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The Nature of the Active Centers of Methyl Methacrylate Anionic Electrochemical Polymerization

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ABSTRACT

By the methods of classical and oscillographic polarography, electrolysis with controlled potential and spectrophotometry, the mechanism of electrochemical generation and the active centers nature of anionic polymerization of methyl methacrylate in dimethylformamide was investigated. It was shown that in dimethylformamide in the presence of tetraalkylammonium cations, methyl methacrylate carbanions exist as solvately divided ion pairs in which the electrostatic interaction is determined by the radius of the cation. It affects the chemical stages rate of the electrochemical generation of carbanions and appears by the anomalous shift of $\zeta_{1/2}$ of polarographic reduction with the increasing of the cation radius of the supporting electrolyte. The replacement of the lithium cation with tetraalkylammonium changes the interaction type of methyl methacrylate carbanion with the counterion.

INTRODUCTION

Ion pairs are formed by direct transfer of the electron centers responsible for initiating anionic polymerization of methyl methacrylate (MMA) in tetrahydrofuran (THF). They have an absorption band at 30 μ m with the lithium counterion [1].

Change of polarity of the solvent and of the cation radius lead to a shift of the absorption maximum due to the change in the interaction energy of MMA with a counterion. Judging by the shift of the absorption maximum, a change of the interaction energy between the MMA ion and the counterion do not usually exceed 5 to 6 kcal/mol [1, 2].

While investigating the electrochemical initiation of anionic polymerization of MMA in dimethylformamide (DMF) in the presence of tetraalkylammonium salts, we detected [3] a very high shift of the maximum absorption band of active particles as compared with the absorption maximum of similar particles obtained in THF by reaction with 1,1-diphenyl-n-hexyllithium [1]. Such a shift corresponds to the decrease of interaction energy of a methyl methacrylate anion with a cation by 14.2 kcal/mol which significantly exceeds the literature values reported for such cases.

This may involve both the mechanism of formation of active particles under conditions of electrochemical generation (ECG) and their properties.

The present paper reports a detailed study of the mechanism formation and properties of the active particles which cause anionic polymerization of MMA under these conditions.

The mechanism of formation of active centers under conditions of electrochemical generation was judged by the data of classical and oscillographic polarography. The properties of the particles formed were determined by spectrophotometry and by measuring the electric conductivity of the system studied.

EXPERIMENTAL

Reagents were purified by methods described in Refs. 4 and 5. Polarograms of MMA against 0.2 M tetrabutylammonium iodide (TBAI) were taken with a LP-60 polarograph equipped with an EZ-2 recorder. Mercury-pool dropping cathode (capillary characteristics were: $m^{2/3}t^{1/6} = 0.71$ and $1.05 \text{ mg}^{2/3} \text{ s}^{-1/2}$) and bottom mercury as an anode were used. Air-tight temperature was regulated at 25°C. Majranovskiy's cells [6] were used in all experiments. Oxygen was carefully removed from polarographic solutions by blowing with a purified and dried argon.

For oscillopolarographic experiments a circuit of polarization of electrodes with a specified alternate current [7] was used. The end face plane of the amalgamated silver wire was used as a cathode. The cathode square was approximately 0.3 mm^2 .

The solution was mixed with a cathode revolving at 500 rev/min. Bottom mercury was used as an anode whose potential was constant and was controlled with a three-electrode circuit [7].

Oscillograms were taken from the screen of a P-576 polaroscope.

Electrolysis with controlled potential was conducted directly in a spectrophotometric cuvette of a specially designed electrolyzer

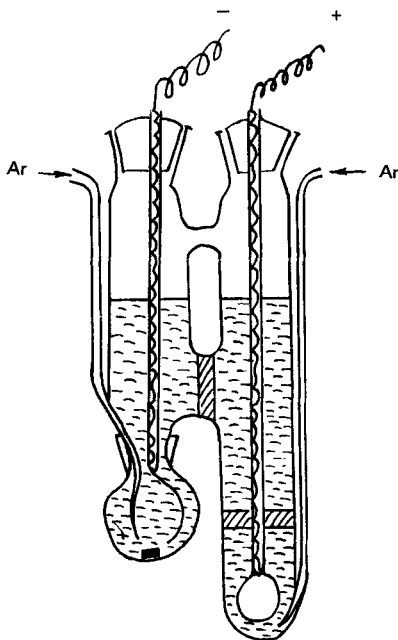


FIG. 1. Electrolyzer for spectrophotometric study of the reduction products.

(Fig. 1). A crescent-shaped platinum cathode was positioned in a quartz vessel with 0.7 to 1 cm thick walls. The design of the cell provides maximum division of the catholyte and the anolyte.

Besides the conventional glass porous diaphragm (Shott filter N3) separating the cathode compartment from the anode compartment, the latter contains one more diaphragm of glass wool.

In addition, the design provides for the position of the anode to be much lower than the cathode to prevent heavy products of oxidation of iodine disactivating carbanions of MMA from penetration into the cathode compartment.

Electron spectra were recorded with a Specord UV VIS automatic. The conductivity of the system was measured with an alternate current bridge circuit [8]. Audio oscillator GA-33 was a source of a supply at a frequency of 2-3 kHz.

Oscillograph EO-7 was used as a zero reader. Conductivity was evaluated by the specific volume resistance of the solution between two platinum electrodes, each of them 1 cm^2 and positioned 1 cm from one another inside the cathode compartment of the electrolytic cell. During the measurements, electrolysis was stopped.

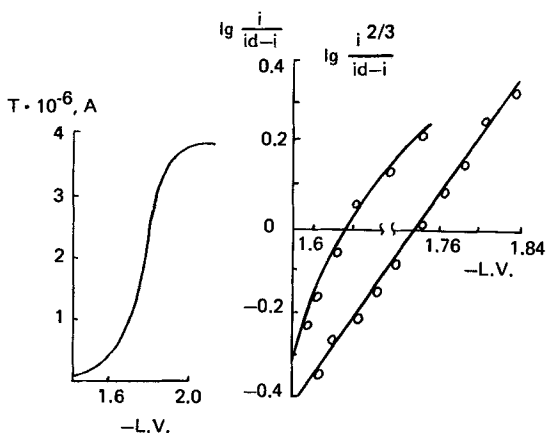


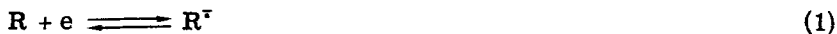
FIG. 2. Polarogram of 0.5×10^{-3} mol/L solution of MMA in DMF against 0.1 mol/L TBAL. Calculation by Koutecky-Hanush equation (left) and Heyrovsky-Ilkovich equation (right).

RESULTS AND DISCUSSION

In DMF in the presence of tetraalkylammonium salts, reduction of MMA takes place to give one polarographic diffuse wave within the potential area -1.7 to ± 0.15 V, respectively, to the nonpolarized mercury anode (Fig. 2).

Results of the investigation of properties of polarographic waves of MMA cited below enabled us to obtain a picture of the mechanism of electrochemical reduction.

The potential of the half-wave ($\zeta_{1/2}$) of MMA is essentially independent on the temperature (Table 1). With increasing MMA concentration and period of drop formation, an anode shift $\zeta_{1/2}$ is observed which is typical for processes where electrochemical reduction is followed by dimerization of the electrode reaction products [9]. In $d\zeta/dt - \zeta$ oscillograms of MMA in the range of potentials close to that for polaroscopic reduction of monomers, cathode and anode teeth are seen (Fig. 3) whose difference in potentials is ~ 0.1 V [$\Delta\zeta_{C,A} = -1.78 - (-1.69) = -0.098$], i.e., it is not higher than 0.2 V which is typical for reversible reduction processes:



At the same time MMA waves do not comply with the Geirovski-Ilkovich equation which describes a thermodynamically reversible

TABLE 1. Dependence of $\xi_{1/2}$ of MMA on Its Concentration, Period of Drop Formation, and Temperature

N	C_{depol} (10 mol/L)	$-\xi_{1/2}$ (V)	τ (s)	$-\xi_{1/2}$ (V)	Temperature (°C)	$-\xi_{1/2}$ (V)
1	0.034	1.82	5.2	1.82	21	1.72
2	0.68	1.78	95	1.79	15	1.73
3	1.36	1.72	2652	1.74	10	1.74

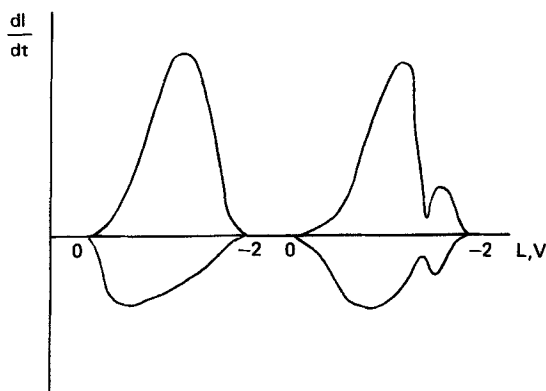


FIG. 3. $d\xi/dt$ vs ξ oscillograms of MMA in DMF against 0.2 mol/L TBAL. Solution of the background (left) and solution 2.2 mol/L of MMA (right).

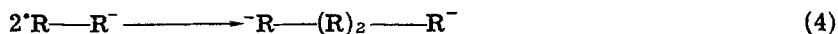
process [10]. This and the compliance of the MMA waves with the Koutecky-Hanus equation [9] is typical for reversible reduction followed by rapid dimerization, and enables us to conclude that one stage of electrochemical reduction of MMA (Reaction 1) is reversible while the other one (chemical), dimerization of the reaction products (I), is irreversible.



In addition, along with Reaction (2), irreversible interaction of the anion radicals of MMA with the nonreduced monomer is possible:



with subsequent recombination of the dimeric anion radical:



According to oscillopolarographic data, the anion radicals of MMA have a lifetime is 2×10^{-2} s which is insufficient for reversibility under conditions of polarization with direct current at the rate of $\sim 7 \times 10^{-3}$ V/s and sufficient for reversibility at the cathode polarization rate of 1×10^2 V/s and a frequency of the alternating current of 50 Hz.

Thus, fast chemical transformation of the products of chemical reduction of MMA, in particular Reactions (2)-(4), is the reason for the general irreversibility of the polarographic reduction of MMA.

Besides the $\zeta_{1/2}$ shift of MMA with a concentration increase and prolongation of the drop-formation period, we detected the $\zeta_{1/2}$ shift of MMA at the transition from TBA to tetramethylammonium iodide (TMAI).

An increase of the radius of the electrolyte cation causes a change in the structure of the double electric layer (the reducing molecule is being moved away from the surface of the electrode [11] and Coulombic interaction in the ion pair of the reduced molecule with the cation of the background is becoming weaker [12]).

The vigor of the Coulombic interaction between cation and anion is known to be inversely proportional to the radius of the cation. Therefore, with an increase of the latter, a shift of the $\zeta_{1/2}$ organic depolarizer toward more negative values is observed.

However, in the polarographic reduction of the MMA, an increase of the cation radius causes a shift of $\zeta_{1/2}$ toward positive values (Table 2), which is not in compliance with generally accepted ideas. To elucidate the reasons for this phenomenon, we studied the products of the electrochemical reduction of MMA.

Since the lifetime of the anion radicals prepared by Reaction (1) is very short and the products of their dimerization (by Reactions 2 and 4), carbanions of MMA, are rather stable and are yellow [13], we were able to study these carbanions by electron spectroscopy in the visible region.

As is seen from Fig. 4, the electron absorption spectra of carbanions of MMA in DMF have a very distinct band with the absorption maximum at 24.8 kK. The intensity of the band is proportional to the electrolysis time and the current intensity (Fig. 4b).

The stability of the MMA carbanions was established by the small change in the intensity of the absorption band with time after electrolysis (Fig. 4c).

Dianions prepared by Reactions (2)-(4) are responsible for initiation of anionic polymerization of MMA, which is substantiated by formation of the polymer in the course of electrolysis of rather concentrated solutions of the monomer at $\zeta = -1.7$ V.

TABLE 2. Dependence of the Maximum of the Absorption Band of MMA Carbanions, $\xi_{1/2}$ MMA, and Dimethylphthalate (first wave) on the Radius [2, p. 248] of the Tetraalkylammonium Cation

N	Cation	Ion radius of the cation (Å)	Frequency of the absorption maximum MMA carbanions (kK)	$-\xi_{1/2}$ (V)	
				MMA	Dimethylphthalate
1	$N(CH_3)_4^+$	3.47	25.2	1.85	1.35
2	$N(C_2H_5)_4^+$	4.00	25.00	1.72	1.37
3	$N(C_4H_9)_4^+$	4.94	24.80	1.70	1.42

The intensity of the band for carbanions of polymethyl methacrylate is proportional to their concentration (Fig. 5), determined by

$$[LE] = 1000(q - q_{ind})/VF \quad (5)$$

where q = charge of electricity, coulombs

q_{ind} = charge of electricity consumed for the reduction of the admixtures during induction from the start of electrolysis to the appearance of the absorption band of the MMA carbanions

V = volume, mL

F = Faraday number

This proves the conformity of the absorption band with the Lambert-Beer law and is substantiated by the data listed in Table 3 which show that, independent of the electrolysis time, current intensity, and initial concentration of MMA, one and the same number of Faradays (i.e., concentration of active particles) corresponds to the same intensity of the band of absorption of MMA carbanions.

To substantiate the nature of the active particles formed under conditions of ECG, the coefficient of the extinction of the band of their absorption was determined and found to be $2150 \text{ L/mol}^{-1} \cdot \text{cm}^{-1}$ which is in good agreement with the evidence obtained by Bywater et al. [1] for carbanions of polymethyl methacrylate in THF with a lithium counterion. At the same time, the frequency of the absorption maximum of MMA carbanions formed during ECG differs from that of Bywater by 5.8 kK, which corresponds to a considerable decrease

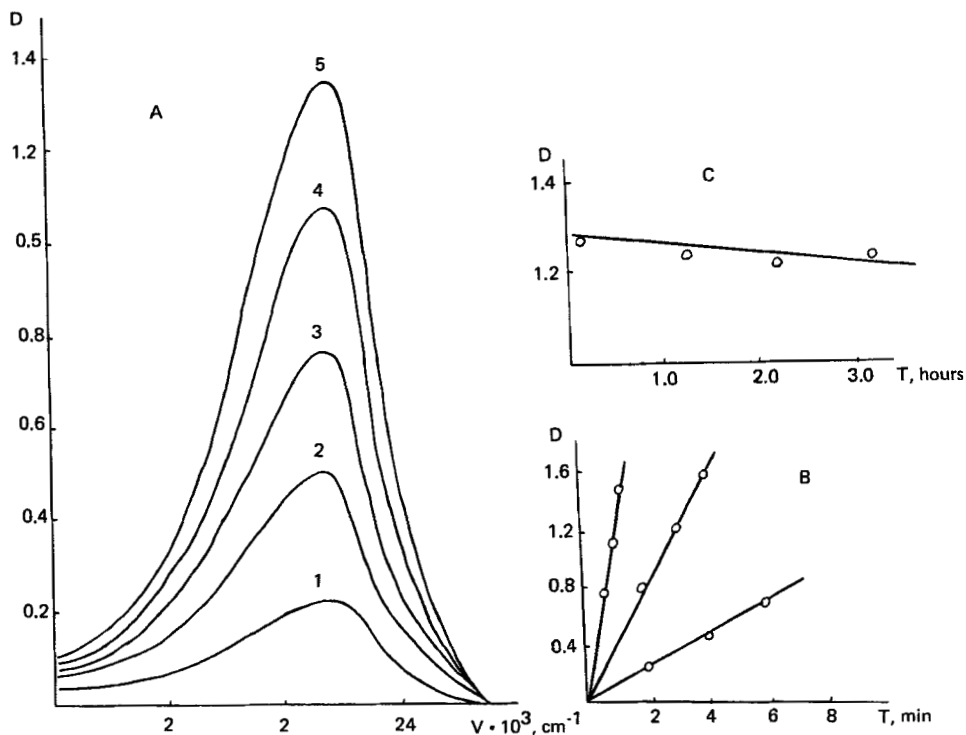


FIG. 4. (a) Electron absorption spectra of electrolysis products of MMA in DMF against TBAI; electrolysis time of 9, 17, 24, 33, and 40 min (Curves 1-5, respectively). (b) Dependence on the time and electrolysis current of the intensity of the absorption bands of MMA carbanions. (c) Dependence on time of the intensity of the absorption band of MMA carbanions after electrolysis.

of the interaction energy between a carbanion of polymethyl methacrylate with a counterion by ~ 14.2 kcal/mol. This enables us to suppose that the character of such an interaction changes, i.e., there is a transition from the contact ion pair with lithium as a counterion in THF to the free ion in DMF. This assumption agrees with temperature dependence of conductivity of the system investigated. Thus, with the decrease of temperature down to 25 to 50°, the specific volume resistance of the "living" polymethyl methacrylate-DMF-TBAI system increases from 200 to 2000 ohm/cm^3 , while the resistance of the system MMA-THF-sodium naphthalenate, where active centers exist in the form of ion pairs, reduces from 5200 to 3000 ohm/cm^3 .

However, as was shown for fluorenyl salts (p. 256 in Ref. 2), the transition from the lithium cation to TBA from the contact to the

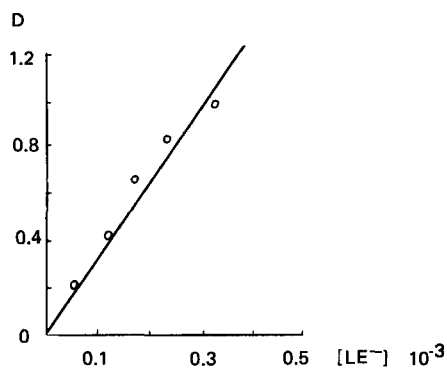


FIG. 5. Dependence of the intensity of the absorption band of MMA carbanions on their concentration, calculated by Eq. (4) at a current density of 0.35 mA/cm^2 .

TABLE 3. Effect of the Electrolysis Time, Current Density, and Initial Concentration of MMA on the Intensity of the Absorption Band 24.8 kK on the Quantity of Electricity (1×10^{-5} Faradays)

N	Current (mA)	Time (s)	Concentration of MMA (mol/L)	Optical density (D)
1	20.0	48.2	0.05	0.80
2	7.5	128.0	0.05	0.78
3	2.5	386.0	0.05	0.77
4	5.0	193.0	0.01	0.80
5	3.5	275.0	0.01	0.78
6	2.1	460.0	0.01	0.72

solvate-divided ion pairs or even to the free ion causes a decrease of the interaction energy by only 5.7 kcal/mol.

Another similar example is furnished by our data obtained by an ECG study of styrene carbanions.

We have found that the maximum of the absorption band of the styrene carbanions in DMF against TBAI is at a frequency of 28.4 kK, while in THF with a lithium counterion the frequency of the absorption maximum of the same carbanions is 29.6 kK [14]; that is, in the transition from the lithium anti-ion to TBA and from THF to DMF

there occurs a bathochromic shift of the absorption maximum by 1.2 kK, which corresponds to the decrease of the anion-cation interaction energy by 3.4 kcal.

Such a sharp difference in the reduction products of MMA and other compounds (styrene, for instance) may be attributable to peculiarities in the structure of the methacrylate carbanion.

According to Eisner and Yerusalimski [15], the extra negative charge of the product of reduction of MMA is delocalized on the carbonile oxygen and β -carbon, the angle between them being $\geq 90^\circ$.

Therefore, for the cations whose ion radius does not exceed 1 Å, formation of the most dense ion pair, the interaction of whose components is determined by not only Coulomb attraction but also by the overlapping of s_{p_2} orbitals of the cation and negatively charged atoms of the carbanion, may be assumed. This assumption agrees with the highest bond strength of a MMA anion with a counterion as compared with other monomers, particularly with styrene in FAF, as found by Tardi and Rouge [16].

Thus, if for carbanions of styrene, fluorenyl, and other compounds of this type, an increase of the radius of the cation causes a decrease of electrostatic interaction with a counterion, for carbanions of MMA in transition from a lithium to a TBA counterion, the type of cation-anion interaction changes.

Schematic representations of carbanions of MMA with lithium and TBA anti-ions cited below (I, II), made with consideration of the Steward-Brigleb models, enable us to clearly imagine possible changes of the type of interaction in the ion pair with increasing anti-ion radius as compared with the same effect for carbanions of styrene (III, IV).

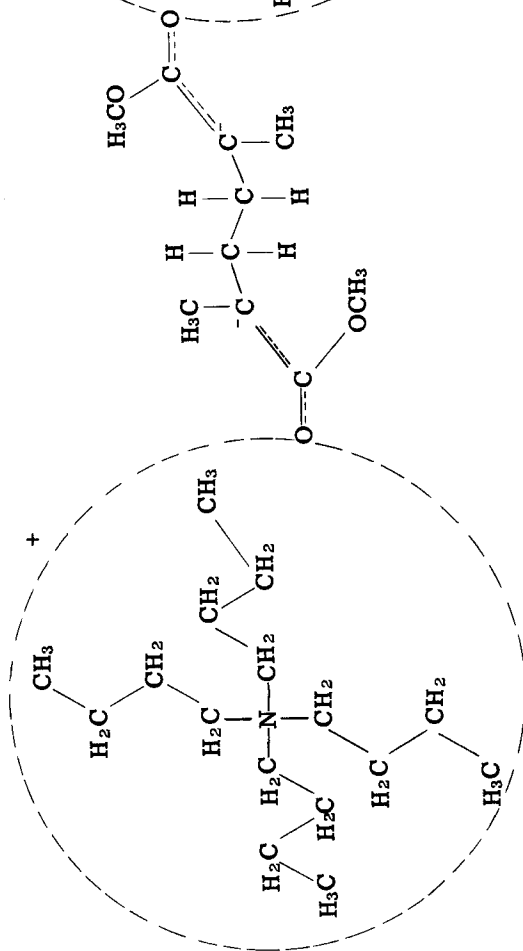
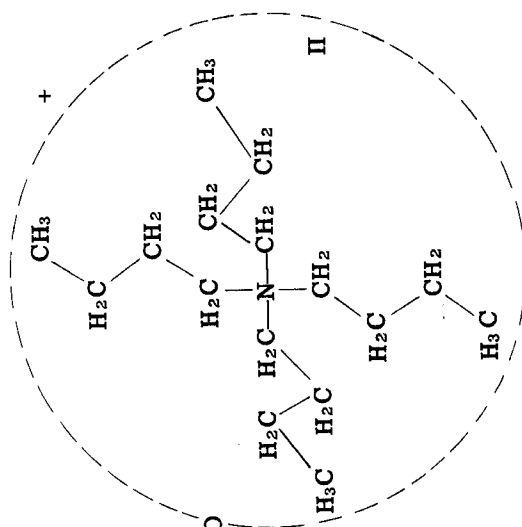
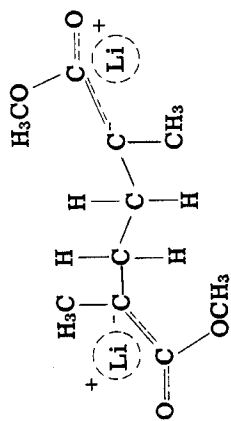
Although an assumption about ion association in the course of electrochemical polymerization of MMA in DMF was earlier put forward by Funt and Bhadani [17], it was based on indirect evidence. By their dielectric permeability and donor number DMF belong to the solvents wherein both coexistence of the ion pairs and free ions [18] depending on the nature of the cation is possible.

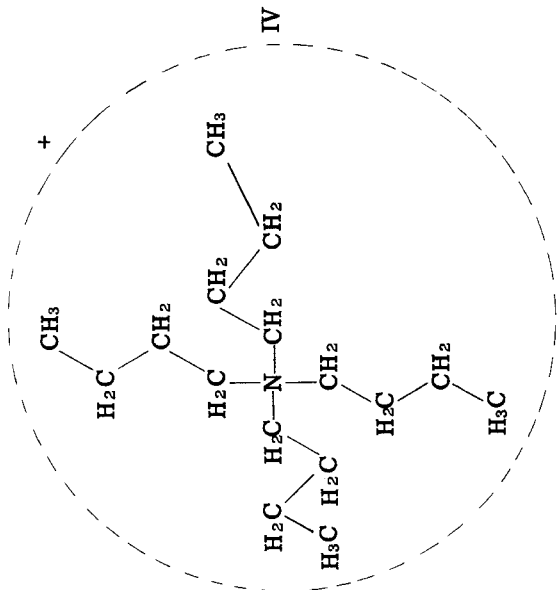
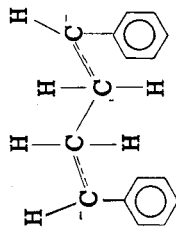
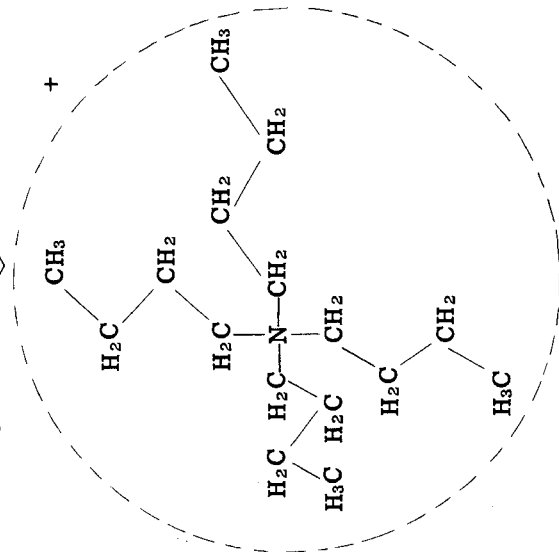
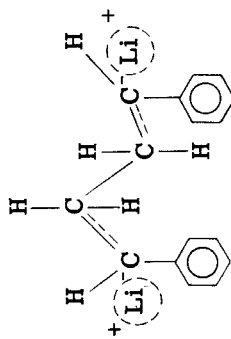
The temperature dependence of conductivity of the MMA-DMF-TBAI system favors the existence of chiefly free ions. In this case the nature of the cation and its radius do not affect the frequency of the absorption maximum of carbanions [2].

It was, however, found by us that during ECG in DMF, a change in the radius of the cation in transition from TBAI to TMAI gives a hypsochromic shift of the absorption maximum of MMA carbanions (Table 2) which corresponds to the change in the anion-cation interaction energy by 1.4 kcal/mol and favors the existence of ion pairs in DMF, whose increasing radius of the anti-ion leads to a decrease of the electrostatic attraction.

Now, the anomalous shift of $\zeta_{1/2}$ MMA with the increasing radius of the tetraalkylammonium cation is understood.

Since $\zeta_{1/2}$ MMA depends on the subsequent chemical reactions, particularly (2) and (3), whose rate grows with decreasing electrostatic





III

IV

interaction in the ion pair, an increase of the radius of the anti-ion causes an anode shift $\zeta_{1/2}$ in contrast to the case of thermodynamically reversible electrochemical reduction not complicated by the subsequent chemical reactions; for example, the electrochemical reduction of dimethylphthalate (Table 2).

The observed reduction of conductivity of the system with decreasing temperature is evidently connected with the solvent with high dielectric permeability. The most essential contribution to conductivity is made by the change in the viscosity of the system and the reduction of the mobilities of the electrolyte ions.

To summarize, it should be noted that various investigations of the mechanism of formation of active particles initiating anionic polymerization of MMA and of their properties enabled us to assume that in DMF in the presence of tetraalkylammonium cations, MMA carbanions are present as ion pairs in which the electrostatic interaction is determined by the ion radius of the cation.

This affects the rate of chemical stages of ECG of carbanions. These assumptions are in good agreement with literature data on the increase of the rate of electrochemical polymerization of MMA in DMF with the increasing radius of the tetraalkylammonium cation [19].

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