Russian Chemical Bulletin, Vol. 43, No. 2, February, 1994

Some features of electrochemically initiated copolymerization of acrylic acid and acrylamide

L. G. Kolzunova, N. Ya. Kovarsky, and A. S. Inberg*

Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences,
159 prosp. 100-letiya Vladivostoka, 690022 Vladivostok, Russian Federation.
Fax: +7 (423) 231 1889

Some features of the electrocopolymerization of acrylic acid and acrylamide in aqueous ammonium persulfate have been studied. UV spectroscopic and polarographic data attest to the intermolecular interaction of acrylic acid with acrylamide with the formation of 3:1, 3:2, and 1:1 complexes; the former complex is the strongest. Electrochemical initiation of polymerization of monomers whose $\varphi_{1/2}$ differ by ~0.3 V can result in a copolymer. The composition of the cathode polymeric coating has been determined by IR-spectroscopy and elemental analysis data. The molar ratios of acrylic acid to acrylamide in this coating and in the complex of the monomers are identical. The role of these complexes as elementary units in copolymerization is noted.

Key words: acrylic acid, acrylamide, intermolecular interaction, copolymerization, electrochemical initiation.

In the electrochemical initiation of polymerization (ECIP) of monomers, the electrode reactions can be complicated by preceding and subsequent chemical transformations, whose contributions are determined by the reactivity of the original compounds and the intermediate products. This must be taken into account when a mixture of monomers undergoes ECIP in which both copolymers and a mixture of homopolymers can be formed. In the majority of cases, the possibility of copolymerization of monomers is qualitatively estimated by the difference in $\varphi_{1/2}$ of the polarographic reduction waves of compounds tested under strictly identical conditions. For copolymerizing monomers the value $\Delta\varphi_{1/2}$ usually does not exceed 0.2 V (see Ref. 1), however, in some case monomers with $\Delta\varphi_{1/2} > 0.2$ V are able to copolymerize. ECIP of acrylic acid (AC) with acrylamide (AA) in an aqueous solution of ammonium persulfate (APS) can serve as an example. This results in the formation of polymer coatings on cathodes.[2] The physicochemical properties of these coatings (transparency; high degree of hardness, electrical resistance, melting and decomposition temperatures; insolubility in water and organic solvents), which do not change for several years, differ from those of homopolymers of AC and AA. This allows one to draw the conclusion that AC and AA form a copolymer product during ECIP, although the $\Delta\varphi_{1/2}$ value of the original monomers is ~0.3 V (Fig. 1). In this work we attempted to elucidate the features of electrochemical copolymerization of AC and AA.

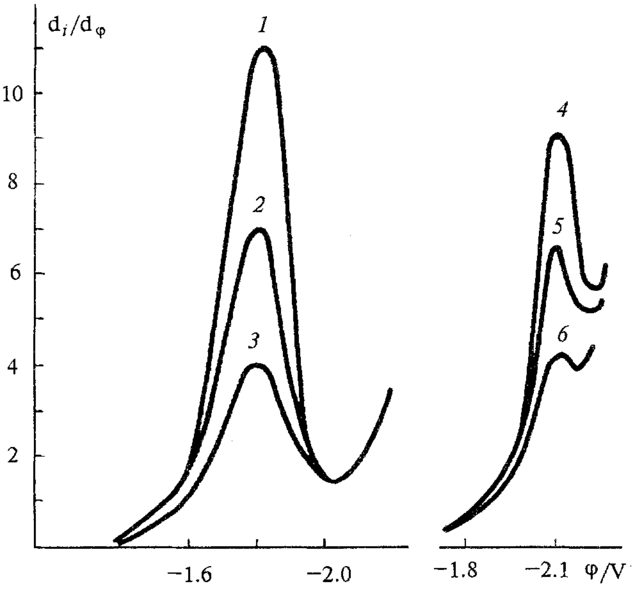


Fig. 1. Differential oscillographic polarograms of acrylic acid (*M*): $8.3\cdot10^{-4}$ (*1*); $4.16\cdot10^{-4}$ (*2*); $2.08\cdot10^{-4}$ (*3*) and acrylamide (*M*): $2.53\cdot10^{-4}$ (*4*); $1.69\cdot10^{-4}$ (*5*); $0.84\cdot10^{-4}$ (*6*) (background is 0.1 *N* $LiClO_4$).

Experimental

Pure grade acrylamide (Reanal) was recrystallized from a benzene—ethanol mixture.[3] Acrylic acid was purified from the inhibitor and the admixture of polymer by vacuum distillation.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 250—254, February, 1994.

A P-5848 potentiostat and a 25-mL glass two-chamber cell were used for potentiodynamic, and potentio- and galvanostatic measurements with a 1X18H9T stainless steel cathode and a platinum anode.

Polarographic analysis was performed with a PO-5122(03) oscillographic polarograph in the differential regime of detection in aqueous solutions degassed by argon against a background of 0.1 *N* $LiClO_4$. A dropping cathode with $m^{2/3}t^{1/6} = 5.1 \cdot 10^{-6}$ kg was used, a saturated calomel electrode served as the reference electrode. The velocity of the change in the polarizing voltage was 3.8 V s^{-1}, the current range was 0.02 mA, delay was 0.15 s. Model mixtures of monomers were prepared directly before polarographic measurements. For polarographic analysis of ECIP, aliquots of catholyte (0.1 mL) were withdrawn at specific time intervals. IR spectra were obtained on a Perkin—Elmer-577 spectrometer in thin films of the polymer or in a pellet with KBr.

UV spectra were recorded on a Perkin—Elmer 555 spectrophotometer.

Results and Discussion

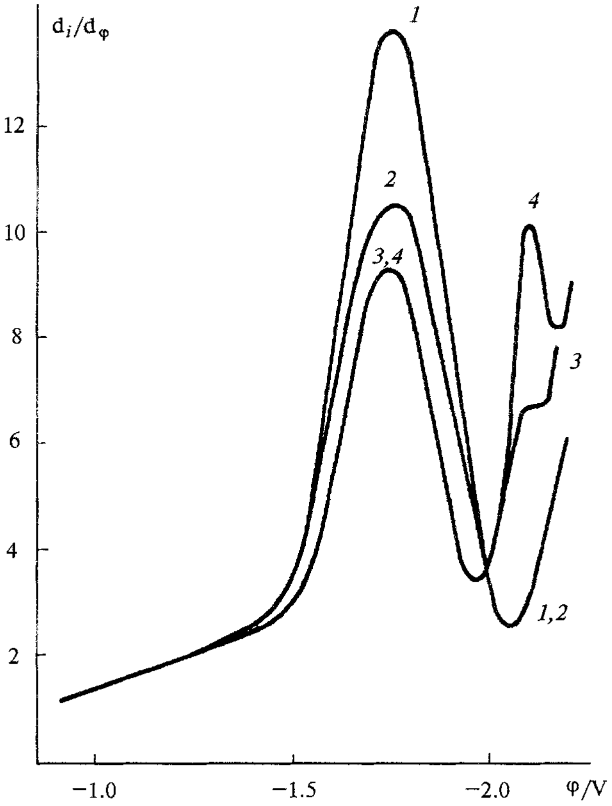


Fig. 3. Differential oscillographic polarograms of the mixture of acrylic acid and acrylamide at concentrations (*M*), respectively: $8.3 \cdot 10^{-4}$ and $0.56 \cdot 10^{-4}$ (*1*), $1.68 \cdot 10^{-4}$ (*2*); $2.8 \cdot 10^{-4}$ (*3*); $4.2 \cdot 10^{-4}$ (*4*) (background is 0.1 *N* $LiClO_4$).

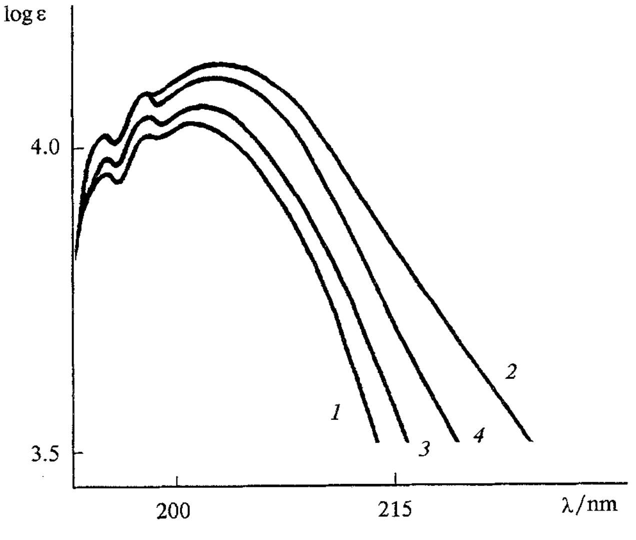


Fig. 2. UV spectra of acrylic acid (*1*), acrylamide (*2*), and their mixtures in molar ratios 3:1 (*3*) and 1:1 (*4*) (concentration of monomers is $8.3 \cdot 10^{-3}$ *M*, *l* = 0.01 cm).

A comparison of the UV spectra of a mixture of monomers with those of the individual compounds (Fig. 2) reveals some deviation of the experimental values of optical density and the extinction coefficient from those calculated with assumption that the components do not interact. This deviation, which reaches 9—11 % in the region of the maximum for the mixture AC:AA=1:1, is possible if intermolecular interaction occurs between the compounds studied. This conclusion is supported by polarographic studies. For individual AC and AA, the height of the peaks of their differential polarograms is proportional to the concentration of these compounds in the solution (see Fig. 1). However, this regularity is violated when both AC and AA are present in the solution (Fig. 3). For example, when AA is added to the solution of AC, some decrease in the height of the differential peak of AC is observed. This phenomenon cannot be explained only by the high surface activity of AA,[1] because, first, increasing the AA concentration in the AC and AA model system shifts the potential of the peak of the AC wave a little to more negative values. Second, addition of AC, which does not possess enhanced sorption ability, to the AA solution causes a decrease in the height of the peak on the differential polarogram of AA (see Fig. 3) and completely suppresses it at the molar ratio of AC and AA equal to 3:1 (Fig. 4, curve *1*). It should be mentioned that the concentration boundary of suppression of the polarographic wave of AA is very sensitive to the molar ratio of the original monomers. Even an insignificant excess in the AA concentration over the indicated ratio [AC]:[AA] = 3:1 leads to the appearance of a distinct differential wave of AA (see Fig. 3, curve *3*; [AC]:[AA] = 3:1.01). On the other hand, dilution of the monomer mixture [AC]:[AA] = 3:1 is accompanied by the appearance of the polarographic peak of free AA, whose height increases with dilution (see Fig. 4). These data allow us to draw the conclusion that acrylic monomers form a complex containing a threefold excess of AC relative to

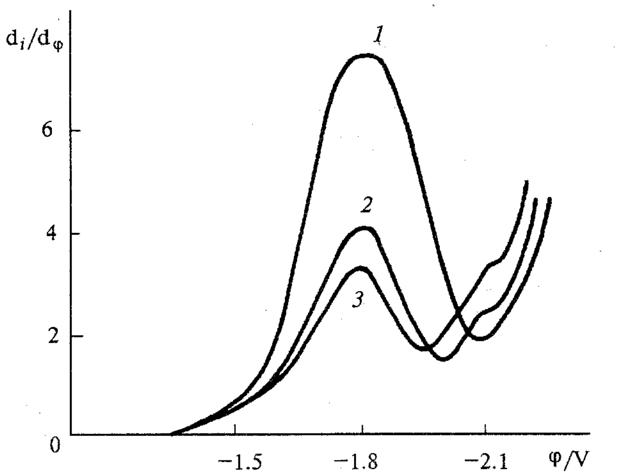


Fig. 4. Differential oscillographic polarograms of a mixture of acrylic acid and acrylamide ($8.3 \cdot 10^{-4}$ and $2.76 \cdot 10^{-4}$ *M* (*1*)) on twofold (*2*) and fourfold (*3*) dilution (background 0.1 *N* $LiClO_4$).

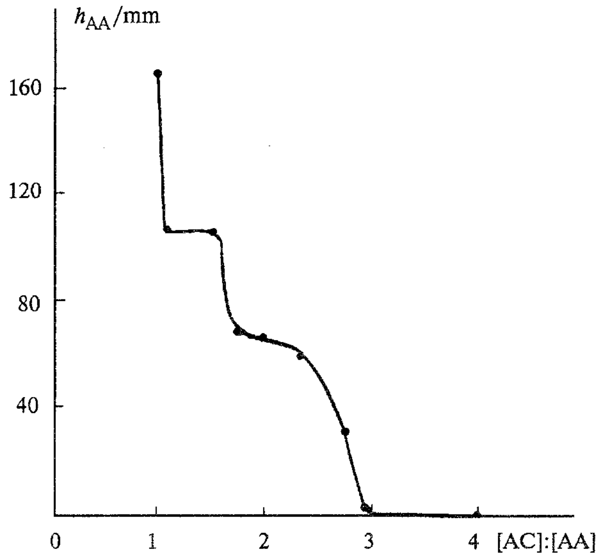


Fig. 5. Dependence of the height of the peak of acrylamide on the differential polarogram on the ratio [AC]:[AA]; [AC] = $8.3 \cdot 10^{-3}$ *M*.

AA in an aqueous solution. The reduction potential of the complex is similar to that of AC.

The decrese in the diffusional current (i_d), which corresponds to the peak on the differential polarogram of AC, as the AA concentration in the solution increases, also favors AC—AA complex formation. This indicates that the diffusional coefficient (D) of AC bound in the complex decreases. At [AC]:[AA] = 3:1, the height of the AC wave is ~77 % of that in the absence of AA. Using the Il'kovich equation, in which $i_d \sim kD^{1/2}$, where k is a proportionality constant, we obtain $D^{1/2}{}_{compl} \approx 0.77 D^{1/2}{}_{AC}$. Taking into account the known value $D_{AC} \approx 5 \cdot 10^{-6}$ cm·s^{-1}, we calculate $D_{compl} \approx (0.77)^2 D_{AC} \approx 3 \cdot 10^{-6}$ cm s^{-1}.

Complex formation is also confirmed by the concentration dependence of the AA peak height on the differential polarogram in the solution at a steady-state concentration of AC. As follows from the data in Fig. 5, the height of the polarographic peak of free AA sharply increases when the ratio of [AC] to [AA] changes from 3:1 to 3:2 and 1:1. This stepwise pattern of the curve can attest to the existence of several stages of dissociation of the complex:

$$[3\,AC \cdot AA] \rightleftharpoons 3\,AC + AA, \quad (1)$$

$$[3\,AC \cdot 2\,AA] \rightleftharpoons [3\,AC \cdot AA] + AA, \quad (2)$$

$$[3\,AC \cdot 3\,AA] \rightleftharpoons [3\,AC \cdot 2\,AA] + AA. \quad (3)$$

Using Eqs. (1)—(3), taking the results presented in Figs. 4 and 5 into consideration, and estimating the concentration of free AA from the height of the corresponding peak on the differential polarogram and the data of the calibration curve obtained for pure AA, we calculated the values of the dissociation constants of tentative complexes* $K_{[3AC \cdot AA]} = 2 \cdot 10^{-15}$ mol^3·L^{-3}, $K_{[3AC \cdot 2AA]} = 0.8 \cdot 10^{-3}$ *M*, $K_{[3AC \cdot 3AA]} = 0.72 \cdot 10^{-2}$ *M*. A comparison of the dissociation constants does not allow us to conclude clearly which of the complexes is most stable. However, the data in Fig. 3 (curve *3*) and Fig. 4 (curve *1*) indicate that the [3AC·AA] complex is the most stable. This was confirmed by polarographic monitoring of the course of ECIP and by a physicochemical analysis of the polymeric film synthesized.

Since $\varphi_{1/2}$ of AC and $\varphi_{1/2}$ of the complex are similar and occur at less negative potentials than $\varphi_{1/2}$ of AA, it is most probable that these are the species that participate most in the polymerization. Actually, the polarography of monomer solutions subjected to ECIP shows that the height of the peak of free AA is almost unchanged, but that of the peak with $\varphi_{1/2}$ in the range of the reduction of AC and the complex compound decreases. However, despite the observed constancy of the concentration of free AA in the solution during electropolymerization, the polymer formed during ECIP contains not only AC, but AA as well. This follows from

---

* The dissociation constant for the [3AC·AA] complex was determined starting from the model mixture [AC]:[AA] = 3:1. The differential polarogram of this mixture does not display the reduction peak of AA. Account is made for dilution of this mixture down to the concentration at which the peak of free AA appears and increases with dilution. The constants for the other complexes were calculated taking into account the change in the height of the reduction peak of free AA as a function of its content in the solution relative to AC.

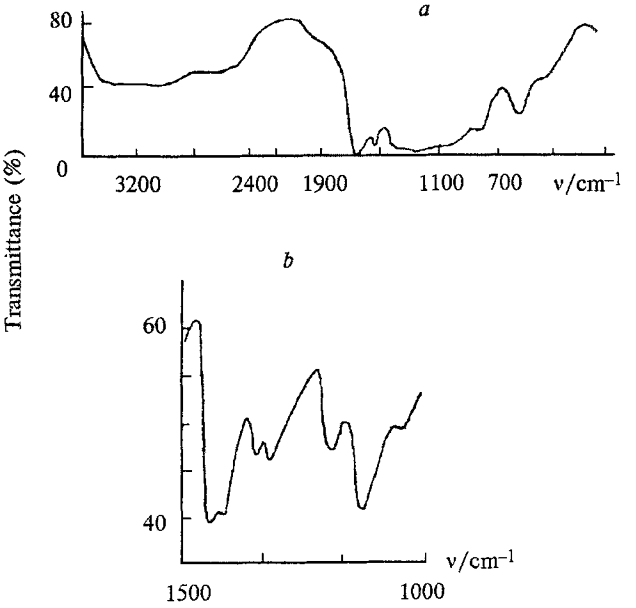


Fig. 6. IR spectra of polymers obtained from AC and AA (*a*) and AC, AA, and F (*b*).

the adsorption band in the 1540—1560 cm^{-1} range observed in the IR spectra of the polymeric film. This band is characteristic of secondary amides and is due to the deformation oscillations of the NH-group (Fig. 6, *a*). This is important when a complex compound containing both of the original monomers is consumed in the formation of the polymeric film. Elemental analysis shows that the nitrogen content in the copolymer film is ~5 %, which corresponds to a threefold excess of AC over AA. This suggests that the copolymerization is preceded by the formation of the [3AC·AA] complex in the solution, which then takes part in propagation of the polymeric chain. The existence of complexes of other compositions is also possible, but their fraction in ECIP is insignificant due to their high instability constants.

Complex formation also decisively affects the composition of the polymers formed during ECIP of more complicated monomer compositions containing components in addition to AA and AC that participate in film formation. In particular, the formation of complexes manifests itself during ECIP of the AA—AC—formaldehyde (F)—APS mixture. Since the coating formed on the cathode surface is a cross-linked copolymer containing ionogenic groups, the composition of the copolymer AC—AA—F can be established by the determination of its exchange capacity with respect to carboxyl groups,[5] which was found to be 10 mg-eq g^{-1}. Since formaldehyde interacts only with AA (see Ref. 6), but not with AC, it becomes obvious that the molar ratio (X) of AA to F in the copolymer must be equal to or greater than one. Then, taking into account that cross-linking is accompanied by polycondensation with detachment of one molecule of water from each of the two elementary units of the copolymer,[7] one can determine the ratio (N) between the number of AC and AA molecules in the copolymer from the formula:

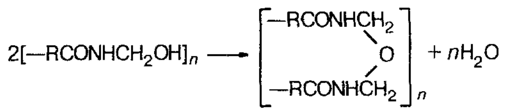
$$N = \frac{\mathrm{MM_{AA}} + x\cdot \mathrm{MM_{\Phi}} - 0.5\mathrm{MM_{H_2O}}}{1 - E\cdot \mathrm{MM_{AC}}}, \qquad (4)$$

where $\mathrm{MM_{AC}}$, $\mathrm{MM_{AA}}$, $\mathrm{MM_F}$, and $\mathrm{MM_{H2O}}$ are the molecular weights of AC, AA, F, and water, respectively; x is the number of F molecules in an elementary unit of the copolymer; E is the exchange capacity of the polymer.

The calculations show that $N = 3$ at $x = 0.75$. The value $x < 1$ suggests either incomplete hydroxymethylation of the amide groups in the copolymer, which is unlikely due to the excess of formaldehyde, or that cross-linking occurs simultaneously according to two mechanisms:

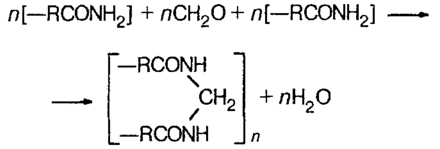
1) by polycondensation of preliminarily hydroxymethylated amide groups[7]

$$n[\text{—RCONH}_2] + n\text{CH}_2\text{O} \longrightarrow [\text{—RCONHCH}_2\text{OH}]_n \qquad (5)$$



$$2[\text{—RCONHCH}_2\text{OH}]_n \longrightarrow \left[\begin{array}{l}\text{—RCONHCH}_2\\ \qquad\quad\;\diagdown\\ \qquad\qquad\text{O}\\ \qquad\quad\;\diagup\\ \text{—RCONHCH}_2\end{array}\right]_n + n\text{H}_2\text{O} \qquad (6)$$

2) by direct interaction between F and AA (Ref. 6)



$$n[\text{—RCONH}_2] + n\text{CH}_2\text{O} + n[\text{—RCONH}_2] \longrightarrow$$
$$\longrightarrow \left[\begin{array}{l}\text{—RCONH}\\ \qquad\;\diagdown\\ \qquad\quad\text{CH}_2\\ \qquad\;\diagup\\ \text{—RCONH}\end{array}\right]_n + n\text{H}_2\text{O} \qquad (7)$$

The existence of such cross-links is confirmed by IR-spectroscopic data: a series of bands in the 1035, 1330, and 1440 cm^{-1} range corresponds to oscillations of the OH group of primary alcohols; the band in the 1540—1560 cm^{-1} range corresponds to oscillations of the NH group of monosubstituted primary amides; the band in the 1130 cm^{-1} range corresponds to oscillations of the group —CH$_2$—O—CH$_2$— in ethers (see Fig. 6, *b*).

In the first case (Eq. (5)) one molecule of formaldehyde interacts with one AA molecule, and in the second case (Eq. (7)), it interacts with two AA molecules. Then, assuming equal probability of both of the cross-linking processes, the molar ratio between AA and F must be 1:0.75. This assumption is confirmed by the composition of the elementary unit of the copolymer [3AC—AA—0.75F] found from experimental estimates of the exchange capacity. The ratio of molar concentrations of AC and AA in the copolymer equals 3:1 as before, which also indicates that the [3AC·AA] complex takes part in ECIP.

As is known, during the cooperative cathode discharge of two substances that produce a chemical compound with a gain of Gibbs energy ΔG, the equilibrium potential of the component that is reduced at more negative potentials shifts to the anode region by the value $\Delta\varphi = \Delta G/n\mathrm{F}$, approaching the equilibrium potential of the second substance.[8] Apparently, a similar effect takes place in the case considered, resulting in the electrochemical synthesis of copolymers from the mixture of monomers AC and AA, whose reduction potentials differ considerably from one another. Owing to this effect and complex formation between AC and AA, their electrocopolymerization occurs more easily than the competing homopolymerization of AA.

References

1. G. S. Shapoval and T. E. Lipatova, *Elektrokhimicheskoe initsiirovanie polimerizatsii* [*Electrochemical Initiation of Polymerization*], Naukova Dumka, Kiev, 1977 (in Russian).
2. L. G. Kolzunova and N. Ya. Kovarskii, *Plasticheskie massy* [*Plastics*], 1974, 28 (in Russian).
3. M. N. Savitskaya, *Zh. Prikl. Khim.*, 1959, **32**, 1797 [*Sov. J. Appl. Chem.*, 1959, **32** (Engl. Transl.)].
4. V. A. Mironov and S. A. Yankovskii, *Spektroskopiya v organicheskoi khimii* [*Spectroscopy in Organic Chemistry*], Khimiya, Moscow, 1985, 5; *Fiziko-khimicheskie metody issledovaniya v organicheskoi i biologicheskoi khimii* [*Physicochemical Studies in Organic and Biological Chemistry*], Prosveshchenie, Moscow, 1977, 4 (in Russian).
5. A. M. Toroptseva, K. V. Belogorodskaya, and V. M. Bondarenko, *Laboratornyi praktikum po khimii i tekhnologii vysokomolekulyarnykh soedinenii* [*Laboratory Manual on the Chemistry and Technology of High-Molecular Compounds*], Khimiya, Leningrad, 1972 (in Russian).
6. A. F. Nikolaev, *Sinteticheskie polimery i plasticheskie massy na ikh osnove* [*Synthetic Polymers and Plastics Based on Them*], Khimiya, Moscow—Leningrad, 1966 (in Russian).
7. L. G. Kolzunova and N. Ya. Kovarskii, *Vysokomol. Soedin., Ser. A*, 1983, **25**, 1702 [*Polym. Sci. USSR*, 1983, **25A** (Engl. Transl.)].
8. K. M. Gorbunova and Yu. M. Polykarov, in *Itogi nauki. Elektrokhimiya* [*Advances in Electrochemistry*], VINITI, Moscow, 1966 (in Russian).

Received November 6, 1992;
in revised form January 15, 1994