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Advances in the chemistry of metal chelate monomers

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ABSTRACT. This review covers the chemistry of metal chelate monomers. Depending on the bonding of the metal to the chelating group, all metal chelate monomers are divided into three main types: molecular chelates, inner-sphere compounds, and macrocyclic complexes. The data are systematised according to methods of preparing similar compounds. Special attention is paid to the specifics of homo- and co-polymerisation of metal chelate monomers. The principal applications of metal chelate monomers and polymers based on them are considered.

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I. Introduction

Problems on the chemistry of macromolecular metal chelates (MMC) have attracted increasing attention over the last few years.[1–8] Polymeric chains and chelating rings are characteristic of MMC. The interest in such compounds is primarily due to their wide use as catalysts,[1–5,9–12] antifriction materials,[13–15] biologically active substances,[16,17] electrically conductive coatings,[18–22] etc. A large number of MMC have already been synthesised (MMC of practically all metals are known). Quantitative characteristics of chelate-formation processes involving polymeric ligands have been defined. Their principal structure features have been revealed.

However, the chelating systems are constructed, as a rule, in many steps including a whole series of successive conversions: the synthesis of the polymeric support, its functionalisation, creation of the chelating groups, synthesis and chelation of the metal complex, and separation of the chemically unbound components. Moreover, chelation in metal–polymer systems is significantly more complicated compared with low molecular weight analogues since both reagents can undergo a variety of reactions. The most important reactions of the transition metal during chelation are redox reactions, dissociation of dimeric complexes, cluster formation, etc. Destruction of the polymer, its conformational transitions, a change in the nature of the functional groups, etc. are also important. It is noteworthy that the compositional inhomogeneity of the MMC, a non-uniform distribution of metal ions on the polymeric support, different valence states, and the modes of coordination of the transition metals significantly affect the properties of the MMC.

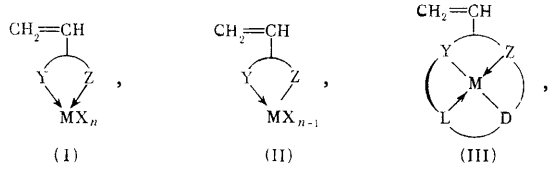
In this respect, much of the attention of the last two decades has been directed toward the development of new methods for synthesising MMC. The most promising of these are polymerisation and copolymerisation of metal chelates of monomers (MCM) containing a metal chelate ring and a multiple bond. This enables preparation of MMC in one step. In such MMC each chelating group contains a metal ion and in most instances has a definite spatial configuration in the metal chelate ring.

Chelation is an effective method of stabilising monomer–metal pairs (MMP). Thus, allyltrichlorotitanium is barely stable whereas its complex with 2,2′-bipyridine (bipy) decomposes only at 180 °C.[23] Unsaturated organocobalt compounds are stable only if they contain bulky chelating ligands, in particular, dimethylglyoxime (DH_2).[24,25] Moreover, MCM are independently interesting owing to the influence of the double bond on the stereochemistry of the coordination sphere and the electronic properties of the metal on the one hand and to the influence of the metal on the reactivity of the multiple bond on the other.

In this review, data for the synthesis, homopolymerisation, copolymerisation and graft polymerisation of MCM are summarised. Routes for the most rational development of this area are outlined.

II. Synthesis

Metal chelate monomers include complexes containing a metal chelate ring and a multiple bond capable of undergoing addition. Depending on the type of metal–chelate bonding, MCM can be classified into the following three types: molecular metal chelates (I), inner-sphere compounds (II) and macrocyclic complexes (III).



where M is the metal, n is the metal valence, X is a ligand, and Y, Z, L and D are the corresponding functional groups.

Type (I) MCM have only coordinate bonds between the metal and the donors of the chelate. Such MCM are formed if the groups have donors positioned to form a metallocycle or are conformationally non-rigid with two or more donors. In type (II) MCM, at least one group forms both a coordinate and covalent bond to the metal. These compounds can be neutral, cationic or anionic and can contain monodentate and chelating ligands. The metal ion in type (III) MCM is bonded to a macrocycle. These three

types of MCM can be further divided into groups depending on the nature of the donors (O,O-; N,N-; N,O-; and P,P-chelates, etc.).

In the modern synthetic chemistry of MCM, general methods and principles for synthesising complexes are widely used.[26,27]

1. Molecular metal chelates

The traditional route for synthesising type (I) MCM is based on reaction of metal compounds (MX_n) with chelating monomers. This method has been used, in particular, to prepare the complex of Cu^{II} chloride with the vinyl ether of monoethanolamine;[28] Ru^{II}, Co^{II} and Fe^{II} complexes with 4-vinyl-, 6-vinyl-, or 4′-vinylterpyridyls;[29] Ru^{II}, Zn^{II} and Ir^{III} complexes with 4-vinyl-4′-methyl-2,2′-bipyridyl;[30–33] the Ru^{II} complex with 6-vinyl-2,2′-bipyridyl;[33] Ni^{II}, Co^{II}, Cd^{II}, Bi^{III}, Hg^{II} and Pd^{II} complexes with 1-allyl-3-(2′-pyridyl)-2-thiourea;[34] Cu^{II}, Ni^{II}, Co^{II}, Mn^{II} and Zn^{II} complexes with 1-vinyl-2-hydroxymethylimidazole and 1-vinyl-2-vinyloxymethylimidazole;[35,36] etc.

A method based on interaction of monofunctional monomers with metal chelates has also been widely employed. For example, chelates of monomers have been prepared for Ru^{II} and Os^{II} with chelates of the type bipy or phen (1,10-phenanthroline) and monofunctional 4-vinylpyridine (4-VP), bis-(4-pyridyl)ethylene, *trans*-4-stilbazole, *N*-(4-pyridyl)-acrylamide, etc.[18–20,37,38]

Molecular metal chelates can be obtained through reaction of metal-containing monomers with chelates. An example of this reaction is the interaction of bipy and phen with transition metal acrylates to give type (IV) MCM:[13,39,40]

$$M(CH_2{=}CHCOO)_n \cdot mH_2O + L \rightarrow M(CH_2{=}CHCOO)_n \cdot L \cdot pH_2O \quad (IV)$$

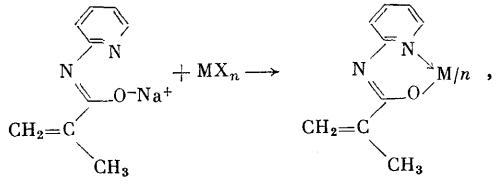
where M = Cu^{II}, Ni^{II}, Co^{II}, Cr^{III}, L = bipy or phen, n = 2, 3; and m and p = 0–2.

2. Inner-sphere compounds

Various methods of synthesising type (II) MCM have been developed. The following examples are typical:

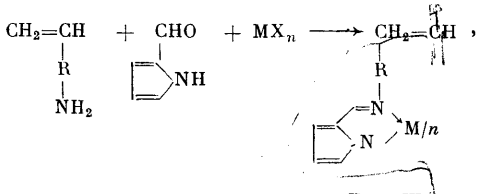
1. direct reaction of MX_n with monomers containing chelating groups. For example, this method was used to prepare Cu^{II} complexes of *N*-vinylsalicylaldimines,[41] complexes of transition[42–44] and rare earth[45] metals with vinyl-β-diketones, chelates of Cu^{II}, Ni^{II}, Co^{II}, Zn^{II} and Cd^{II} with 3-allyl-1-[2-mercapto-4-oxo-3(4*H*)-quinazolinyl]-2-thiopseudourea[46] or 1-isonicotinoyl-4-allyl-3-thiosemicarbazide,[47] a palladiated monomer based on *N*-allylsalicylaldimine,[48] complexes of Cu^{II}, Ni^{II} and Cd^{II} with 5-hydroxyl-5-hydroxy-3-vinyl-3-vinyl-1*H*-benz[*f*]indazole-4,9-dione,[49] etc.

2. Exchange of an alkali or alkaline earth metal in the chelate monomer for a transition metal:[50]



where M = Cu^{II}, Ni^{II}, Co^{II}, Fe^{III}, Cr^{III}; n = 2, 3.

3. Template synthesis of MCM, for example, according to the scheme:[51,52]



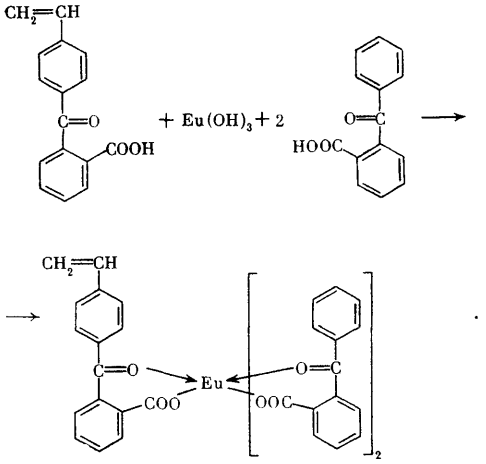
where R = $-C_6H_4-$ or $-CH_2-$; M = Cu^{II}, Co^{III}; n = 2, 3.

4. Addition of acetylenic monomers to metal chelates, in particular, phenylacetylene to dimethylglyoxime complexes of Co:[24,25]

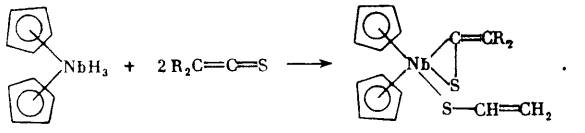
$$HCo(DH)_2 + CH{\equiv}CPh \rightarrow CH_2{=}C(Ph)Co(DH)_2 \ .$$

5. Covalent bonding of metal chelates to monomers. An example is the reaction of Co chelates with *p*-chloromethylstyrene to give cobalt chelate monomers with a cobalt–carbon bond.[4]

6. Neutralisation reactions. Thus, the chelate monomer of Eu^{III} was synthesised by neutralisation of $Eu(OH)_3$ by a mixture of 4-vinylbenzoyl-2′-benzoic and 2-benzoylbenzoic acids in a 1:2 mole ratio:[53]



7. Reaction of metal hydrides with thioketenes:[54,55]

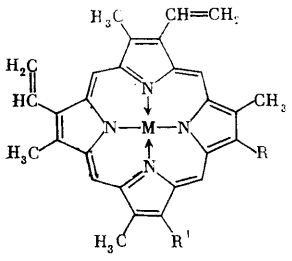


3. Macrocyclic complexes

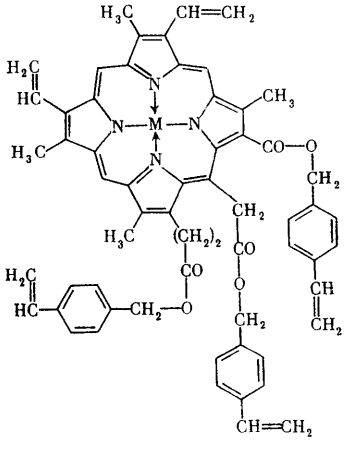
The macrocyclic type of MCM have been synthesised using a whole range of methods. One of these consists of direct reaction of MX_n with unsaturated macrocycles, for example, reaction of nickel acetate with vinylporphyrin.[56] Other metalloporphyrins, in particular, Co^{II}, Fe^{III}, Fe^{II}, Mg^{II}, Zn^{II}, Cu^{II}, etc. containing one or

two vinyl substituents were prepared analogously.[57–59] Typical representatives of these are shown in Scheme 1.

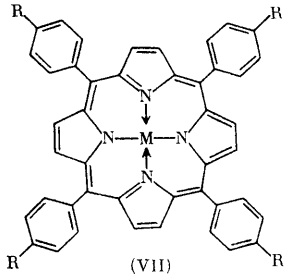
Scheme 1



(V)



(VI)

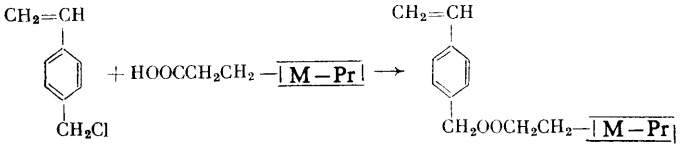


(VII)

where (V) are metal complexes of protoporphyrin-IX [R = R′ = $(CH_2)_2CO_2H$], the dimethyl ester of protoporphyrin-IX [R = R′ = $(CH_2)_2CO_2CH_3$], the vinylbenzyl ester of protoporphyrin-IX [R = R′ = $(CH_2)_2CO_2CH_2C_6H_4CH{=}CH_2$], *N*-(*p*-vinylbenzyl)-*N*′-(imidazolylpropyl)dipropylamidoprotoporphyrin-IX {R = $(CH_2)_2CONHCH_2C_6H_4CH{=}CH_2$, R′ = 1-[$(CH_2)_2CONH.(CH_2)_3$]pyrrole}, and the dimer of protoporphyrin-IX [R = $(CH_2)_2.CONHCH_2-$, R′ = $(CH_2)_2CO_2CH_2C_6H_4CH{=}CH_2$]; (VI) are metal complexes of the porphyrin chlorine; and VII are metal complexes of tetra(*p*-styryl)porphyrin (R = $CH_2{=}CH-$) or acrylamidotetraphenylporphyrin (R = $NHCOCH{=}CH_2$).

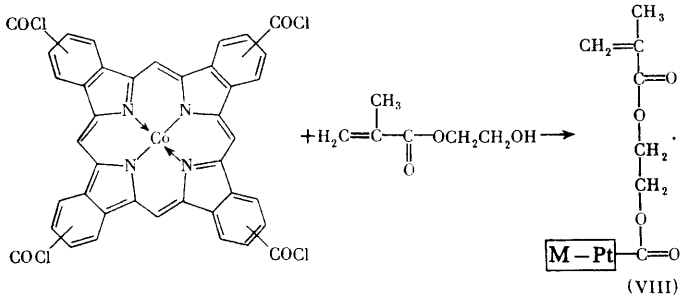
Another method is based on the well known ability of planar metalloporphyrins and -phthalocyanines to accept another ligand owing to coordinative unsaturation of the metal. The additional ligands occupy the fifth and sixth sites in the inner sphere of the transition metal.[60] Such ligands can be vinylpyridines, vinylimidazoles, etc.

However, the method used most widely to synthesise metalloporphyrin monomers consists of interaction of reactive peripheral groups of transition metal porphyrinates (for example, metal complexes of chlorophyll, chlorine, etc.) with monomers:[58,59,61]



where the symbol M–Pr denotes the metalloporphyrin. The most frequently used peripheral groups are carboxyls, sulpho and amino groups. Analogous MCM can be synthesised by reaction of acryloyl chloride with M^{II} tetra-*p*-aminophenylporphyrinate acetate.[61]

These approaches were also used to synthesise metallophthalocyanine monomers. Thus, synthesis of Co phthalocyaninate (VIII) has been described.[62]



(VIII)

Here the symbol M–Pt denotes the metallophthalocyanine. This can also be accomplished using the reaction of acryloyl or methacryloyl chlorides with metal tetra-*p*-carboxyphenylphthalocyaninates.[63]

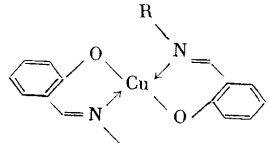
Therefore, analysis of the existing data indicates that the synthesis of MCM is rather well developed and continues to be improved. There appear at present to be no significant synthetic difficulties in synthesising MCM of practically any metals in various valence states. However, as for other types of MCM,[64] aspects of homo- and copolymerisation of MCM are largely unstudied.

III. Homopolymerisation

The kinetics of homopolymerisation of MCM and the properties of the MMC formed have begun to be studied only recently. Thus, the first radical polymerisation of haemin dimethyl ester was effected in 1977.[65] The possibility was demonstrated[18] of polymerising 4-VP complexed to Ru^{II} {complexes *cis*-$[Ru(bipy)_2(4\text{-VP})X]^{n+}$, where n = 1, X = Cl, n = 2, X = CO or 4-VP}. However, the properties of the polymers obtained were not described.

Radical polymerisation of the appropriate monomers produces Er^{III} and vanadyl(II) poly(*p*-acryloyloxyphenyltriphenylporphyrinates). The elemental analyses are consistent with 100% occupancy of the coordination sites by metal.[66] In contrast, the usual method (polymerisation of the corresponding chelate monomer with subsequent binding of metal by the macroligand obtained) gives only 50% metal incorporation. It is interesting that, in contrast with the starting chelate monomer of vanadyl with a weak antiferromagnetic exchange interaction (the Curie–Weiss θ value is −25 K), the polymer obtained that is based on it exhibits strong antiferromagnetic interaction (θ = −170 K). This indicates that the polymer chains play an important role in the magnetic interaction.

Salicylaldimine (Salim) chelates of Cu^{II}, CuL_2



(IX)–(XI)

(IX): R = 4-$CH_2{=}CH-C_6H_4-$ (L = Salim′),
(X): R = 4-$CH_2{=}C(CH_3)-CO_2C_6H_4-$ (L = Salim″),
(XI): R = $CH_2{=}C(CH_3)-CO_2-(CH_2)_2-$ (L = Salim‴),

were polymerised in the presence of azobisisobutyronitrile (AIBN) in the ratio AIBN : MCM = 0.12 : 1.[41] The rate of polymerisation was much less than that for the corresponding salicylaldimines (Table 1). Moreover, homopolymerisation of MCM of Cu^{II} was entirely impossible in a number of other attempts. For example, polymerisation of Cu^{II} methacryloylacetonate in the presence of very different initiators was unsuccessful.[42] Their ineffective homopolymerisation may be due to intramolecular chain termination:

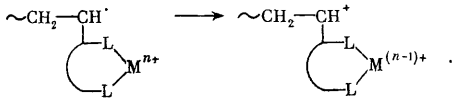


Table 1. Rate of polymerisation of type (IX)–(XI) MCM and the corresponding salicylaldimines.

L	CuL_2	W_{tot}, 10^5 mol dm^3 sec^{-1}		W_{sp}, 10^5 (dm^3)^2 sec^{-1}	
		L	CuL_2	L	CuL_2
Salim′	(IX)	2.59	0.23	5.28	2.10
Salim″	(X)	9.26	1.95	18.89	17.73
Salim‴	(XI)	0.34	0.0079	0.69	0.0718

It should be noted that allyl derivatives of metal β-diketonates do not undergo radical homopolymerisation.[44]

The mechanism of reductive electrochemical polymerisation of Ru^{II}, Os^{II} and Fe^{II} perchlorate and hexafluorophosphate mixed-ligand chelates of monomers has been studied in more detail.[19,20,38,67–69] Such complexes contain a chelating group of the type bipy, phen or terpyridyl (terpy) and a monofunctional monomer of the type 4-VP, *trans*-4-stilbazole, etc. Polymerisation occurs by repeated cycling of the electrode potential (Pt, vitreous carbon, etc.) near values corresponding to ligand reduction. This causes the electrode surface to be covered with an even film of polymer. The MCM in which the vinyl group is bonded to the chelating group polymerise in a similar way (for example, Zn^{II}, Ru^{II} and Ir^{III} complexes of 4-vinyl-4′-methyl-2,2′-bipyridyl).[31] In this instance the film forms much more effectively (the number of moles of polymer per mole of starting MCM).

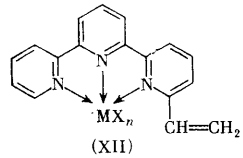
The mechanism of the electrochemical polymerisation includes formation of an anion–radical, for example, by the following reaction:

$$[Ru(bipy)_2(L)_2]^{2+} + \bar{e} \rightarrow [Ru(bipy)(bipy^{\cdot-})(L)_2] + \bar{e} \rightarrow [Ru(bipy^{\cdot-})_2(L)_2]^0,$$

where L is a monofunctional monomer. However, polymerisation is initiated by one-electron reduction based on an intramolecular redox equilibrium involving the thermodynamically less stable isomer in which the electron is localised on L;

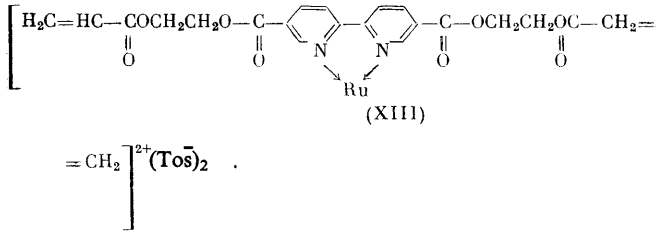
$$[Ru(bipy)(bipy^{\cdot-})(L)_2]^+ \rightleftarrows [Ru(bipy)(bipy^0)(L)(L^{\cdot-})]^+.$$

The dependence of polymerisation rate on the number of vinyl groups in the MCM and their position relative to the coordinated nitrogen atoms was studied for the example of Co, Fe and Ru complexes of various vinyl derivatives of terpy.[29] In particular, it was found that increasing the number of vinyl groups in the complex leads to significantly increased polymerisation. This was noted in a number of other instances.[64] Also, introduction of a vinyl group in the α-position relative to the nitrogen of the pyridine ring [complex (XII)] inhibits polymerisation of the MCM.



(XII)

Similar metal polymer coatings can be prepared by another method, deposition of MCM solution on the electrode surface with subsequent thermal polymerisation. The effectiveness of such an approach was demonstrated for polymerisation of 5,5′-bis-[(3-acryloyl-1-propoxy)carbonyl]-2,2′-bipyridylruthenium(II) toluenesulphonate (Tos) (XIII).[70–73]

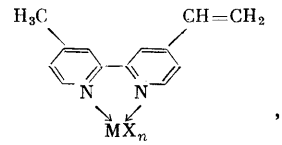


(XIII)

The thickness of the coating is regulated by the polymerisation conditions.

IV. Copolymerisation

Copolymerisation of MCM with traditional monomers is more common than their homopolymerisation. Thus, copolymers containing complexed rare earths (Eu^{III} and Tb^{III}) were prepared by copolymerisation of MCM of type (XIV)–(XIX) with methylmethacrylate (MMA) in a block or methanol.[45]

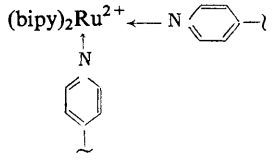


M = Tb^{III}, X = bipy(XIV), phen(XV), terpy(XVI);
M = Eu^{III}, X = bipy(XVII), 1-furyl-4-trifluoroacetylacetone(XVIII), dibenzoylmethane(XIX).

As it turns out the nature of the ligand X had a considerable influence on the fluorescence intensity of the copolymers obtained. In particular, the fluorescence intensity of the Tb complexes decreased in the order: (XVI) > (XIV) > (XV). That for the Eu complexes followed the order: (XIX) > (XVIII) > (XVII). Moreover the fluorescence intensity of the copolymers was much greater than a mixture of the starting monomers. This is consistent with fluorescence quenching by the double bond in the MCM.

Radical copolymerisation of *cis*-$[Ru(bipy)_2(4\text{-}VP)Cl]ClO_4$ and *cis*-$[Ru(bipy)_2(4\text{-}VP)_2](ClO_4)_2$ with styrene (St), MMA and 4-VP has also been achieved.[18] The copolymers based on Ru^{II} complexes

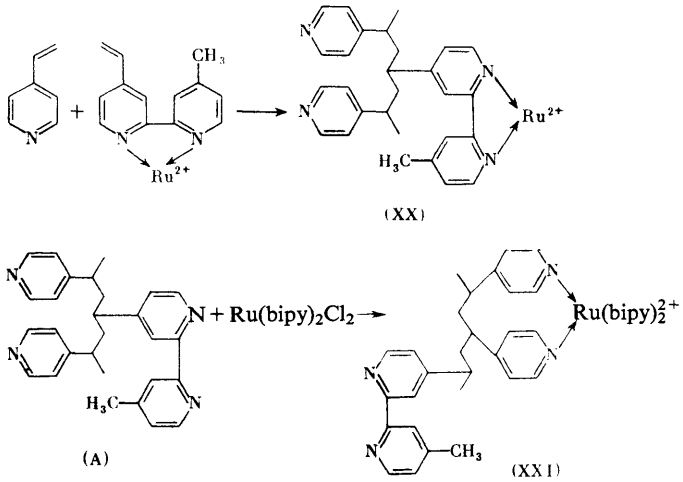
containing one 4-VP molecule were soluble in CH_2Cl_2 and methanol whereas the product of $[Ru(bipy)_2(4\text{-VP})_2](ClO_4)_2$ copolymerisation (comonomer of 4-VP, starting ratio [4-VP]:[MCM] = 20) were insoluble in organic solvents owing to crosslinking through metal atoms:[18]



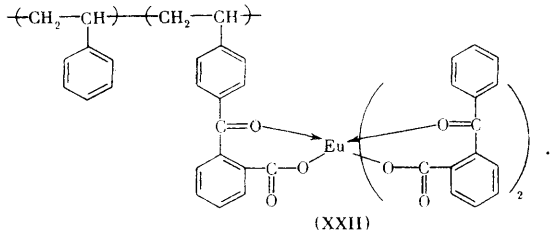
It was demonstrated that MX_n has much less influence if the ratio [4-VP]:[MCM] is increased to 200, for which a soluble product is formed.

It is interesting that copolymerisation of MCM can produce MMC of different structure from those formed by reaction of MX_n with analogous chelating macroligands prepared in advance. For example, copolymerisation of 4-VP with the Ru complex based on 4-vinyl-4′-methyl-2,2′-bipyridyl produces the polymer (XX) (Scheme 2),[31] whereas reaction of the chelating macroligand (A) with $Ru(bipy)_2Cl_2$ gives polymer (XXI).

Scheme 2



Unfortunately, kinetic aspects of the copolymerisation are not treated in the majority of studies of MCM copolymerisation. The mechanism of copolymerisation also is not described in detail for such MCM as Eu[2-(4′-vinylbenzoyl)benzoate]-di(2-benzoylbenzoate) with St to form (XXII).



This MMC characteristically has a high fluorescence intensity proportional to metal content, in contrast with complexes prepared by reaction of $EuCl_3$ with macroligands containing 2-carboxybenzoyl (XXIII) or 2-carboxynaphthoyl (XXIV) groups (Fig. 1).[53] The Eu^{III} complex of 1-(*p*-vinylphenyl)-3-phenylpropane-1,3-dione was copolymerised with MMA in an analogous manner.[45]

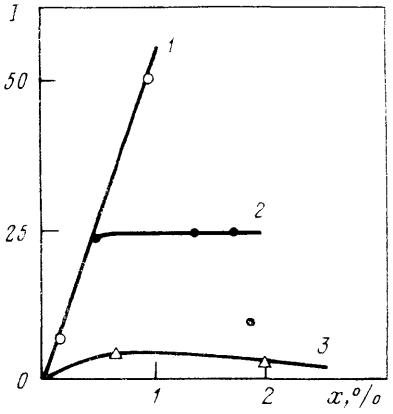
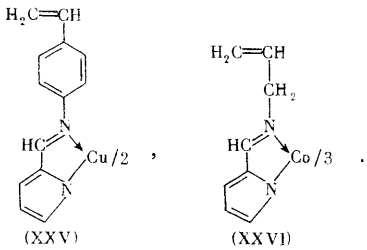


Figure 1. Dependence of fluorescence intensity (*I*) on Eu content (*x*) in complexes (XXII) (curve *1*), (XXIII) (*2*), and (XXIV) (*3*).

Radical copolymerisation of the Co^{II} complex of *N,N′*-bis-[4′-(*p*-vinylbenzyloxy)salicylaldehyde]-1,2-diaminocyclohexane with St and divinylbenzene (DVB) led to ternary copolymerisation in which 20 St and DVB molecules were added for each MCM.[74]

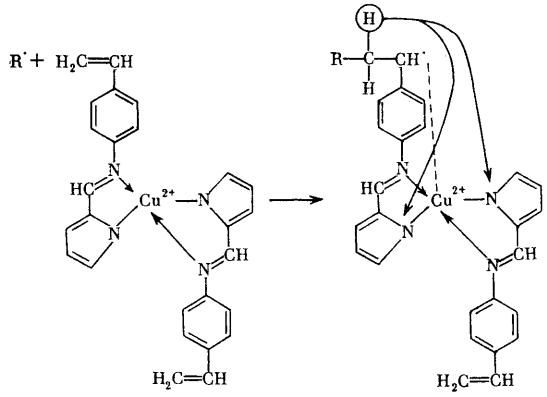
In contrast with the qualitative work mentioned above, the mechanism of copolymerisation of St, MMA, acrylonitrile (AN) or acrylic acid (monomer M_1) with MCM (monomer M_2), represented by the Cu^{II} complex with pyrrolylmethyleneiminostyrene (PIS) of type (XXV) or the Co^{III} complex with pyrrolylmethyleneiminopropene (PIP) or type (XXVI), has been studied.[51]



As seen from Fig. 2, the mole fraction of monomer M_2 in the copolymers formed is greater for MCM than for its metal-free analogue. The reactivity of the comonomer increases on adding metal (Table 2). This is comparatively rare in the polymerisation and copolymerisation of MCM.[64] Furthermore, only one or two out of the three multiple bonds in the Co^{III} chelate of type (XXVI) are involved in the copolymerisation of MCM. The third multiple bond is incorporated into the copolymer. For the Cu chelate, all vinyl groups are involved in the process. However, the polymerisation of this MCM is initiated along a complicated path (Scheme 3). The primary radical first attacks the vinyl group of the monomer. The free electron then transfers from this group to the central metal ion. This process is enhanced by conjugation (a long coplanar π-electron

system). The chain does not propagate until Cu^{II} is completely reduced to Cu^{I}. β-Elimination of a proton from the vinyl group attacked by the primary radical and addition of the proton to the pyrrole nitrogen atom occur simultaneously.

Scheme 3



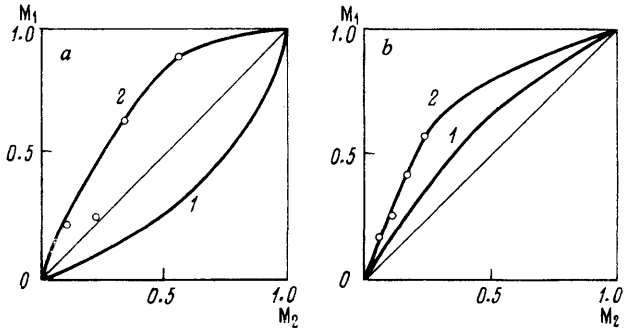


Figure 2. Composition diagram of copolymerisation of MCM (*2*) and their metal-free analogues (*1*) with AN (*a*) and St (*b*). *a* is copolymerisation of complex (XXVI); *b*, complex (XXV).

Copolymerisation of macrocyclic MCM is less well studied. The comonomers used for this are classified according to the Q parameter (resonance stabilisation of the monomer during copolymerisation). Monomers with high Q values (St, MMA, π-conjugated monomers) copolymerise with haemin and its dimethyl ester. During the copolymerisation Fe^{III} is reduced to Fe^{II}.[75,76] The haemin content in the copolymer with St is basically the same as that in the mixture of monomers (Table 3). As the ratio [MCM]:[St] increases, the yield, relative molecular mass, and viscosity of the polymer decrease owing to the influence of the metalloporphyrin on chain propagation (the coefficient of chain propagation C_s = 2.3).

However, copolymerisation of non-conjugated monomers (with a low Q value) does not occur as a result of addition of a radical to haemin to form stable adducts. Therefore, attempts to copolymerise haemin with vinylpyrrolidone (VPr) and vinylimidazole (VIA) were unsuccessful.[75] It is interesting that non-conjugated monomers can be copolymerised with haemin in the presence of a third conjugated comonomer, for example, to form the ternary copolymer haemin–VIA–St.[65,75,76] Copolymerisation of haemin with VPr under the influence of γ-irradiation from ^{60}Co or with 2-hydroxyethylmethacrylate in a buffer (Na_2CO_3–$NaHCO_3$, pH 10) has been described.[77] The MCM obtained through reaction of Mn tetra-*p*-aminophenylporphyrinate-acetate with acryloyl chloride readily copolymerises with MMA or 4-VP to form soluble MMC.[61] Tetra(*p*-vinyl)benzyl esters of the dinuclear Mg^{II} complex with chlorophyll copolymerise through a cationic mechanism (BF_3 etherate) with α-methylstyrene.[78] A three-dimensional structure with the metal monomer immobilised in the bulk of the polymeric gel is formed as a result of copolymerisation of the vinylporphyrin monomers of Co^{II}, Fe^{II} and Ni^{II} containing one or two vinyl substituents with acrylamide or *N,N'*-methyl-bis-acrylamide.[57] The parameters of such a networked structure are easily regulated by the ratio of comonomers.

Table 2. Copolymerisation activity of metal chelate monomers (XXVI) and (XXV) and their corresponding free ligands.

M_1	M_2	Copolymerisation constant	
		r_1	r_2
АН	ПИП	2.30	0.40
АН	(XXVI)	0.86	8.60
Ст	ПИС	0.50	1.80
Ст	(XXV)	0.45	6.90

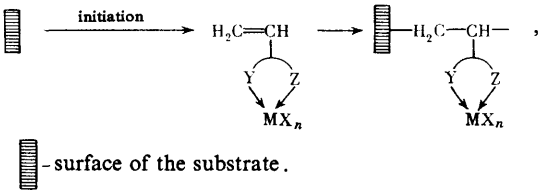
Table 3. Radical polymerisation of styrene with haemin[76] and its dimethyl ester.[75]

Porphyrin	Amount of porphyrin, mol%		Polymer yield, %	$\bar{M}_\eta \cdot 10^{-4}$	[η], 10^2 dm^3 g^{-1}
	in the monomer mixture	in the polymer			
Haemin dimethyl ester*	0	0		12.3	
	0.025	0.1		8.3	
	0.05	0.12		5.9	
	0.125	0.31		3.0	
Haemin**	0.49	0.53	75.6		9.96
	1.95	1.94	60.7		8.66
	3.44	3.31	41.7		7.65

* Copolymerisation in pyridine with AIBN at 358 K.
** Block polymerisation with AIBN at 333 K.

Copolymerisation of a type (VIII) monomer with 9-vinylcarbazole is an example of copolymerisation of metallophthalocyanine monomers.[62]

A special type of MCM copolymerisation is graft polymerisation, where the initiators are fixed to a polymeric or other kind of substrate.



Unfortunately, data on graft polymerisation of MCM are very limited, the majority of them being recently obtained.[13,40,79–85] Nevertheless, it is noteworthy that a distinguishing feature of the grafting of these MCM is the nearly complete absence of the homopolymer. The kinetic dependences of polymerisation are similar to those found for other types of MCM.[64,86,87] In particular, the kinetic dependences exhibit an identical nature for all chelates studied (Fig. 3). The rate is maximal during the first 0.5 h and then quickly drops. Moreover, the nature of the transition metal has a substantial effect on the grafting. Absorption bands of the C=C bond at 1640 cm^{-1} in the IR spectra of grated polymers containing metals are consistent with a certain amount of unpolymerised vinyl groups. In other words, only part of the vinyl groups polymerise during grafting of the MCM. The similarity of the spectral and magnetic properties of the monomers and polymers based on them (Table 4) indicates that the valence state and the coordination sphere of the metal do not change during grafting. However, the splitting parameter (Dq) decreases and the Racah interelectron repulsion parameter (B') increases on going from MCM to their polymers. Considering[88] that $Dq \approx d^{-6}$, it can be assumed that the decrease of the splitting parameter indicates an increase of the metal–ligand distance (d) in the indicated order. Moreover, the nephelauxetic parameter β increases in this same order. This indicates a decrease of the covalency of the metal–ligand bond.

V. Applications

Metal chelate monomers and polymers based on them find very diverse applications stimulating the direction of investigations in this area of chemistry.

1. Improvement of operating and physicomechanical properties of polymers

As a rule, polymers based on MCM are stable up to 473–523 K. Introduction of even a small amount of these monomers to copolymers of common monomers leads to crosslinked polymers with increased thermoplasticity and stability toward organic solvents. In particular, bis-(aminoethyleneamido-maleate-tetrahydrate)zinc prepared from zinc maleate and ethylenediamine was used to crosslink polyethylene in order to increase its resistance to thermal ageing and cracking.[89,90]

The reduced products of electrochemical polymerisation of vinyl derivatives of Fe^{II}, Ru^{II} and Os^{II} containing bipy are photoconductive (λ_{max} = 420–520 nm).[91] It should be noted that the metal ions in MMC, as a rule, have the same photophysical properties as in the corresponding MCM. Thus, monomeric Eu^{III} and Tb^{III} complexes with 4-vinyl-4′-methyl-2,2′-bipyridyl, like their copolymers with MMA, are excited at λ_{max} = 335 and λ_{max} = 500–600 nm, respectively. This is characteristic of these ions.[45] It is interesting that the polymeric products exhibit more intense fluorescence than the MCM. These substances may have utility in lasers.

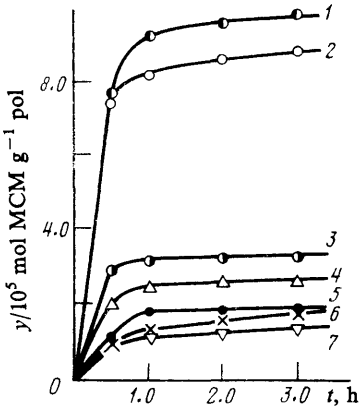


Figure 3. Kinetic curves of yield of grafted MCM polymers based on methacryloylacetophenone: Co^{II} (*1*), Ni^{II} (*2*), Pd^{II} (*3*), Mn^{II} (*4*), Cu^{II} (*5*), Fe^{III} (*6*), Cr^{III} (*7*) (ethylacetate, [MCM] = 0.04 and dm^{-3}, 70 °C, D = 200 kJ kg^{-1}).

Table 4. IR, electron-spectroscopic, and magnetochemical data for type (IV) MCM and their grafted polymers.

Complex	M	L	IR spectrum (principal frequencies), cm^{-1}			Dq, cm^{-1}	B', cm^{-1}	β	μ_{eff}, μ_B
			ν(C=C)	ν (heterocycle)	ν(COO–)				
Monomer	Ni	bipy	1635	1605	1565	1134	773	0.743	3.16
Polymer	Ni	bipy	1639	1606	1560	1028	837	0.804	2.96
Monomer	Co	bipy	1637	1610	1560	1152	834	0.859	4.53
Polymer	Co	bipy	1638	1608	1560	1018	883	0.909	4.75
Monomer	Ni	phen	1637	1600	1565	1166	830	0.797	3.17
Polymer	Ni	phen	1640	1600	1560	990	857	0.823	2.95
Monomer	Co	phen	1635	1605	1565	1163	849	0.874	4.75
Polymer	Co	phen	1639	1608	1565	1016	884	0.911	4.87

Macromolecular metal chelates based on $[Ru(bipy)_2(4\text{-}VP)_2]^{2+}$ and $[Ru(bipy)_2(4\text{-}VP)Cl]^+$ exhibit luminescence in methanol or dilute acids at room temperature.[18] Thus, absorption of the metal ions in poly-$[Ru(bipy)_2(4\text{-}VP)Cl]_n^+$ in methanol at 455 nm leads to a broad emission with a maximum at 615 nm.

Electroactive polymeric coatings are prepared by reductive electrochemical polymerisation of MCM consisting of vinylpyridine derivatives of Fe^{II}, Ru^{II} and Os^{II} complexes with chelates.[19] They are unique in that the redox centres are localised on each monomeric nucleus.

It also seems interesting to use grateful metal chelate polymers as antiwear and anticorrosion additives to lubricants.[15,40] In particular, addition to TsIATIM-201 lubricant of the type (IV) Cu acrylate

complex of bipy grafted to the surface of polytetrafluoroethylene (PTFE) improves its tribiological characteristics (corrosion index, seizing load and weld load) (Fig. 4). Whereas this MMC is more effective than grafted Cu acrylate,[92] this is apparently related to the involvement of the chelating ligand (bipy) in the transfer of Cu from one contacting surface to another. A very thin film of Cu metal (protective film) can be seen on the frictional surface after the tests. This is consistent with a "wearless" regime in these systems.[93,94]

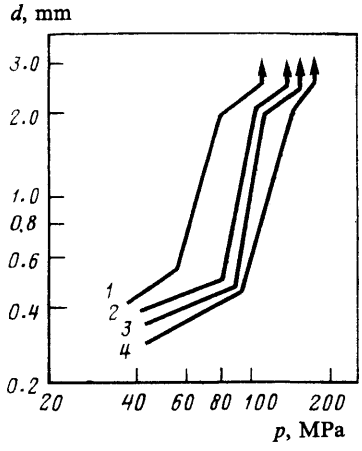


Figure 4. Dependence of average wear-spot diameter (d) of a four-ball machine on applied axial loading (P) for TsIATIM-201 lubricant: without PTFE additive (*1*), with PTFE additive (*2*), with PTFE additive and grafted Cu acrylate (*3*), with PTFE additive and grafted Cu acrylate complex with bipy (*4*).

2. Catalytic activity

Macromolecular metal chelates based on chelate monomers include immobilised catalysts[9,10] that combine the high activity and selectivity of homogeneous systems with the technology of heterogeneous ones. Chelation is one of the simplest methods of surmounting the principal drawback of immobilised catalysts, the relatively unstable metal–polymer bond during the catalysed reaction.[12] Moreover, such MMC can be prepared in one step. This is important in planning practical applications of these catalytic systems. Finally, an important advantage of such catalysts is the possibility of rather simple determination of the metal complex structure (the valence and electronic state of the metal, its ligand environment, the geometric structure of the metal chelate group, etc.) in addition to the controlled distribution of metal complexes along the polymer chain. This is due to the ease of separating intermediates at any step of the catalysed reaction.

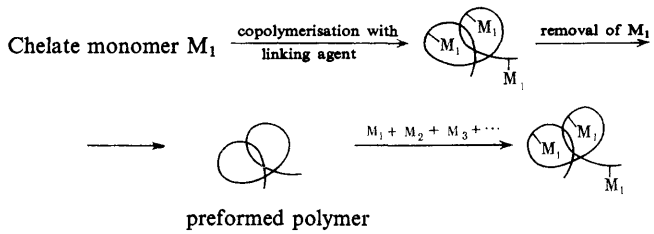
Examples of the use of MMC based on MCM are numerous. Therefore, let us point out the most typical ones. Soluble metalloporphrin polymers prepared by copolymerisation of MMA or 4-VP with macrocyclic MCM, represented by the product of reacting Mn tetra-*p*-aminophenylporphyrinate-acetate and acryloyl chloride, were capable of catalysing oxidation of olefins by molecular oxygen.[61] The copolymer of acrylamide and *N,N'*-methylene-bis-acrylamide with the Ni^{II} vinylporphyrin complex (in combination with H_2O_2) has been used to create effective redox systems for initiating polymerisation of acrylamide in aqueous medium.[57] Effective catalysts for ethylene dimerisation have been prepared by radical polymerisation of type (IV) Ni^{II} acrylate complexes with bipy and phen.[95]

As expected, more active catalysts are obtained by graft polymerisation of MCM since in this instance the catalytically active centres are localised on the support surface. For example, the grafted Pd^{II} chelate of a diketone ligand showed high activity for hydrogenating isomers of chloronitrobenzene.[82] This catalyst remains active for 15 cycles.

3. Template effect in macromolecular metal chelates

As applied to metal polymer systems, the template effect refers to the "recognition" and binding of those metal ions that were used as templates for synthesis of metal polymer complexes.[94,96–99] Ordinary chelate polymers do not selectively bind particular metal ions. As a rule, the selectivity is determined by the formation constants of the corresponding complexes and reaction conditions such as pH, solvent, temperature, etc.[7,8] Also, MMC prepared by copolymerisation of MCM with crosslinking agents exhibit "superstructure". The sorption capacity, sorption rate and selectivity of superstructured polymers increases dramatically after metal ions are removed. The mechanism of this effect is depicted in Scheme 4. The bond length and angle between the central metal ion and the coordinated ligand are strictly determined by their nature. When the chelating groups of the MMC are somehow immobilised and the metal ion is then removed geometrically, i.e., with retention of the preformed structure, the remaining polymeric ligand can have "pockets" specifically disposed to the same metal ions (templates) that were removed from the polymeric matrix.

Scheme 4



Thus, although the copolymer of 4-vinyl-4'-methyl-2,2'-bipyridyl, St and DVB from solutions of Ni^{II} and Cu^{II} salts of identical concentrations to a large extent binds Cu^{II} (as a result of the large binding constant of this complex), this same polymer preformed in the presence of Ni^{II} exhibits a template effect for Ni (Fig. 5).[100]

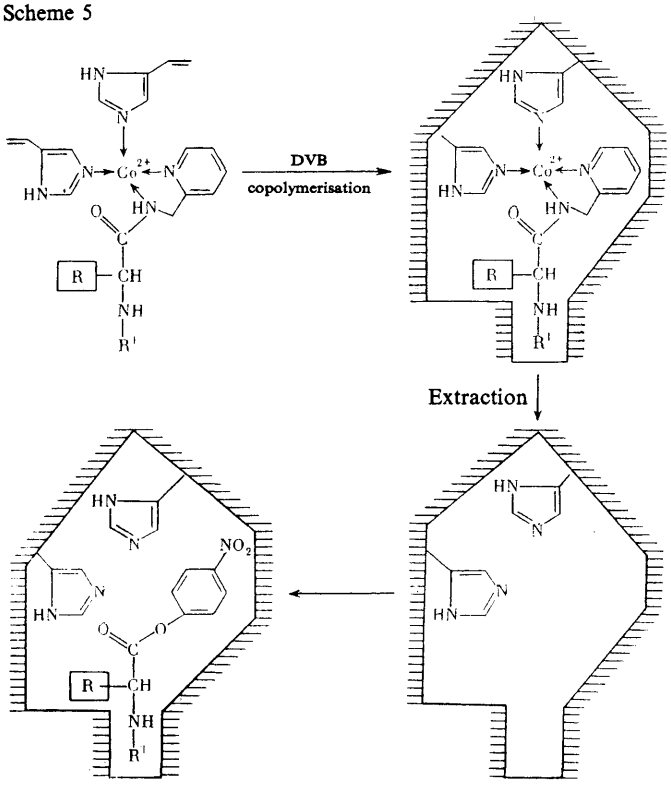
Polymeric chelates prepared by copolymerisation of dithiophosphate complexes, for example bis-[di(4-vinylphenyl)dithiophosphato].Ni^{II} or -Co^{II} and -Cr^{III}, with St and ethyleneglycolmethacrylate exhibit selectivity for the particular ion after removal of the metal. The enrichment factor (ratio of metal bound by the structured and unstructured polymers) for Ni^{II} is 1.4; for Co^{II}, 2.4.[101]

It should be noted that template syntheses can be effected using MMC. For example, it is possible to separate the racemate of D- and L-phenylalanine.[74] In this instance the separation is carried out as follows. The chelate monomer of Co^{II} with the Schiff base is initially synthesised. Then D-phenylalanine is added. Copolymerisation with St and DVB is carried out. The D-phenylalanine is extracted using HCl. The polymer obtained, structured for the

D-isomer, exhibits a template effect relative to the D-isomer of the racemic mixture (with optical purity 74 ± 1%).

New types of structured polymers that model active group histidine have been synthesised.[102] Complexes of Co^{II} with 4(5)-vinylimidazole and leucine-2-picolinimide or with leucine are copolymerised with DVB in a mixture of water, alcohol and butanol. The polymer particles (200–500 nm) are subjected to extraction with methanol for 12 h. The template molecules are then removed using bipy. The structured polymer formed is used as a catalyst for hydrolysis of *p*-nitrophenyl esters to amino acids (Scheme 5). The hydrolysis rate in the presence of polymers structured for the corresponding methionine or leucine derivatives is significantly greater than in the presence of unstructured ones. This is explained by the creation in the structured polymers of discrete voids with imidazole groups. The effect is retained after repeated use of the structured polymers. This is indicative of the catalytic nature of such action.

Scheme 5



IV. Conclusion

Analysis of existing data on the synthesis, homopolymerisation and copolymerisation of MCM indicates that significant progress has been made in solving several problems on the chemistry of MCM and that extensive investigations are being carried out in this area. Among the most important questions, the solutions of which would reveal general principles of the chemistry of MCM, we note the following:

1) development of new methods for preparing MCM;
2) establishment of the activation pathways of the multiple bonds of MCM, a detailed analysis of the influence of the metal on the separate polymerisation steps, discovery of new methods of initiating polymerisation;
3. investigation of the reactivity of the multiple bonds of MCM in other reactions (hydrogenation, isomerisation, oxidation, ozonolysis, hydroformylation, etc);
4) study of the copolymerisation of MCM with each other and with common monomers;
5) determination of the structures of metal polymer chains, investigation of the changes experienced by the metal ion during polymerisation, and the study of cooperative effects in MMC and their topochemistry;
6) study of the stereoregulation and supermolecular organisation in MMC;
7) discovery of new applications of MCM and polymers based on them, including their industrial use.

The final resolution of these problems requires joint efforts of specialists on the chemistry of polymers, coordination compounds, organic synthesis, catalysis, etc.

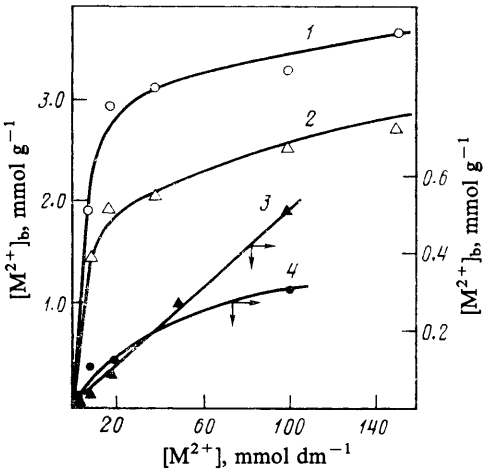


Figure 5. Binding of Cu (curves *1* and *3*) and Ni (curves *2* and *3*) by the copolymer of 4-vinyl-4′-methyl-2,2′-bipyridyl, styrene and divinylbenzene (*1*, *4*) and this same copolymer synthesised with a Ni template (*2*, *3*).

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