
metakrilonitril
ravnoteža ionski par – slobodni ion
tetrahidrofuran
trietilfosfin
utjecaj vanjskoga električnog polja

Utjecaj polarnosti reakcijske sredine i električnog polja na hibridnu ionsku polimerizaciju

Sažetak

Istraživan je mehanizam polimerizacije metakrilonitrila inicirane trietilfosfinom u dimetilformamidu i tetrahidrofuranu. Elementarnom analizom pokazano je da je fosfor kemijski vezan na polimerne molekule. Analiza NMR spektroskopijom, kao i mjerenja električne vodljivosti potvrđuju da tijekom inicijacije nastane hibridna ionska struktura.

Adicijom monomera na karbanion nastaje makrohibridni ion. Reakcija inicijacije je spora i određuje brzinu polimerizacije. Spontana monomolekulna terminacija prisutna je u procesu. Tijekom postojanja aktivni centar može biti u obliku ionskog para ili slobodnog iona. Slobodni ion mnogo je reaktivniji u reakciji rasta lanca. U dimetilformamidu ionski parovi praktički ne sudjeluju u reakciji rasta lanca i polimer nastaje rastom slobodnih iona. Monomolekulna konstanta ravnoteže ionski par – slobodni ion ovisi o dužini makrohibridnog iona. Posljedično, i brzina polimerizacije ovisi o dužini rastućeg lanca. Dobiveni su eksperimentalni dokazi za to i određene elementarne konstante za makrohibridnu ionsku polimerizaciju.

Moglo se očekivati da na hibridnu ionsku polimerizaciju snažno utječe polarnost reakcijske sredine. Zbog toga smo istraživali polimerizaciju metakrilonitrila iniciranu trietilfosfinom u tetrahydrofuranu te utjecaj vanjskoga električnog polja na ovaj sustav.

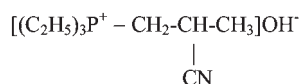
U tetrahydrofuranu polimerizacija je vrlo spora i nastaju samo oligomeri. Dodatkom dimetilformamida smjesi tetrahydrofurana i monomera, tj. porastom dielektrične konstante reakcijske smjese, raste brzina polimerizacije i molekularna masa polimera. Vanjsko električno polje snažno povećava brzinu polimerizacije i molekularnu masu polimera u tetrahydrofuranu. Ti rezultati sugeriraju da porast dielektrične konstante reakcijske sredine, kao i primjena vanjskoga električnog polja omogućuju disocijaciju slabo reaktivnih ionskih parova u jako reaktivne slobodne ione.

Introduction

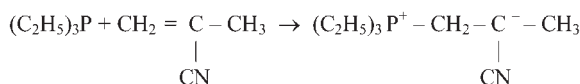
The zwitter-ion mechanism of polymerization of methacrylonitrile initiated by triethylphosphine in dimethylformamide has been proven by three different methods.¹

(1) Elemental analysis has shown that phosphorous is contained in the polymer, approximately one atom per each polymeric chain. The content of phosphorus: (a) does not depend on the initial concentration of triethylphosphine, (b) is increased with decreasing of molecular weight of the polymer, and (c) does not change during the repeated precipitation of polymers. This means that phosphorus is chemically bound to polymeric molecule.

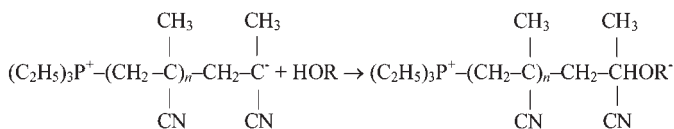
(2) NMR spectroscopy has shown that chemical shifts of ³¹P in the low molecular weight polymer and the model compound are specific for quaternary phosphonium salts. Proton magnetic resonance results also confirm the presence of quaternary phosphonium group in the polymer. The comparison of the NMR spectra parameters of the low molecular weight polymer and the model compound have made it possible to determine the structure of the product formed by the addition of the first methacrylonitrile molecule to triethylphosphine as:



As an intermediate product there appears apparently the zwitter-ion formed according to the reaction:



The growth of a polymeric chain proceeds by the monomer addition to carbanion with the conservation of the zwitter-ion. The interaction of an active centre with hydroxyl containing compounds (water, alcohols) leads to chain termination:



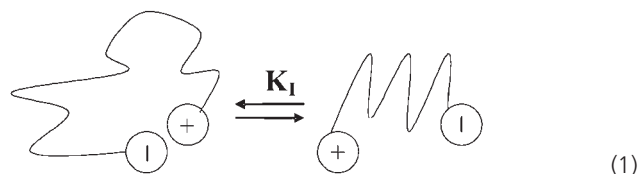
Spontaneous termination reaction is also possible.

(3) The conductivity has been found to increase during the reaction in the presence of terminating agent because the electrostatically bound ions are produced by the termination reaction. The concentration of these ions increases during the course of the reaction because the initiation reaction is slow. There is no conductivity increase during the polymerization in a dry system, because in zwitter-ions opposite charges are covalently bound to each other.

In macrozwitter-ion polymerization active centres can exist in the form of ion pairs and free ions.² Ion pairs can be formed in two

principally different ways: (a) monomolecularly through the interaction of the anion with the cation of the same polymer chain, i.e., by intramolecular cyclization, or (b) bimolecularly through the interaction with the counter ion of the neighbouring growing zwitter-ion, or with the counter ion which is preserved in terminated polymeric chains according to the proposed mechanism.

Accordingly, possible ion equilibrium in macrozwitter-ion polymerization can be represented schematically:



At the beginning of polymerization the ratio of free ions-ion pairs is determined by the equilibrium I, because the concentration of active centres and terminated polymeric chains is low due to the slow initiation reaction. Transition constant K_d^n of the equilibrium I depends on polymerization degree (n) of macrozwitter-ions and is given by the expression:

$$K_d^n = K_d' n^{3/2} \quad (2)$$

The concentration of free ions (R_n) is determined as:

$$R_n = K_d^n r_n \quad (3)$$

where r_n is the concentration of ion pairs.

The investigation of the kinetics of polymerization^{3,4} has revealed that the reaction in steady-state conditions is of first order with respect to the monomer concentration. Reaction order with respect to the initiator concentration has been found to be 2.5. This has been explained by the fact that in the very beginning equilibrium I is dominating and the rate of chain growth is increased with the increase of its length, the probability of finding an active centre in a form of more reactive free ion being larger. In this case, taking into account the slow initiation, fast growth reaction only on the free ions, termination of the ion pairs and free ions, initial polymerization rate W_0 is given by the equation:

$$W_0 = \frac{k_i k_- I_0 M_0^2}{k_t} \exp(2k_t / k_- K_d' M_0) \quad (4)$$

where k_i , k_- , k_t' and k_t are the rate constants for initiation, chain growth, and termination on free ions or ion pairs, i.e. I_0 - initiator concentration, and M_0 - monomer concentration.

The ratios of rate constants have been determined from the dependence of initial rate upon the monomer concentration as follows:

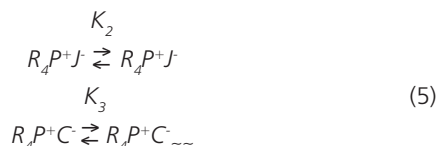
$$k_i k_- / k_t' = 3.5 \text{ (dm}^3\text{)}^2 \text{ mole}^{-2} \text{ min}^{-1}; k_t / k_- K_d' = 0.3 \text{ mole dm}^{-3}$$

During the course of polymerization reaction the concentration of terminating polymer molecules is increased, and the ratio between the concentrations of free ions and ion pairs is dependent on the interactions of growing free anions with cations of terminated molecules (1) (equilibrium II). It has been found that a great reduction of polymerization rate really takes place upon the addition of low molecular weight polymer previously synthesized.

Decrease of polymerization rate and yield is not determined by the quantity of polymer but by the concentration of polymeric chains, i.e., inhibitory effect of polymer is due to its ending groups (quaternary phosphonium groups).

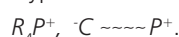
This has been proved experimentally⁵ by finding that the addition of salt $\text{Ph}_3\text{MeP}^+\text{J}^-$, which is dissociated in a solvent, has the same effect upon polymerization. If the concentration of electrolyte is high enough the reaction is practically stopped. This shows that the growth through ion pairs can be neglected as compared to the growth through free ions.

In the presence of salt the dissociation of active centres is determined by the equilibrium:



where K_2 and K_3 are equilibrium constants for dissociation of electrolyte and *linear* ion pairs containing carbanion, respectively.

The addition of adequate quantity of electrolyte transforms all *cyclic* ion pairs to *linear*, of the type



The initial polymerization rate in the presence of completely dissociated salt (concentration S_0) is given by the expression:

$$W_0 = \frac{k_i k_- K_3 I_0 M_0^2}{k_t' K_3 + S_0 k_t} \quad (6)$$

i.e., initial polymerization rate should be proportional to the square of monomer concentration.

The measurements of the initial rate have shown that the reaction in the presence of salt is of second order with respect to the monomer concentration, or, in other words, the addition of salt cancels out the effect of self-accelerated growth of macrozwitter-ions, because dissociation constant K_3 of *linear* ion pairs does not depend on the length of polymer chain.

The dependence of the polymerization rate and the polymer molecular weight on concentration of electrolyte ($\text{Ph}_3\text{MeP}^+\text{J}^-$) enabled determination of the initiation rate constant

$$k_i = 5.6 \cdot 10^{-4} \text{ dm}^3 \text{ mole}^{-1} \text{ min}^{-1}$$

and ratios of rate constants

$$k_-/k_t' = 6.25 \cdot 10^3 \text{ dm}^3 \text{ mole}^{-1}$$

$$k_t/k_-K_3 = 4.8$$

where K_3 is the dissociation constant of *linear* ion pairs: R_4P^+, C^-

In the beginning of the polymerization there is an induction period whose duration depends on the monomer concentration and is independent of the initiator concentration. Molecular weight of poly(methacrylonitrile) increases during the time equal to 2 to 3 induction periods, which indicates non-stationarity of active centres in this period.⁶

Strict mathematical analysis of the polymerization kinetic scheme, including non-stationarity on the active centres and consideration of the dependence of the ion pair-free ion equilibrium constant on the length of the growing polymer zwitter-ion provides the following expression for an induction period τ vs. monomer concentration M_0 :

$$\tau = \frac{1}{k_t'} + \frac{2}{k_- k_d^{(0)}} \frac{1}{M_0} \quad (7)$$

Using this equation and the relations for the constants defined above, we obtain all the elementary constants:^{7,8}

$k_i = 5.6 \cdot 10^{-4} \text{ dm}^3 \text{ mole}^{-1} \text{ min}^{-1}$, rate constant of initiation,

$k_- = 2.5 \cdot 10^4 \text{ dm}^3 \text{ mole}^{-1} \text{ min}^{-1}$, rate constant of chain growth of free ions,

$k_{\pm} = 2.0 \text{ dm}^3 \text{ mole}^{-1} \text{ min}^{-1}$, rate constant of chain growth of ion pairs,

$k_t' = 4 \text{ min}^{-1}$, rate constant of termination of free ions,

$k_t = 0.84 \text{ min}^{-1}$, rate constant of termination of ion pairs,

$k_{H_2O} = 1.3 \cdot 10^3 \text{ dm}^3 \text{ mole}^{-1} \text{ min}^{-1}$, rate constant of termination of free ion with water,

$K_d^{(1)} = 10^{-4}$, monomolecular constant of ion pair transition in free ion for the active centre of the degree of polymerisation 1,

$K_3 = 0.07 \cdot 10^{-4} \text{ mole dm}^{-3}$, dissociation constant of *linear* ion pairs $R_4P^+C^-$

It could have been expected that the zwitter-ion polymerisation is strongly influenced by the polarity of reaction medium. Therefore, we investigated the polymerisation of methacrylonitrile initiated by triethylphosphine in tetrahydrofuran as well as the influence of an external electric field on this system.

Experimental

Methacrylonitrile (MAN) and dimethylformamide (DMF) were purified by the usual methods, dried over calcium hydride, distilled and dried in vacuum over calcium hydride until no hydrogen generation could be detected. Tetrahydrofuran (THF) was stirred in vacuum with sodium-potassium alloy to obtain the characteristic blue colour of potassium ion as an indication of absence of water in THF. Monomer and solvent were transferred to the reaction vessels by vacuum distillation. Triethylphosphine was added by condensation in vacuum from the vapour phase. The concentration of initiator was determined from the pressure of triethylphosphine vapour prior to condensation.

Kinetics of polymerization was followed dilatometrically. For conductivity measurements and for polymerization under electric field special cells containing electrodes in reaction vessel were used.⁹ The molecular weight of the polymer was determined viscosimetrically using the relation:¹⁰

$$\eta = 3.06 \cdot 10^{-3} M^{0.503}$$

Results and discussion

Investigation of methacrylonitrile polymerization initiated by triethylphosphine in tetrahydrofuran has shown that in this solvent reaction proceeded very slowly and could not be followed by dilatometry in the usual way and within reasonable time. The concentration of monomer was 2.1 mol dm^{-3} and the concentration of initiator $10^{-2} \text{ mol dm}^{-3}$ as in previous experiments in dimethylformamide where polymerization was effective. The appearance of a yellow-red colour after one day of heating of polymerizing system at 40°C indicated that the polymer was formed. After evaporation of solvent and monomer poly(methacrylonitrile) has been detected by IR spectroscopy.

At least two factors could be responsible for slowing down of the reaction in tetrahydrofuran:

- 1) The initiation reaction involving charge separation in zwitter-ion is slow in tetrahydrofuran.
- 2) During its lifetime, before spontaneous termination, active centre exists mainly in the form of low reactive ion pair.

In order to provide the evidence on the effect of the polarity of reaction medium, we investigated the polymerization in binary solvent mixtures dimethylformamide-tetrahydrofuran. First of all we checked that in the investigated range the dielectric constant of dimethylformamide-tetrahydrofuran-methacrylonitrile mixtures decreases monotonously and linearly as the mole fraction of tetrahydrofuran increases.

There are wide evidences that free energy of an ionic reaction depends on the dielectric constant of the medium. The dissociation of an ion pair into free ion is a typical example of such dependence. In this particular case the logarithm of K_{dis} is very often found to be a linear function of $1/\epsilon$, ϵ representing the bulk dielectric constant which could differ from that one in the immediate vicinity of ion

pairs. Therefore Kirkwood's approach¹¹ considering the medium surrounding the cavity in which the reaction takes place seems to be more appropriate. According to Kirkwood the linear dependence between the free energy and $(\epsilon-1)/(2\epsilon+1)$ should exist.

Only a few systematic results exist on anionic polymerization in mixed solvents.¹² It was shown that in the anionic polymerization of polystyrellithium in tetrahydrofuran – benzene mixture linear dependence between the logarithm of the rate constant of propagation on ion pairs and Kirkwood's function $(\epsilon-1)/(2\epsilon+1)$ exist¹³ and this is not the case in tetrahydrofuran-dioxan mixture.¹⁴

Our system is much more complex because besides the propagation rate, the rates of initiation and termination can be changed by changing dielectric constant of reaction medium. Nevertheless, we obtained fairly good linearity for logarithm of initial rate of polymerization as a function both of $1/\epsilon$ and $(\epsilon-1)/(2\epsilon+1)$ in investigated range (Figure 1).

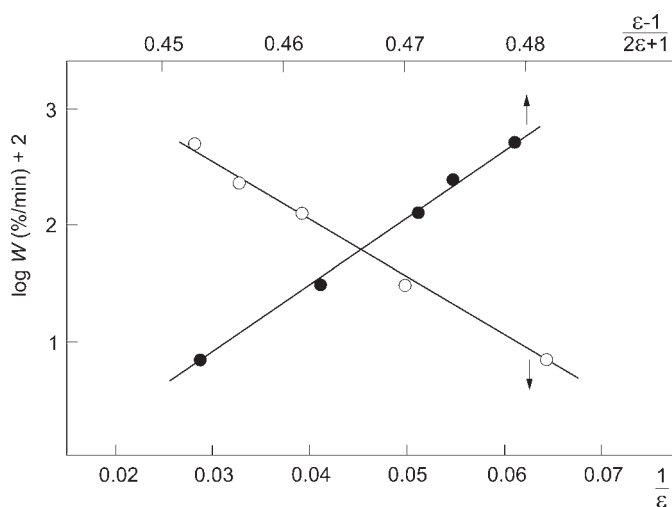


FIGURE 1 - Dependence of the polymerization rate on dielectric constant of reaction mixture MAN-DMF-THF. $[\text{MAN}] = 2.1 \text{ mole dm}^{-3}$, $[\text{TEF}] = 10^{-2} \text{ mole dm}^{-3}$, $T = 313.9 \text{ K}$.

In order to determine which reaction steps are affected by changing dielectric constant of reaction medium we investigated the molecular weight of polymer. The logarithm of polymerization degree as function of $1/\epsilon$ and $(\epsilon-1)/(2\epsilon+1)$ is plotted in Figure 2. The degree of polymerization decreases with decreasing dielectric constant of reaction medium and again linear dependence is obtained. These results indicate that propagation reaction rate is affected by changing dielectric constant of reaction medium.

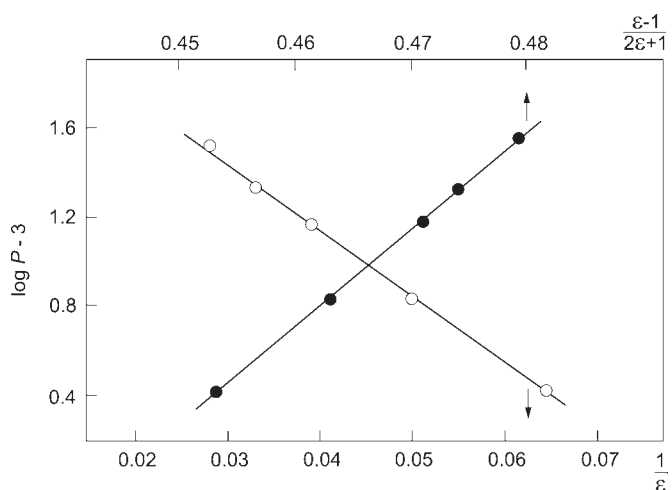


FIGURE 2 - Dependence of the polymerization degree on dielectric constant of reaction mixture MAN-DMF-THF. $[\text{MAN}] = 2.1 \text{ mole dm}^{-3}$, $[\text{TEF}] = 10^{-2} \text{ mole dm}^{-3}$, $T = 313.9 \text{ K}$.

The shape of the kinetic curves does not indicate any specific effect by addition of THF in the reaction mixture methacrylonitrile – dimethylformamide (Figure 3). It suggests that decrease of dielectric constant does not influence the rate constant of propagation but it causes the decrease of equilibrium constant ion pair – free ion. During its lifetime in THF active centre exist mainly in the form of ion pair and high molecular polymer could not be formed as indicated by the rate constants of propagation of ion pairs and free ions listed in introduction. This statement was the basis for our assumption that an external electric field could influence the equilibrium ion pair – free ion and in this way could promote the polymerization in tetrahydrofuran.

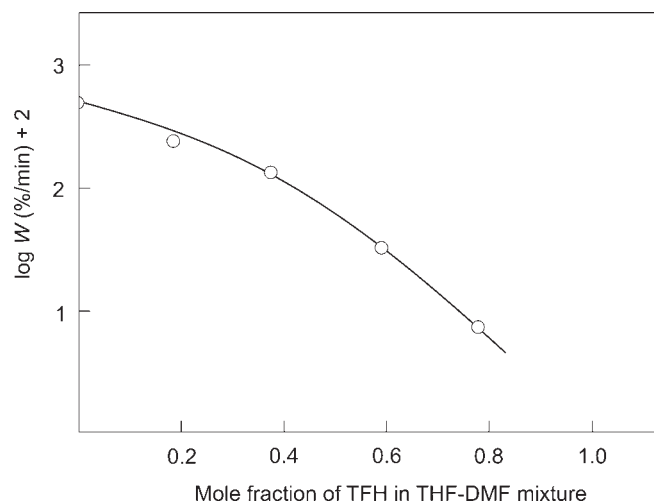


FIGURE 3 - Dependence of the polymerization rate on the mole fraction of THF in mixture THF-DMF. $[\text{MAN}] = 2.1 \text{ mole dm}^{-3}$, $[\text{TEF}] = 10^{-2} \text{ mole dm}^{-3}$, $T = 313.9 \text{ K}$.

Investigating the polymerization of methacrylonitrile initiated by triethylphosphine in THF and in the presence of an electric field we have found a strong increase in polymerization rate and high molecular poly(methacrylonitrile) was formed. The polymerization rate increases as the field strength increases (Figure 4).

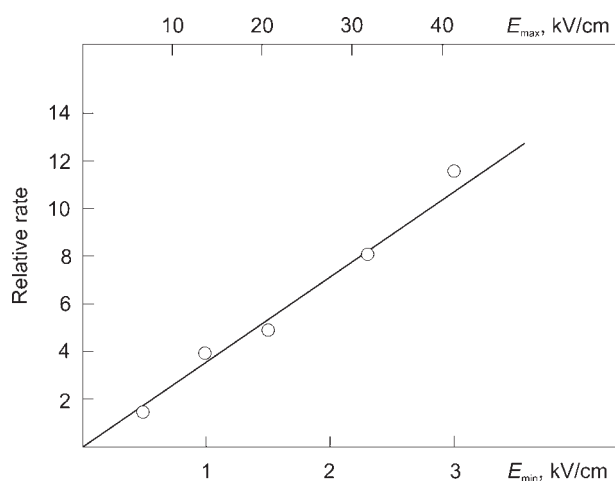


FIGURE 4 - Dependence of the polymerization rate on the strength of electric field (Both minimum values E_{min} of the field strength at external electrode and corresponding maximum values E_{max} at internal electrode are plotted on abscissa). $[\text{MAN}] = 2.1 \text{ mole dm}^{-3}$, $[\text{TEF}] = 10^{-2} \text{ mole dm}^{-3}$, $T = 313.9 \text{ K}$.

In our experiments, the field strength was inhomogeneous with minimum values at external electrode (helicoïd platinum wire situated at inner wall of the glass cylinder vessel) – increasing exponentially to maximum values at internal electrode, metal rod situated in the

centre of reaction vessel. In Figure 4 both the minimum values of the field strength on external electrode and the corresponding maximum values of the field strength on internal electrode are plotted on abscissa.

To understand the effect of the electric field in the case of the polymerization of methacrylonitrile initiated by triethylphosphine in THF, the following experimental facts should be taken into account:

- (1) Without the electric field polymerization is very slow and initiation could be detected by conductivity measurements but only low molecular weight polymer is formed.
- (2) Without initiator (triethylphosphine) in the system methacrylonitrile-tetrahydrofuran no polymerization in an electric field could be observed.
- (3) By increasing the concentration of initiator by two orders of magnitude in the absence of monomer neither current nor conductivity increase could be observed.
- (4) In our experiments field strength was more than an order of magnitude higher than in some earlier work¹⁵ and ion pair – free ion equilibrium constant in the case of zwitter-ion could be more than one order of magnitude higher than in the case when identical counter ion is electrostatically bonded in ion pair with carbanion as our previous results summarized in the introduction of this paper indicate.

Observed experimental facts suggest that strong enhancement of the polymerization rate in an electric field in our case probably could be explained by dissociation of low reactive ion pairs into high reactive free ions.

It should be noted, however, that in most cases the effect of an electric field on polymerization reaction was explained by electroinitiation.^{16,17} The redistribution of ionic species under influence of an electric field and in this way possible variations of local concentration of reaction components should be taken into account as well.¹⁸ Very little has been published on zwitter-ion polymerization.^{19,20}

Conclusion

We have shown that triethylphosphine initiated the zwitter-ion polymerization of methacrylonitrile in dimethylformamide and high molecular weight polymer was formed. Ion pairs practically do not take part in the propagation step and polymer is formed through the propagation of free ions. In tetrahydrofuran polymerization proceeded very slowly and only low molecular weight polymer was formed. In order to provide the evidence on the effect of the polarity of reaction medium the polymerization was investigated in binary solvent mixture dimethylformamide – tetrahydrofuran. Linear dependence of the logarithm of initial rate of polymerization as well as the logarithm of polymerization degree on reciprocal dielectric constant of reaction medium was determined. The shape of the kinetic curves does not indicate any specific effect by addition of tetrahydrofuran in reaction mixture methacrylonitrile – dimethylformamide. It suggests that a decrease of dielectric constant does not influence the rate constant of propagation but it causes the decrease of equilibrium constant ion pair – free ion. During its lifetime in tetrahydrofuran active centre exist mainly in the form of ion pair and high molecular polymer could not be formed. The application of an external electric field may also enable the dissociation of low reactive ion pairs in high reactive free ions and may

increase polymerization rate and molecular weight of polymer as observed.

Acknowledgements

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