Preparation and reactivity of metal-containing monomers

37.* Redox properties and electrochemical polymerization of methacryloylacetone and its Fe^{III} and Cu^{II} complexes

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Electroreduction of methacryloylacetone and its Fe^{III} and Cu^{II} complexes was studied by cyclic voltammetry and preparative electrolysis on a Hg electrode. The possibility of the electropolymerization of the compounds at highly negative potentials (−2.0 V, vs sce) has been demonstrated. The polymers obtained were characterized by elemental analysis, electronic, IR-, and Mössbauer spectroscopy.

Key words: methacryloylacetone, polymethacryloylacetone, methacryloylacetonates, polymethacryloylacetonates, electrochemical polymerization, voltammetry.

Earlier we described the synthesis, properties[2] and regularities of radical polymerization[3] of some first-row transition-metal methacryloylacetonates and reported the characreristics of the polymers produced. It has been noted that Fe^{III} and Cu^{II} methacryloylacetonates practically do not polymerize under the conditions studied. This fact is assumed[4] to be due to the intramolecular termination of the chain resulting from the transfer of an electron from the growing macroradical to the metal ion. EXAFS data support this suggestion, confirming partial reduction of the metal ion during the polymerization of Cu^{II} methacryloylacetonate.[5]

The termination of the polymer chain can be avoided by reducing the metal ions in the monomeric complexes beforehand or by constantly regenerating the active radical centers. Both of these conditions are feasible during the electrochemical polymerization of metallomonomers. The advantages of this method are that it is possible to strictly control for chain initiation and termination, and to produce electrodes modified by metallopolymers and possessing electrocatalytic activity. In the present work we studied the redox properties and the possibility of electropolymerization of Cu^{II} and Fe^{III} methacryloylacetonates and methacryloylacetone designated hereinafter as $(MAA)_2Cu$, $(MAA)_3Fe$, and (MAA), respectively.

Results and Discussion

On a Pt electrode in Bu_4NClO_4/MeCN, weak waves of reduction and oxidation are observed for all three of the compounds. Multiple cycling of the potential in the anodic and cathodic regions is followed by a gradual decrease and then disappearance of all of the noticeable signals. This points to electrodeposition of insulating films, which block the electrode surface, and in principle confirms the possibility of electropolymerization of the compounds studied. More distinct signals can be observed on a Hg electrode. Therefore the processes that occur on this electrode during electroreduction (ER) will receive primary emphasis.

Methacryloylacetone. There are three reduction waves, I, II, and III (Table 1), in the cyclic voltammograms of MAA (Fig. 1). The height of wave I is close to that of the one-electron oxidation of ferrocene to the

Table 1. Electrochemical properties of MAA, $(MAA)_3Fe$, and $(MAA)_2Cu$

Compound	Wave	$E_{1/2}$ ($E_{p/2}$/V)	ΔE_{ca} ($\Delta E_{p-p/2}$/mV)
MAA	I	(−1.64)	(110)
	II	−1.88	80
	III	(−2.30)	(50)
$(MAA)_3Fe$	I	+0.13	130
	II	−1.84	80
$(MAA)_2Cu$	I	−0.565	250
	II	(−2.860)	(40)
	III	−0.255	70
	IV	−0.150	80

Note. $E_{1/2} = (E_p{}^c + E_p{}^a)/2$; $\Delta E_{ca} = (E_p{}^c - E_p{}^a)/2$; $\Delta E_{p-p/2} = E_p - E_{p/2}$, where $E_p{}^c$ and $E_p{}^a$ the are potentials of the cathodic and anodic waves; $E_{p/2}$ is the half-height potential.

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* For part 36, see Ref. 1.

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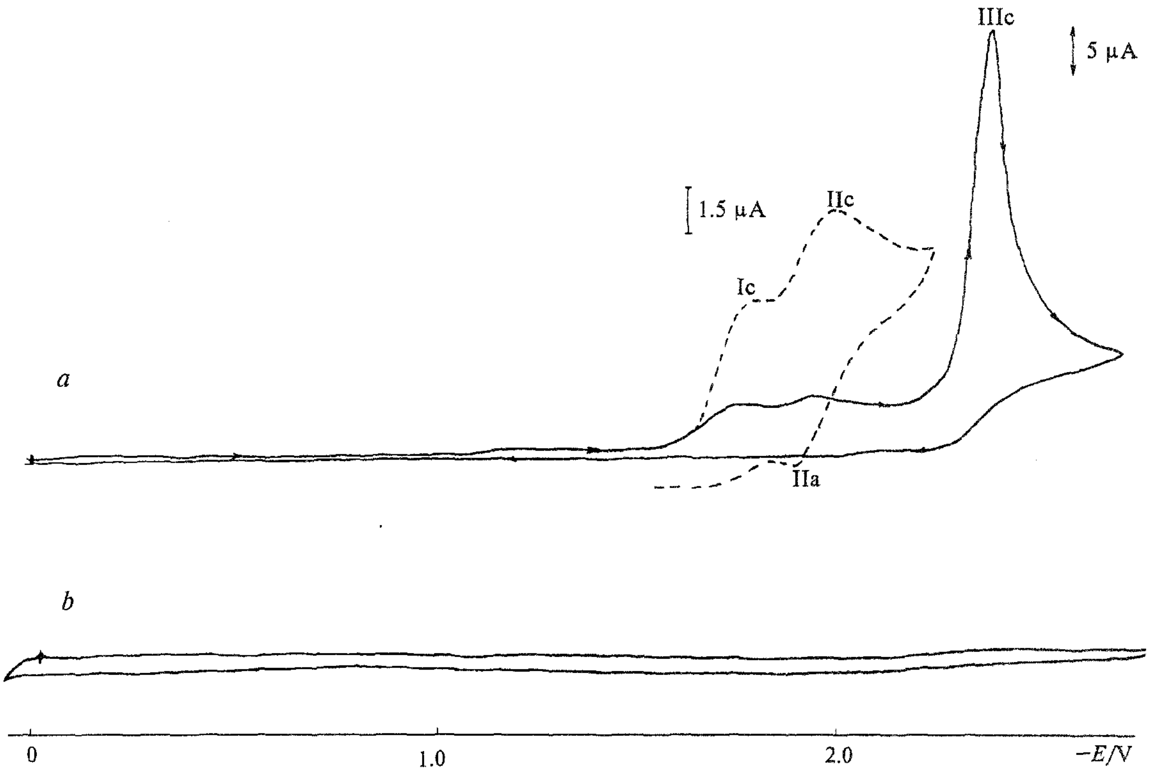


Fig. 1. Cyclic voltammogram of MAA (10^{-3} mol L^{-1}) on a Hg electrode in 0.05 mol L^{-1} Bu_4NClO_4/MeCN at v = 200 mV s^{-1} (*a*) and background curve (*b*).

ferricinium ion and increases proportionally to the square root of the scanning rate (v) in the region 20—500 mV s^{-1}. This fact attests to diffusion-controlled one-electron transfer with the formation of the $MAA^{\cdot -}$ radical anion at this stage of ER. The absence of the corresponding reoxidation wave in the anodic region of the voltammogram points to the chemical instability of $MAA^{\cdot -}$. The height of wave II also increases proportionally to $v^{0.5}$, moreover, with increasing v the ratio of the heights of the waves I/II drops from 5.6 at 20 mV s^{-1} to 2.7 at 500 mV s^{-1}, which proves again the chemical instability of the product of one-electron reduction of MAA. By analogy to the electropolymerization of such vinylic monomers as acrylonitrile, methyl acrylate, methyl methacrylate, vinyl acetate,[6] and vinylferrocene derivatives,[7] which demonstrate similar redox properties, one can propose the formation of the dianion MAA^{2-} at the second stage of ER. In this case, an oxidation wave (IIa), whose height exceeds the overall height of waves Ic and IIc and increases proportionally to v appears in the anodic region of the voltammogram at $E = -1.84$ V, which points to the adsorption character of this wave. When the multicycling potential is applied between −1.0 and −2.0 V the height of wave I gradually decreases, and simultaneously waves IIc and IIa increase. This points to the formation of a product, that is adsorbed on the electrode surface. As in the ER of acrylonitrile and methyl acrylate,[6] the instability of $MAA^{\cdot -}$ may result from dimerization of the electrogenerated radical anions followed by the formation of the respective dianion. This assumption is supported by the shift of the potential of wave I to the cathodic region as v increases from 20 to 200 mV s^{-1} and as MAA concentration decreases from 10^{-2} to 10^{-3} mol L^{-1}. When v increases by an order of magnitude the current function $i \cdot v^{0.5}$ decreases by only 12.4 %.[8]

The qualitatively similar character of the IR spectra of polymethacryloylacetone (PMA) produced by both electrochemical (Fig. 2) and radical polymerization[3] proves that the ER of methacryloylacetone involves the vinylic group. The fact that the band at 1713 cm^{-1} in the spectra of electrochemically generated PMA is more intense than that of PMA produced conventionally points to the increasing ratio of the keto-form in the keto-enolic mixture of the polymer. This is also supported by the relative decrease in intensity of the broad band at 3600 cm^{-1} due to the vibration of the enolic OH groups.

Unlike the majority of the known[6,7] cases of ER of vinylic monomers, electropolymerization of MAA is extremely slow under electrolysis conditions and stops immediately when the current is switched off. When the potential of MAA^{2-} formation is achieved the polymer film readily deposits on the electrode surface and the polymerization continues after the current is switched

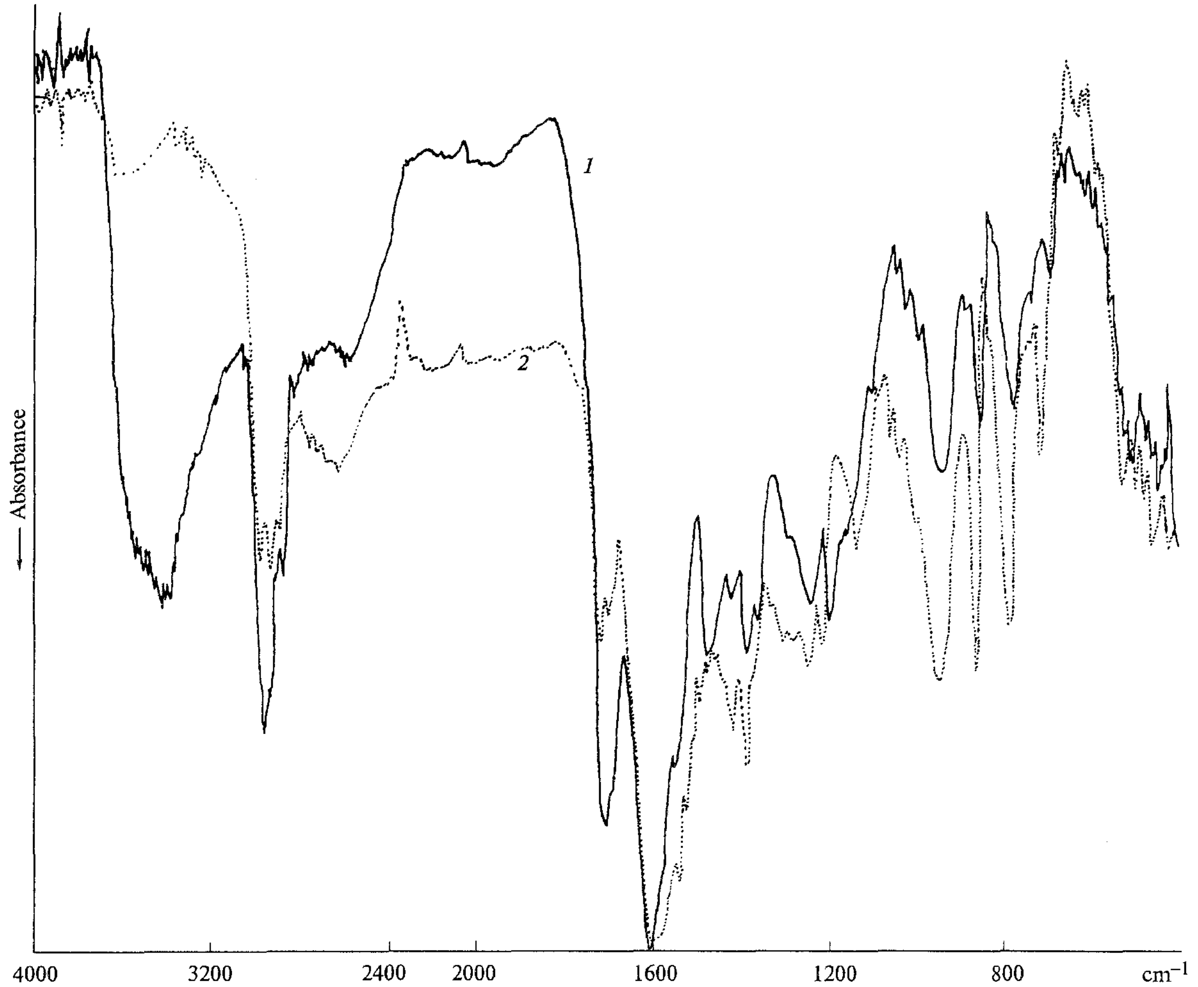
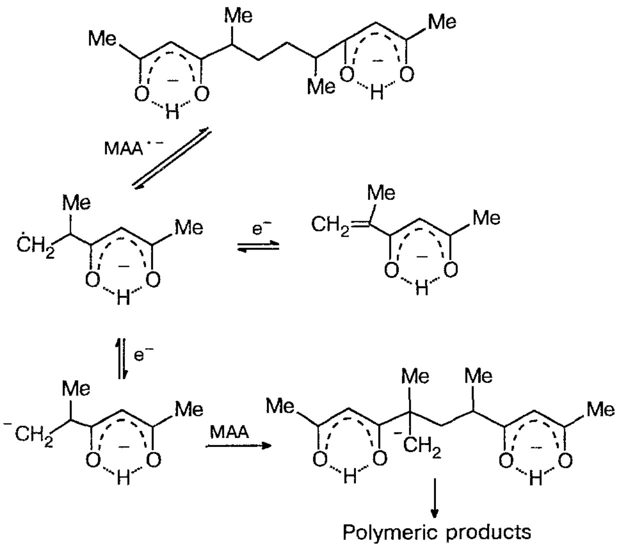


Fig. 2. IR spectra of polymethacryloylacetone produced by electrochemical (*1*) and radical polymerization (*2*).

off, which attests to the chain process. In this region of potentials, the polymerization of methacryloyl may be generally described by the following scheme:



The unusual shape and the height of wave III, which increases proportionally to v, point clearly to its adsorption character. The product of this ER stage completely blocks the electrode surface, and even at the multiple cycling potential no redox signals are observed in the voltammogram in the anodic region. Most probably, further ER of the MAA^{2-} dianion involving the β-diketone fragment and resulting either in the formation of the cross-linked polymer or in the decomposition of methacryloylacetone and/or its polymeric derivatives and producing compounds that are strongly adsorbed occurs at this stage.

Fe^{III} methacryloylacetonate. Two systems of redox signals are distinctly observed on the cyclic voltammogram of (MAA)$_3$ Fe (Fig. 3) in the regions +0.1 and −1.85 V (Table 1). The heights of peaks Ic and Ia are proportional to $v^{0.5}$ and the distance between them is 260 mV, which points to the quasi-reversible reduction of the complex in this region of potentials. The similar redox properties of Fe, Co, Mn, Ce tris(β-diketonates)[9] and particularly Fe tris(acetylacetonate),[10] have been discussed earlier, where ER has been considered to be

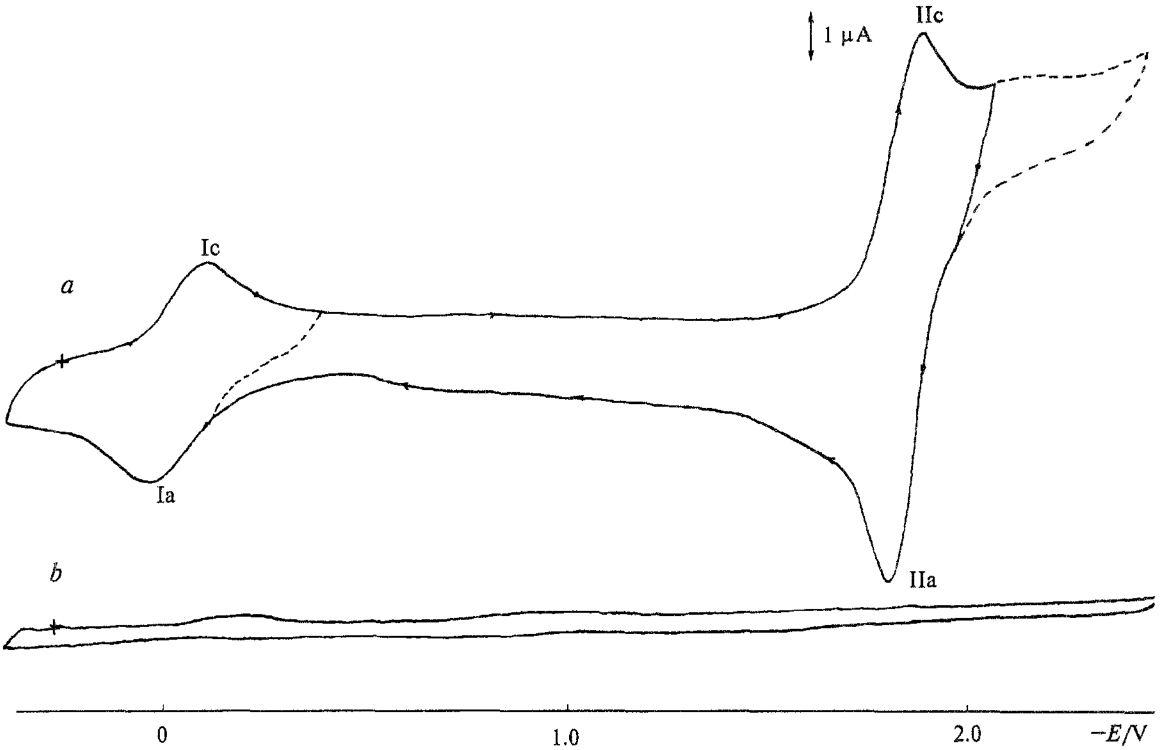


Fig. 3. Cyclic voltammogram of $(MAA)_3Fe$ (10^{-3} mol L^{-1}) on a Hg electrode in 0.05 Bu_4NClO_4/MeCN at v = 200 mV s^{-1} (*a*) and background curve (*b*).

the transfer of one electron to the MO (with a considerable contribution from the AO) of the complex. With respect to the similarity in the redox properties and to the inactivity of methacryloylacetone at these potentials (Fig. 1, Table 1), one can assume that $(MAA)_3$ Fe undergoes quasi-reversible reduction to the corresponding Fe^{II} derivative.

Some peaks of quasi-reversible reduction (IIc) and reoxidation (IIa) (Table 1) are observed on cyclic voltammograms of Fe methacryloylacetonate (Fig. 3) in the region of MAA redox activity. The heights of these peaks increase at the multicycling potential in this region. One can suggest that at these potentials an electron is transferred to the ligand resulting in the formation of a radical anion, which, unlike ER of methacryloylacetone, is active in the propagation reactions (see below). A comparison of the potential of wave II and the MAA reduction potential (wave I) (Table 1) allows one to conclude that the coordination of the MAA vinylic group by the Fe ion lowers the reactivity of this group. This assumption is in accordance with the data on the radical polymerization of transition-metal methacryloylacetonates obtained earlier.[2]

A yellow-brown metallopolymer with a metal content equivalent to the calculated (molar) value is formed during electrolysis at the potential −2.0 V. The polymer PMAFe is cross-linked and is insoluble in organic solvents. The value $\overline{M}_w/\overline{M}_n$ = 1.28 (Table 2) obtained by indirect methods indicates a narrow molecular-weight distribution, and the average degree of polymerization ($\overline{P}$ = 130) correlates well with the results of radical polymerization of Co^{II}, Ni^{II}, and Mn^{II} complexes.[3] IR spectra of the aforementioned transition-metal polymethacryloylacetonates[2] and the polymer produced are alike. In the latter spectrum the M—O stretching bands (450—600 cm^{-1}) and the bands due to the chelate structure (1350—1570 cm^{-1}) are retained and the intensity of the C=C stretching bands (1634—1640 cm^{-1}) considerably decreases, which indicates that the chelate structure is preserved during polymerization.

By comparing the Mössbauer spectra of Fe acetylacetonate ($(AA)_3Fe$) and Fe methacryloylacetonate (Fig. 4, Table 3) it can be seen that the spectral parameters do not vary much when the acetyl group is replaced by a methacryloyl group. Qualitatively, this comparison permits one to note that the local cubic symmetry of the Fe—O bonds in the structure of the nearest surroundings of the Fe atom becomes more asymmetric.[11] The iso-

Table 2. Molecular weights of polymethacryloylacetone and Fe^{III} and Cu^{II} polymethacryloylacetonates

Polymer	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{P}$
PMA	27050	48690	1.80	215
PMACu	5500	9185	1.67	44
PMAFe	16440	21040	1.28	130

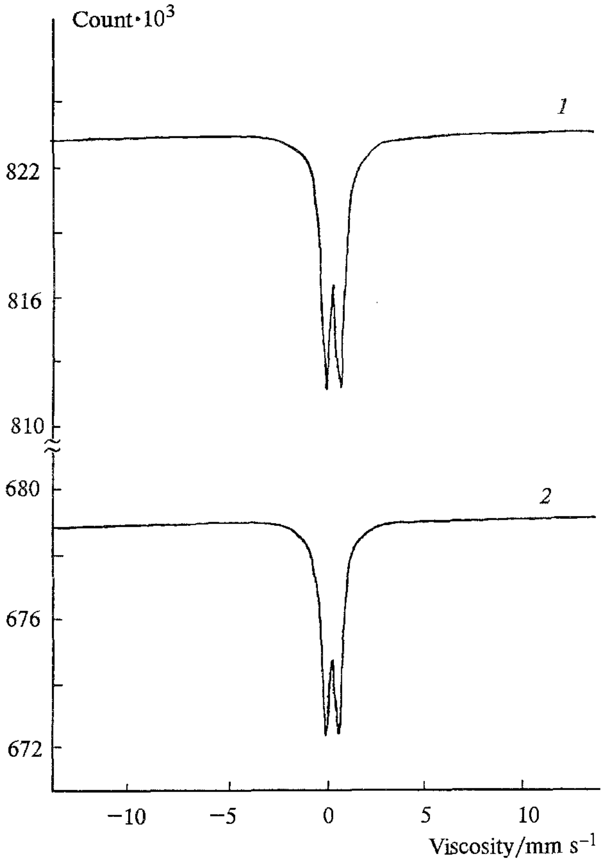


Fig. 4. Mössbauer spectra of Fe^{III} methacryloylacetonate (*1*), and Fe^{III} polymethacryloylacetonate (*2*).

meric shift of the lines attributed to the electron charge density at the Fe nucleus is proportional to the average Fe—O length in the complex and practically does not vary. The value σ_i corresponds to the high spin state of Fe^{+3} ($S = 5/2$). But the noticeable narrowing of the Γ_i line in $(MAA)_3Fe$ compared to $(AA)_3$ Fe indicates that the rate of spin-lattice relaxation of the Fe^{+3} ions decreases.

By analyzing parameters of the Mössbauer spectra of Fe polymethacryloylacetonate (PMAFe) (Fig. 4) one can conclude that during the electropolymerization of metallomonomers the valence of Fe changes very little. The average length of the Fe—O bond decreases and the structure of the nearest surroundings of Fe becomes more asymmetric. Retention of the valence of Fe is of interest because the potentials at which the transfer of an electron to the ligand occurs should cause the ER of the Fe ion. The most probable explanation for this apparent discrepancy is the chain character of polymerization, in which the radical anion $[(MAA)_3Fe^{II}]^{\cdot +}$ reacts with the initial $(MAA_3)Fe$ complexes to form electroinactive macromolecules. The chain character of the process is confirmed again by the fact that the current drops to zero after passage of 14.4 C of electricity during the electrolysis of a solution containing 2.2 10^{-4} mol Fe. It is not difficult to determine that this corresponds to the transfer of $1.4 \cdot 10^{-4}$ moles of electrons, which is 1.5 times less than required for the one-electron reduction of all of the Fe^{+3} ions.

Table 3. Mössbauer spectral parameters of Fe(III) acetylacetonate, methacryloylacetonate, and polymethacryloylacetonate

Compound	δ_i/mm s^{-1}	Δ_i/mm s^{-1}	f (%)	Γ_i/mm s^{-1}
$(AA)_3Fe$	0.41±0.01	0	1.1	2.00±0.02
$(MAA)_3Fe$	0.40±0.01	0.80±0.02	1.2	0.56±0.02
PMAFe	0.33±0.01	0.67±0.02	0.9	0.51±0.02

Cu^{II} methacryloylacetonate. Two reduction peaks are clearly observed in the regions −0.6 V (I) and −2.9 V (II) in the cyclic voltammograms of $(MAA)_2Cu$ (Fig. 5, Table 1). The one-electron (ferrocene standard) peak I is quasi-reversible and diffusion-controled limited ($i \cdot v^{0.5}$ = const.) because in the anodic region of the voltammogram the corresponding peak of reoxidation (Ia) is present at −0.44 V. The considerable shift (250 mV) between the cathodic and the anodic peaks (ΔE_{ca}) is probably due to conformational changes occurring during the reduction of the complex.* In addition to peak Ia, yet another oxidation peak whose height depends on v is observed at $E = -0.22$ V in the anodic region of the voltammogram (IIIa). At 20 mV s^{-1} the height of peak Ia is similar to that of IIIa, but at 500 mV s^{-1} peak IIIa virtually disappears. In this case the intensity of the cathodic signal (Ic) remains also the same as the overall intensity of the anodic signals (Ia+IIIa). The multiple cycling potential in the region from 0 to −1.0 V results in a new ER peak at −0.29 V (IIIc). The heights of this peak and the corresponding reoxidation peak (IIIa) increase during the initial 7—8 cycles as the intensities of redox signals I and I′ decrease. The higher the scan number the more gradual the shift of the reduction and oxidation peaks to the cathodic and anodic regions, respectively, and subsequently the weaker the intensities of all of the noticeable redox signals. Taking into account that methacryloylacetone has no redox-activity at these potentials (Fig. 1), one can assign peak I to the transfer of one electron to the MO of the complex (with the main contribution from the AO of Cu). In this case, an unstable anionic complex is formed and the product of its conversion, which is active in reversible redox-reactions ($\Delta E_{\chi\alpha}$ = 70 mV), is gradually deposited on the surface of the Hg electrode. At the potential −0.8 V, electrolysis results in

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* The original solid $(MAA)_2Cu$ has a square-planar configuration;[2] its interaction with MeCN should result in a square-pyramidal configuration, as is in the case for copper acetylacetonate.[12] However, Cu^{I} derivatives possess a tetrahedral configuration.[13]

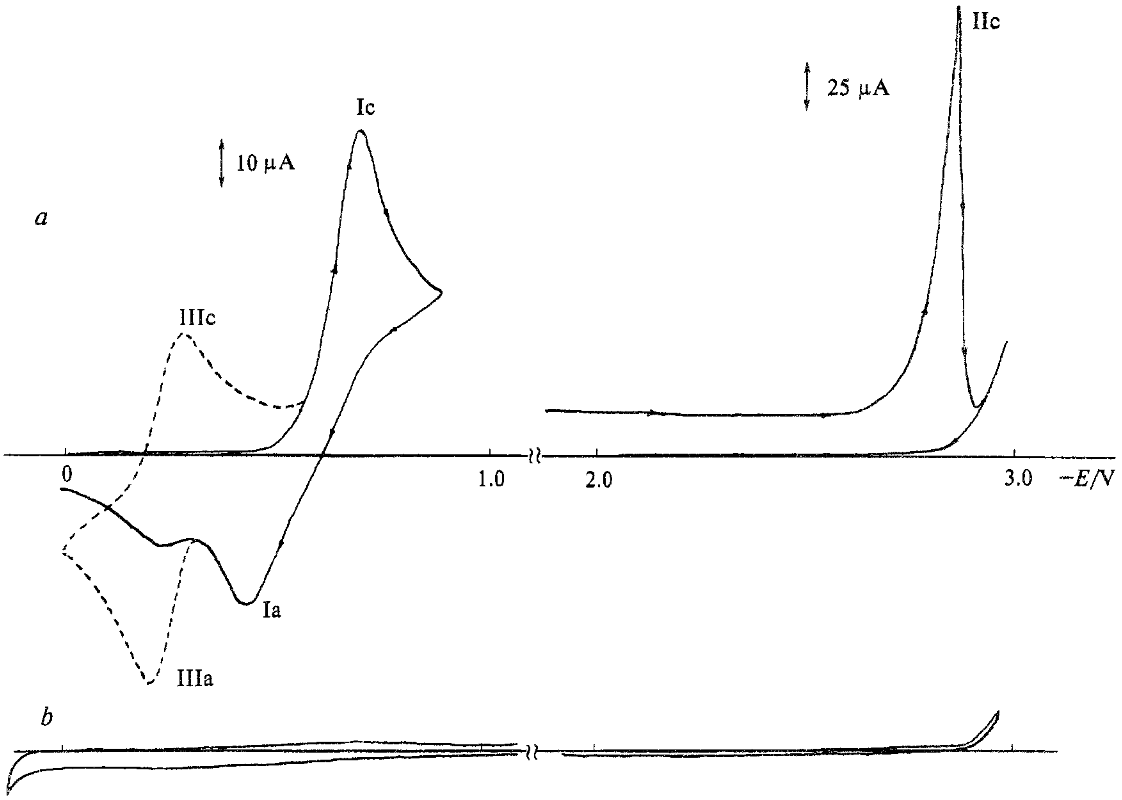

Fig. 5. Cyclic voltammograms of $(MAA)_2Cu$ ($2 \cdot 10^{-3}$ mol L^{-1}) on a Hg electrode in 0.05 mol L^{-1} Bu_4NClO_4/MeCN at v = 200 mV s^{-1} (*a*) (first cycle — solid line, seventh cycle — broken line) and background curve (*b*).

a gradual decrease in the intensity of the band at 1600 cm^{-1} and then (when 2F is passed) its disappearance (Fig. 6). In this case, peaks Ic, Ia, and IIIc also disappear completely in the cyclic voltammograms, and a new oxidation peak, IVa, appears. This indicates that the Cu^{I} complex is stable in the time-scale of cyclic voltamperometry and is chemically unstable in the time-scale of electrolysis.

As in the ER of Cu^{II} acetylacetonate,[9] a chemical reaction that accompanies electron transfer is the substitution of the anion ligand MAA^- for MeCN, which produces the neutral $(MAA)Cu^{I}(MeCN)_2$ complex, which oxidizes at the potential of peak IIIa. In addition, Cu^{I} complexes easily undergo disproportionation[3] into Cu^{II} derivatives and Cu^{0} (an amalgam should form on the Hg electrode). In this case, in spite of the fact that only a one-electron peak I observed in the voltammogram, the overall ER should be considered to be a two-electron process. According to the data from elemental analysis, after electrolysis the Cu concentration in the solution drops to practically zero (622.75 μg mL^{-1} in the initial solution and 1.8 μg mL^{-1} after electrolysis), which is in favor of the formation of a Cu amalgam during ER of $(MAA)_2Cu$.

It is of interest to note that although no visible redox processes are observed during electrolysis at −2.0 V, a poorly soluble yellow-green product with a low molecular weight and a low degree of polymerization is formed (Table 2). The metal content in this metallopolymer is close to the value estimated for Cu polymethacryloylacetonate (PMACu), and bands due to M—O stretching (450—600 cm^{-1}) and chelate ring vibrations (1350—1570 cm^{-1}),[3] respectively, remain in the IR spectra. Keeping in mind the chemical instability of $(MAA)_2Cu$ during ER, one can assume that the electropolymerization occurs owing to the ER of the MAA^- anions, producing dianions active in chain reactions with the initial complexes.

The unusual shape of the ER peak at −2.9 V (II) and the fact that its height increases proportionally to v point to its adsorption character, and the product of this stage of ER of $(MAA)_2Cu$ blocks the electrode surface completely. This follows from the absence of redox signals in the anodic region of the voltammogram and under further potential cycling. Comparing the redox properties of $(MAA)_2Cu$ and MAA one can draw the conclusion that in this potential region the reduction of the coordinated methacryloylacetonate occurs with participation of the chelate ring functional groups, which results in the decomposition of the metallocomplex (see above).

Thus, the experimental data confirms that it is possible to prepare Fe^{III} and Cu^{II} polymethacryloylacetonates by means of electrochemical polymerization. The

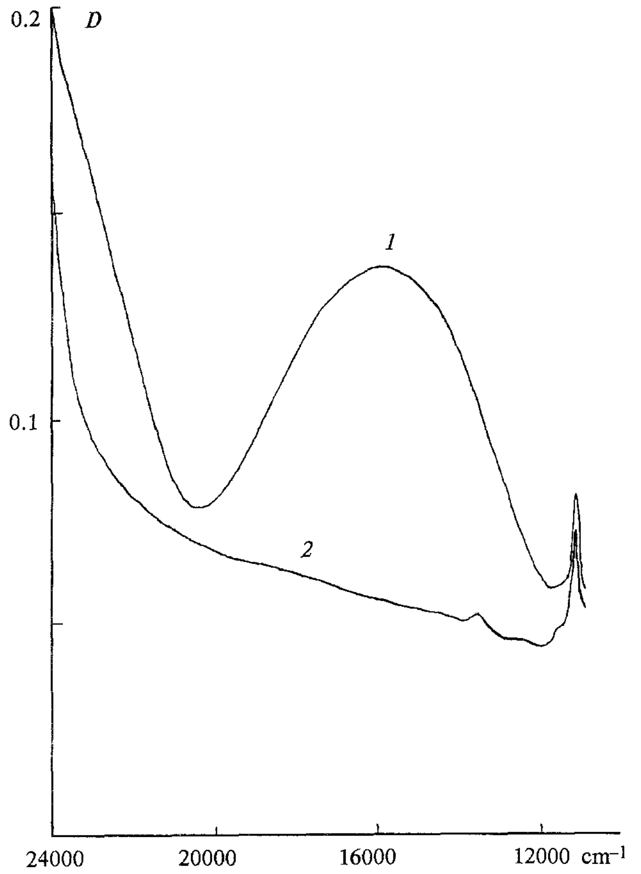

Fig. 6. Visible spectra of $(MAA)_2Cu$ (10^{-3} mol L^{-1}) before (*1*) and after passage of 2F (*2*); l = 1 cm.

structures of the polymers obtained by electrochemical and conventional radical polymerization are alike. Contrary to the previous assumption[4] on the nature of the low efficiency of the radical polymerization of Fe^{III} and Cu^{II} methacryloylacetonates, virtually no electron transfer occurs from the ligand to the metal, which was shown in the studies of the redox properties and the mechanism of the electrochemical polymerization of MAA and its Fe^{III} and Cu^{II} complexes. The results obtained seem to support the assumption that the metallocomplexes interact with the initiator (azobisisobutyronitrile[3]), which results in reduction of the metal ion and rapid chain termination.

Experimental

The synthesis and physicochemical properties of $(MAA)_2Cu$ and $(MAA)_3Fe$ have been reported earlier.[2]

Acetonitrile was refluxed over $KMnO_4$ (1 g L^{-1}) to remove unsaturated compounds and distilled, then distilled three times from P_2O_5 (1 g L^{-1}) and once again from K_2CO_3 to remove water. All procedures were carried out in an atmosphere of dry Ar.[14]

Cyclic voltammograms were obtained using a PAR 370-8 (USA) electrochemical system. A SMED-1 (Czechoslovakia) stationary mercury dropping electrode was used as the working electrode and the counter-electrode was a 1 cm^2 platinum disk. A PI-50-1 potentiostat equipped with a PR-8 program controller was used for preparative electrolysis.

The reference electrode (Ag/AgCl/4 mol L^{-1} aqueous LiCl) was separated from the solution by a bridge with a background electrolyte and was calibrated relative to the potential of the redox transition $[(C_6H_5)_2Cr]^{0/+}$(E^0 = −0.68 V, saturated calomel electrode). All of the mentioned potentials were measured relative to the reference saturated calomel electrode. The procedure of the electrochemical experiments has been reported in more detail earlier.[15]

Methacryloylacetone and Fe^{III} and Cu^{II} methacryloylacetonates were polymerized in 0.05 mol L^{-1} Bu_4NClO_4/MeCN on a Hg cathode by potentiostatic techniques using a cell with divided cathodic and anodic compartments.

The degree of polymerization of the polymethacryloylacetonates was estimated by an indirect method,[3] consisting of estimating the degree of polymerization of the polymethacryloylacetone obtained after the removal of metal ions from the metallopolymer. The molecular-weight distribution of the polymer formed was determined by gel-permeation chromatography on a Waters-200 instrument. The solvent (THF) was passed at a rate of 1 mL min^{-1} through a bar column with exclusion limits $3\cdot10^5$ — $3\cdot10^3$ E (Set B) at 298 K. The calibration curve was obtained using monodisperse polystyrene standards (Waters).

The metal content in the samples was determined by atomic adsorption using an ASS-3 spectrometer.

IR spectra of samples as pellets with KBr were measured in the region 400—4000 cm^{-1} using a UR-20 spectrometer. Absorption spectra of solutions were recorded on a Specord M-40 spectrophotometer.

Mössbauer spectra were obtained using a constant acceleration spectrometer coupled to a multi-scanning multichannel SMSA-4 (Wissel) analyzer. The spectrometer was calibrated with a ^{57}Co-in-Cr source and the six-line spectum of a metallic iron foil (20 mm) adsorber. The value of hyperfine splitting was assumed to be 330 kGs. The spectra were obtained at room temperature, and were treated by using the least-squares method to fit the experimental data to a doublet of Lorenz lines.[11]

References

1. T. I. Movchan, T. I. Solovyeva, L. A. Petrova, I. S. Voloshanovskii, G. P. Belov, and A. O. Pomogailo, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 43 [*Russ. Chem. Bull.*, 1994, **43**, 35 (Engl. Transl.)].
2. T. I. Movchan, V. I. Starikov, I. N. Ivleva, I. S. Voloshanovskii, and A. D. Pomogailo, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 694 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 545 (Engl. Transl)]
3. T. I. Movchan, I. S. Voloshanovskii, and A. D Pomogailo, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1993, 2060 [*Russ. Chem. Bull.*, 1993, **42**, 1972 (Engl. Transl.)].
4. A. D. Pomogailo and V. C. Savostyanov, *Metallomonomery i polymery na ikh osnove* [*Metal-containing Metallomonomers and Polymers Based on Them*], Khimiya, Moscow, 1988, 384 (in Russian).
5. T. I. Movchan, D. Sci. (Chem.) Thesis, Odessa, 1992 (in Russian).

6. *Organicheskaya electrokhimia* [*Organic Electrochemistry*] Ed. M. M. Baiser, Khimiya, Moscow, 1988, 1024 (in Russian).
7. X.-Z. You, Z.-F. Ding, X. Peng, and G. Xue, *Electrochim. Acta*, 1989, **34**, 249.
8. *Physical Methods of Chemistry*, Eds. B. W. Rossiter and J. F. Hamilton, Wiley and Sons, New York, 1986, **2**, 321.
9. O. Sock, P. Lemoine, and M. Gross, *Electrochim. Acta*, 1981, **26**, 99.
10. M. K. Kalinowski and A. Cmiel, *Inorg. Chim. Acta*, 1981, **49**, 178.
11. *Khimicheskoe primenemie messbauerovskoy spectroskopii* [*Mössbauer Spectroscopy in Chemistry*], Mir, Moscow, 1979, 421 (Russ. Transl.).
12. M. K. Kalinowski and A. Galazka, *Electrochim. Acta*, 1980, **25**, 1205.
13. A. Cinquantini, G. Opromolla, and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1991, 3161.
14. *Recommended Methods for Purification of Solvents and Tests for Impurities*, Ed. J. F. Coetzee, Pergamon Press, 1983, 10.
15. A. B. Gavrilov, S. B. Kukharenko, and V. V. Strelets, *Metalloorg. Khim.*, 1990, **3**, 2406 [*Organomet. Chem. USSR*, 1990, **3** (Engl. Transl.)].

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