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MACROMOLECULE - METAL COMPLEXES BASED ON SALTS OF UNSATURATED MONO- AND DICARBOXYLIC ACIDS: SYNTHESIS AND CHARACTERIZATION

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Abstract: The radical polymerization and copolymerization of salts of unsaturated carboxylic acids were used for the production of metal-containing polymers. The kinetic peculiarities and copolymerization parameters were estimated. The synthesis and structure of transition metal acrylates, maleates, fumarates, and itaconates are discussed. The influence of the metal atom on salt reactivities and reaction rates is observed.

INTRODUCTION

Metal-containing monomers (MCM) have recently drawn much attention of researchers (Ref.1). Upon polymerization, MCMs give rise to composite materials having new physicochemical and functional properties, catalytically and biologically active macromolecule-metal complexes, etc. Salts of unsaturated mono- and dicarboxylic acids have found extensive applications in the synthesis of metal-containing polymers. The simplicity of the experimental setup and their stability make these MCMs among the most convenient species. This paper reports on synthesis and (co)polymerization of transition metal acrylates, maleates, fumarates, itaconates as well as characterization of their polymers.

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RESULTS AND DISCUSSION

Synthesis of Metal Carboxylates

The neutralization of metals oxides, hydroxides or carbonates with the calculated amounts of unsaturated acids is a simple and convenient method of metal carboxylate synthesis:

$M_2O_n + 2RCOOH \rightarrow M(OOCR)_n + nH_2O$

$M(OH)_n + nRCOOH \rightarrow M(OOCR)_n + nH_2O$

$MCO_3 + nRCOOH \rightarrow M(OOCR)_n + nCO_2 + nH_2O$

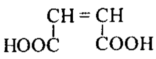
These reactions are straight forward and the side-products (water and carbon dioxide) are easily removed. Using this technique we prepared a number of metal acrylates ($MAcr_n$):

$Ni(OCOCH{=}CH_2)_2{\cdot}H_2O$, ($NiAcr_2$), $Co(OCOCH{=}CH_2)_2{\cdot}H_2O$, ($CoAcr_2$), $Cu(OCOCH{=}CH_2)_2$, ($CuAcr_2$), $[Fe_3O(OCOCH{=}CH_2)_3{\cdot}3H_2O]OH$, ($FeAcr_3$), $Cr_3O(OCOCH{=}CH_2)_3{\cdot}3H_2O)]$, ($CrAcr_3$), $V_3O(OCOCH{=}CH_2)_3{\cdot}3H_2O$, ($VAcr_3$), etc. (Refs. 2-4). The elemental analyses and infrared spectra of the monomers synthesized are given in Tab. 1.

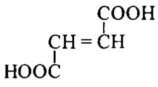
Tab. 1. The elemental analyses and key infrared absorptions for $MAcr_n$ synthesized in this work.

$MAcr_n$	Found/Calcd, %			IR spectral characteristic band frequencies, cm^{-1}				
	C	H	M	ν, >C=C<	ν, =CH C	ν_{as}, COO	ν_s, COO	ν, M-O
CuAcr	34.5/ 34.95	2.94/ 2.91	29.9/ 31.06	1645	1065	1580, 1560	1370	315
CoAcr	32.6 32.8	3.71/ 3.65	27.5/ 26.94	1640	1070	1595, 1585	1370	280
$NiAcr_2$	32.4 32.8	3.70/ 3.65	26.6/ 26.94	1640	1065	1560	1360	290
$FeAcr_3$	31.7 31.9	3.67/ 3.05	24.6/ 24.06	1635	1065	1575, 1515	1435, 1370	525
CrAcr	32.0/ 32.29	3.91/ 3.73	24.6/ 23.32	1635	1065	1575, 1525	1440, 1370	540
$VAcr_3$	32.1/ 32.43	3.43/ 3.75	21.5/ 22.97	1635	1065	1590, 1527	1444, 1375	

The general method for the preparation of salts of unsaturated dicarboxylic acids is the reaction of metal hydroxides, carbonates, or acetates with the corresponding acids. In our recent work, Co(II), Cu(II), Ni(II), Zn(II), Fe(III), and Fe(II) salts of maleic (**1**), fumaric (**2**), and itaconic (**3**) acids were studied (Ref. 5).


$HOOC{-}CH{=}CH{-}COOH$

1


$HOOC{-}CH{=}CH{-}COOH$

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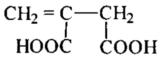
$CH_2{=}C(COOH){-}CH_2{-}COOH$

3

Structure of Metal Carboxylates

Metal acrylates. IR-spectra of metal acrylates exhibit absorption bands at 1530 - 1570 cm^{-1} and 1370 cm^{-1} associated with the antisymmetric and symmetric stretching vibrations ($\nu_{as}(COO)$ and $\nu_s(COO)$, respectively) of the carboxyl group which have bridging coordination (Ref. 6). In addition, for $FeAcr_3$, $CrAcr_3$, and $VAcr_3$, very intense bands are observed at 1515-1527 cm^{-1} and 1435-1444 cm^{-1}. These can be attributed to the antisymmetric and symmetric stretching vibrations of carboxyl groups possessing bidentate coordination (Ref. 6).

The synthesis of some metal acrylates is accompanied by an increase in metal ion nuclearity. The metal acrylates synthesized in this work have mono- ($NiAcr_2$, $CoAcr_2$), bi- ($CuAcr_2$) and tri- ($FeAcr_3$, $CrAcr_3$, $VAcr_n$) nuclear structures. The binuclear structure of $CuAcr_2$, $[Cu_2(OCOCH{=}CH_2)_4(ROH)_2]ROH$ (R = CH_3 or C_2H_5) was determined by X-ray analysis (Ref. 2). Its structure consists of the formation of a binuclear cluster with Cu-Cu distance equal to 2.617 Å.

Salts of dicarboxylic acids. We performed the X - ray diffraction study of crystals of Co(II) and Fe (II) hydrogen maleates of the composition $M(C_4H_3O_4)_2{\cdot}4H_2O$, Co (II) maleate $CoC_4H_2O_4{\cdot}3H_2O$, and Co (II) fumarate $CoC_4H_2O_4{\cdot}5H_2O$. Acid Co and Fe maleates are isostructural to similar Zn (II) and Mn (II) compounds (Ref. 7, 8). In the center-symmetric complex, two monodentate residues of compound **1** are linked with the metal atom. In the condensed phase, Co (II) neutral maleate is a three-dimensional coordination polymer. The coordination polyhedron of cobalt is a somewhat distorted octahedron, where the residue of **1** is linked with the metal ion by two oxygen atoms of both carboxyl groups to form the chelate seven-membered ring and the coordination of two other oxygen atoms of **1** with the Co atoms results in the formation of the three-dimensional cage structure (Fig. 1). Fumaric acid acts as the bidentate ligand. The crystals of Co(II) fumarate have the composition $[CoC_4H_2O_4{\cdot}4H_2O]_n \cdot nH_2O$. Two O

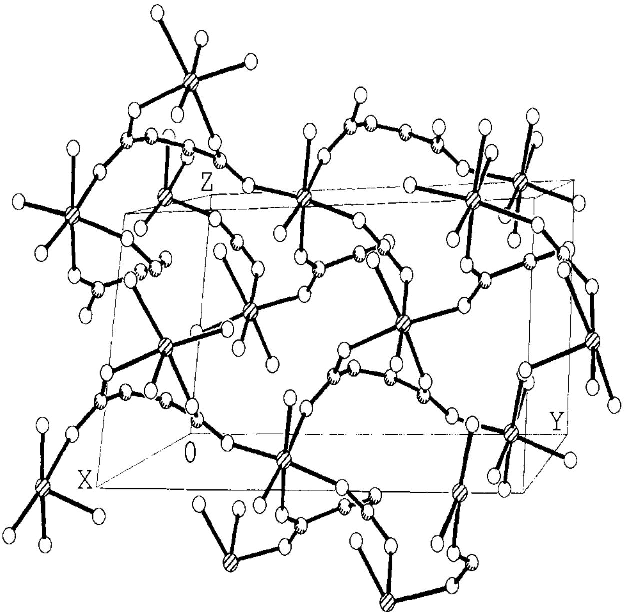

Fig. 1. Structure of the three-dimensional coordination polymer of Co (II) maleate

atoms of the carboxyl groups are linked with two Co atoms. Two crystallografically independent Co atoms are localized in particular sites on the double axis, which results in the formation of an infinite chain of the coordination polymer with the *cis*-arranged residues of **2**, whose fragment is presented in Fig. 2.

Polynuclear metal carboxylates. Trinuclear transition metal μ_3-oxocarboxylates containing $[M_3O(OCOR)_6]^+$ (R = H, CH_3, C_6H_5 etc.) cluster cation are well known (Refs. 9-11). They have a cluster structure in which the metal atoms form an equilateral triangle with the oxygen atom at the center. The carboxylic groups form bridges between the metal atoms. However, there is no information in the literature on polynuclear carboxylates with unsaturated carboxyl ligands. We have obtained the first trinuclear chromium, iron and vanadium acrylates, as well as chromium and iron maleates, itaconates. Their structure was identified by time-of-slight mass spectrometry with the extraction of dissolved ions. Fig. 3 shows the mass spectrum of the positive ion extracted from a solution of the chromium itaconate. The main peaks in the mass spectrum (*m/z* =

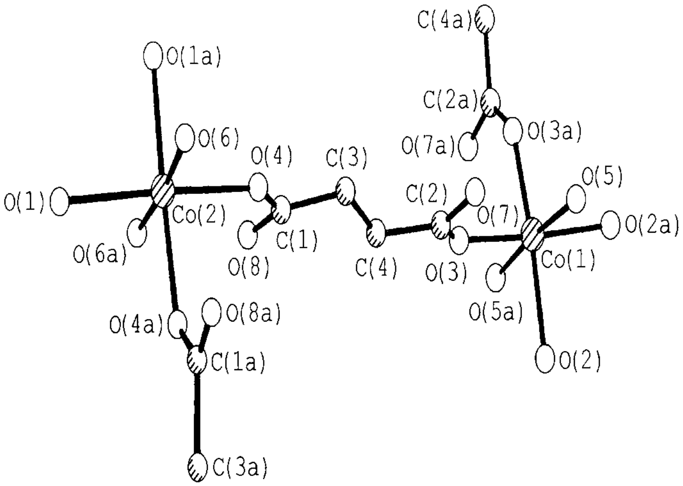

Fig. 2. Fragment of the chain of the coordination polymer of Co(II) fumarate

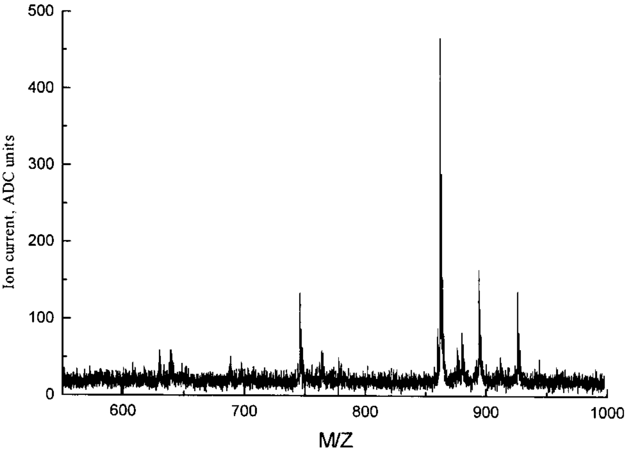

Fig. 3. Mass spectra of $[Cr_3O(HOOCCH{=}CHCOO)_6]^+$ cation extracted from an alcohol solution recorded at U = 110V

862, 894, and 924) agree with the value calculated for the free and solvated (by one or two methanol molecules) cluster cations, respectively.

Radical Polymerization of MCM

The rate of transition metal acrylate polymerization (azobisisobutironitrile (AIBN) initiation, in ethanol) decreases as follows: Co(II)>Ni(II)>Fe(III)>Cu(II) and in all cases it is lower than that of acrylic acid polymerization. Kinetic analysis of transition metal acrylate homopolymerization indicates that this process is characterized by the same elemental steps encountered with ordinary vinyl-type monomers. However, it is sometimes complicated by a purely individual effect of the transition metal (Ref. 12). Considering the initial $[M]_o$ and the current monomer $[M]$ concentrations to be related to the conversion α by the relationship $[M] = [M]_o\ (1-\alpha)$ and a quasi steady state approximation with respect to the macroradicals to be valid, the polymerization rate is expressed as follows:

$$d\alpha / dt = k_p(k_i / k_t)^{1/2} I^{1/2}(1-\alpha) \qquad (1)$$

Provided that $I = I_o e^{-k_i t}$, its solution yields the following equation

$$\ln\{\ln(1-\alpha) + 2k_p[I_o / k_i k_t]^{1/2}\} = \ln 2k_p[I_o(k_i k_t)]^{1/2} - 1/2k_i t, \qquad (2)$$

which provides a good description of the kinetics of polymer formation. Also, such an analysis characterizes the observed dependence of the limiting conversion on the initial initiator concentration:

$$-\ln(1-\alpha_\infty) = 2k_p[I_o / (k_p k_t)]^{1/2} \qquad (3)$$

The value of k_i is found from these equations to be $3.16 \cdot 10^{-2}$ min which is close to the published data (Ref. 13).

Copolymerization of MCM

Metal acrylates. Copolymerization of a MCM with both conventional vinyl monomers and with another MCM permits one to obtain new polymers and also to modify well-known polymers. The rate of radical initiated metal acrylate copolymerization with styrene depends upon the cation's type and correlates with the reactivity of the acrylate double bond in homopolymerization. Diagrams of the feed (M_2) versus copolymer (m_2) compositions for styrene/CoAcr$_2$ or NiAcr$_2$ copolymers indicate a tendency to alternation (Fig. 4): r_1 = 0.43-0.55, r_2 = 0.30-0.32 (M_1 - styrene, M_2 - CoAcr$_2$, NiAcr$_2$).

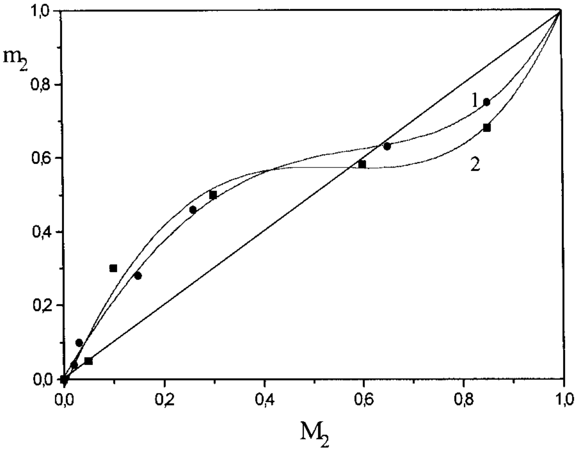

Fig. 4. The mole composition curves of copolymers : 1 - Co(II) acrylate - styrene; 2 - Ni(II) acrylate- styrene

Metal dicarboxylates. We studied copolymerization of Co acid ($Co(C_4H_3O_4)_2{\cdot}4H_2O$ - **I**) and neutral ($CoC_4H_2O_4{\cdot}3H_2O$ - **II**) maleates with styrene in methanol at 70 °C. AIBN has been used as an initiator. The values of reaction orders with respect to initiator are equal to 0.53 and 0.55 for **I** and **II**, respectively. This suggests that the mechanism of termination of kinetic chains growth is bi-molecular. In the case of **I** the copolymerization rate monotonically falls with increasing of the molar fraction of MCM in the mixture of comonomers, but for **II** the rate dependence vs. the molar fraction of MCM is extreme with maximum at the equimolar ratios of comonomers (Fig. 5).

The composition of copolymers is presented in Tab. 2. The monomer reactivity ratios determined are equal to $r_1 = 0.34 \pm 0.001$, $r_2 = 1.45 \pm 0.001$ (**I** - M_1, styrene - M_2) and r_1 = 0,07 ± 0.004, $r_2 = 0.45 \pm 0.004$ (**II** - M_1, styrene - M_2). These data show that the reactivities of monomeric salts are lower than that of styrene. The tendency to alternation is much more in the copolymerization of styrene with **II**. The distribution of units in the macromolecular chain constitutes an important characteristic of the copolymer, which defines their properties. The r_1 anr r_2 values were useful in calculating of the probabilities of structure formation ($-m_2-m_1-$ ... $-m_1-m_2-$ and m_1-m_2- ... $-m_2-m_1-$)

and the corresponding functions of the copolymerization chain units distribution. For example, in the **II**-styrene copolymer the regularly alternating structures are responsible for more 50 % of all the monomeric units.

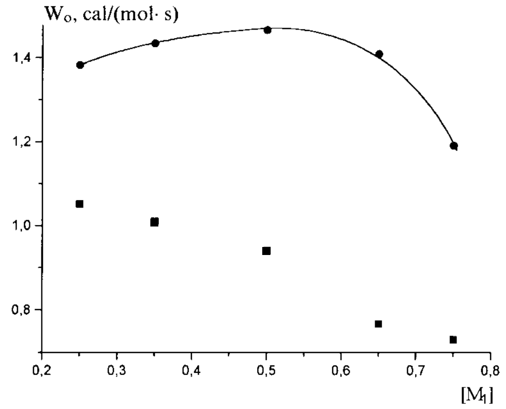

Fig. 5. The dependence of copolymerization rate on the molar fraction of MCM in the starting mixture for the pairs: ■ – Co(II) acid maleate - styrene, ● - Co(II) maleate - styrene

Tab. 2. Copolymerization of **I** (M_1) and (II) (M_1`) with styrene
(70 °C, [AIBN] =1.0 ·10^{-2} mol/l, [M_1]+[M_2] = 1. 0 mol/l

[M_1]	[M_1`]	ω %	ω` %	[m_1]	[m_1`]
molar fraction		Co	Co	molar fraction	
0,25	0.25	8.47	15.20	0.20	0.33
0.35	0.35	10.24	16.60	0.27	0.36
0.50	0.50	12.89	19.40	0.38	0.44
0.65	0.65	15.12	20.50	0.51	0.48
0.75	0.75	16.37	21.80	0.59	0.52

CONCLUSION

The polymerization and copolymerization of salts of unsaturated carboxyl acids are convenient methods for the production of metal-containing polymers. The main methods of synthesis of these metal-containing monomers are elaborated. The compounds obtained have both the monomeric and polymeric chain or three-dimensional structure . MCM under discussion are mono-, bi- and polynuclear complexes. The (co)polymerizations reveal the influence of metals on salt reactivities, reaction rates and molecular weights of the products.

REFERENCES

(1) A. D. Pomogailo, V. S. Savost'yanov, "*Synthesis and Polymerization of Metal-Containing Monomers"* CRC Press, Boca Raton 1994, 164 p.

(2) G. I. Dzhardimalieva, A. D. Pomogailo, V. I. Ponomarev, L. O. Atovmyan, Yu. M. Shulga, A. G. Starikov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1525 (1988) (*Bull. Acad. Sci. USSR, Div. Chem. Sci.* **37**, 1352 (1988) (Engl. Transl.))

(3) Yu. M. Shulga, O. S. Roshchupkina, G. I. Dzhardimalieva, I. V. Chernushchevich, A. F. Dodonov, Yu. V. Baldokhin, P. Ya. Kolotyrkin, A. S. Rozenberg, A. D. Pomogailo, *Izv. Akad. Nauk, Ser. Khim.* 1739 (1993) (*Russ. Chem. Bull.,* **42**,1661 (1993) (Engl. Transl.)

(4) Yu. M. Shulga, I. V. Chernushchevich, G. I. Dzhardimalieva, O. S. Roshchupkina, A. F. Dodonov, A. D. Pomogailo, *Izv. Akad. Nauk, Ser. Khim.* 1047 (1994)

(5) N. P. Porollo, Z. A. Aliev, G. I. Dzhardimalieva, I. N. Ivleva, I. E. Uflyand, A. D. Pomogailo, N. S. Ovanesyan, *Izv. Akad. Nauk, Ser. Khim.*, 375 (1997) (*Russ. Chem. Bull.,* **46**, 362 (1997) (Engl. Transl.)).

(6) K. Nakamoto, *"Infrared and Raman Spectra of Inorganic and Coordination Conpounds*," Wiley, New York (1986).

(7) A. S. Antsyshkina, M. A. Porai-Koshits, M. G. Guseinov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 273 (1974) (*Bull. Acad. Sci. USSR, Div. Chem. Sci.* **33** (1974) (Engl. Transl.))

(8) M. P. Gupta, B. Mahanta, *Cryst. Struct. Comm.,* 179 (1978)

(9) B. N. Figgis, G. B. Robertson, *Nature* , **205**, 694 (1965)

(10) G. J. Long, W. N. Robinson, W. P. Tappmeyer, D. L. Bridges, *J. Chem. Soc., Dalton Trans.* 573 (1973)

(11) R. C. Mehrotra, R.Bohra. *"Metal Carboxylates*", Academic Press, London New York (1983).

(12) G. I. Dzhardimalieva, A. D. Pomogailo, S. P. Davtyan, V. I. Ponomarev, *Izv. Akad. Nauk SSSR, Ser. Khim.*,1531 (1988) (*Bull.Acad Sci USSR, Div Chem.Sci.*, **37**,1352 (1988)

(13) Kh. S. Bagdasar'yan. "*Theory of Radical Polymerization*," Nauka, Moscow (1966).