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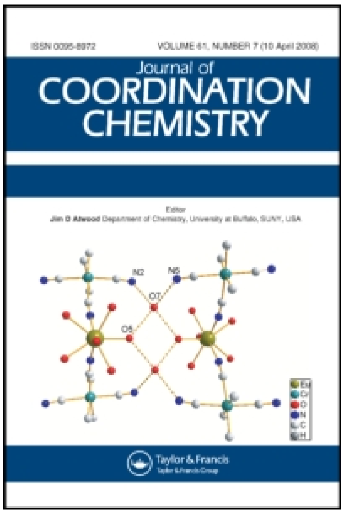

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Metal Chelate Monomers

I. E. Uflyand[a]; A. D. Pomogailo[b]
[a] Department of Chemistry, State Pedagogical Institute, Rostov-on-Don, USSR [b] Institute of Chemical Physics, Academy of Sciences, Chernogolovka, Moscow region, USSR

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METAL CHELATE MONOMERS

I. E. UFLYAND*

Department of Chemistry, State Pedagogical Institute, Engelsa 33, Rostov-on-Don 344082, USSR

and A. D. POMOGAILO

Institute of Chemical Physics, Academy of Sciences, Chernogolovka, Moscow region 142432, USSR

The principal advances and problems of the synthesis, properties, poly-, homo-, co- and graft polymerization of metal chelate monomers based on the metals of IVA–VIIA and VIII groups of the Periodic Table are analysed. The metal chelate monomers are classified by the type of metal bond with chelating ligands consisting of three principal groups: molecular metal chelates, intracomplex compounds and macrocyclic complexes. Special attention is paid to the effect of a transition metal on both the polymerization and properties of the products formed. The basic fields of application of the metal chelate monomers and macromolecular metal chelates based on them have been summarized.

Keywords: Metal chelate monomers, polymerization, copolymerization, graft polymerization, macromolecular metal chelates

CONTENTS

1. INTRODUCTION

Progress in many fields of science and engineering is connected to macromolecular metal chelates (MMC). MMC are high-molecular weight compounds that incorporate metal chelate cycles. The major achievements in synthesis and investigations of MMC have been summarized recently.[1,2] The construction of MMC is, as a rule, multistage and includes the following steps: polymer carrier → its functionalization

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* Author for correspondence.

and creation of chelating fragments → synthesis and chelation of metal compound (MX_n) → separation of chemically free reagents. Besides, the chelation in the polymer-MX_n systems are more complicated than the reactions of low-molecular weight ligands because both reagents may undergo various transformations. The most significant transformations of transition metal compounds in chelation reactions are oxidation-reduction processes, dissociation of dimer complexes, clusters formation, and changes of geometry. The polymer destruction, conformational changes, structure formation, and change of functional group nature may play an important role. It is important that the compositional non-uniformity of MMC, the different character of metal distribution on the carrier, and the different valence states and coordination of transition metals, strongly influence the properties of MMC.

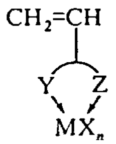
At the same time, the most distinctive feature of MMC is the possibility of incorporation of metal chelate units through direct polymerization and copolymerization of metal chelate monomers (MCM). The polymerization and copolymerization of MCM is a unique method of synthesizing MMC wherein practically all chelating fragments contain the metal. However, only limited studies have been conducted on the synthesis and characteristics of MCM, their polymerization and copolymerization behaviour. What this means is that the presence of a transition metal atom in the molecules of these monomers leads to various coordination reactions, and redistribution of the electron density at the growing sites, which in turn governs all the elementary stages of the polymerization process.

This review is connected with the major advances and problems of the preparation, investigation of structure, polymerization, copolymerization, graft polymerization, and applications of MCM and MMC based on them, and also outlines the most rational future developments in this field.

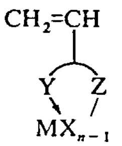
2. METHODS OF SYNTHESIS AND STRUCTURE OF METAL CHELATE MONOMERS

MCM are compounds that include a double or triple bond capable of polymerization, and a metal chelate cycle. Multiple-bonded metal chelates, a priori incapable of polymerizing and copolymerizing, such as acetylacetonates, enaminoketonates, enaminoiminates, metal chelates with bulky substituents at the multiple bond, etc., are not metal chelate monomers.

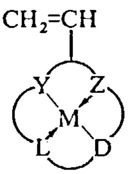
According to the type of bond between the metal and the organic molecule, MCM can be classified into the following types:



molecular chelates(I)



intracomplex compounds(II)



macrocyclic complexes(III)

(M is metal, n is the metal valence, X is the metal ligand, and Y, Z, L, D are the respective functional groups.)

The MCM type I are characterized by coordination bonds of the metal ion with the donor atoms of the chelating fragments. Such MCM are formed with the aid of fragments having the obviously metallocyclization arrangement of the donor sites or conformationally nonrigid groups with two or more donor sites. In the second class of monomers (II) at least one fragment is linked with the metal ion via both a valent and coordination bond. It should be noted that such compounds can be neutral, cationic, anionic or contain, in addition to chelating ligands, monofunctional varieties. In the MCM type III the metal ion is bound by macrocyclic grouping. Within these types the MCM are subdivided depending on the nature of the donor atoms (O,O-; N,N-; N,O-; P,P-chelates, etc.).

Modern synthetic MCM chemistry uses widely general methods and principles of complex compound synthesis. At present, some synthetic approaches have been developed which allow us to prepare MCM with practically all metals and, at least in principle, in any of their valent states.

2.1. *Molecular metal chelates*

The most widely used syntheses of MCM type I involve coordination binding of monofunctional monomer with the metal chelate. Thus, the complexes of M(II) compounds (M is Ru and Os) have been synthesized via substitution reactions with cis-$M(Dipy)_2Cl_2$ (Dipy is 2,2′-dipyridyl) in aqueous-alcohol solutions on heating in the presence of vinyl ligands such as 4-vinylpyridine (4-VP), bis(4-pyridyl)ethylene, trans-4-stilbazol, and N-(4-pyridyl)acrylamide.[3-5] In the Ru(II) complexes, one or two chlorine atoms can be substituted, whereas the synthesis of the Os(II) disubstituted complexes relies on the use of cis-$Os(Dipy)_2CO_3{\cdot}2H_2O$. The complexes cis-$[Ru(Dipy)_2(4\text{-}VP)X]^{n+}$ (n = 1, X = Cl; n = 2, X = CO or 4-VP) have been synthesized from $Ru(Dipy)_2Cl_2{\cdot}2H_2O$, 4-VP, and $NaClO_4$ or NH_4PF_6.[6,7]

One convenient way to synthesize metal chelate monomers of molecular type is the interaction of MX_n with chelating monomers. This method has been instrumental, for instance, in the synthesis of complex of $CuCl_2$ with the vinyl ether of monoethanolamine,[8] Ru(II), Co(II), Fe(II) complexes of 4-vinyl, 6-vinyl, and 4′-vinylterpyridines,[9] Cu(II), Ni(II), Co(II), Mn(II), Zn(II) complexes with 1-vinyl-2-hydroxymethylimidazol and 1-vinyl-2-vinyloxymethylimidazol,[10,11] etc.

In order to obtain molecular chelates, the interaction of metal-containing monomers and chelating agents can be used, e.g., the action of Dipy and Phen (Phen is 1,10-phenanthroline) on the metal acrylates:[12]

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

where M is Co(II), Ni(II), Cr(III), L is Dipy or Phen, $m, p = 0\text{–}2$, $n = 2, 3$.

The most typical representatives of molecular MCM and methods of their preparation are listed in Table I.

2.2. *Intracomplex compounds*

To prepare the intracomplex MCM the following methods are used:

(i) the direct interaction of MX_n with monomers containing chelating groups. Thus, for example, this method was used to obtain a Eu(III) complex with 1-(*p*-vinylphenyl)-3-phenyl-1,3-propanedion;[17]

TABLE I
Synthesis of molecular MCM

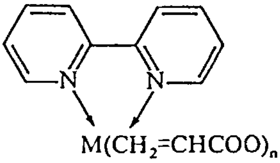
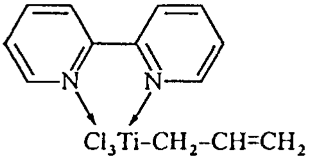
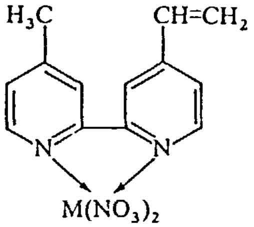
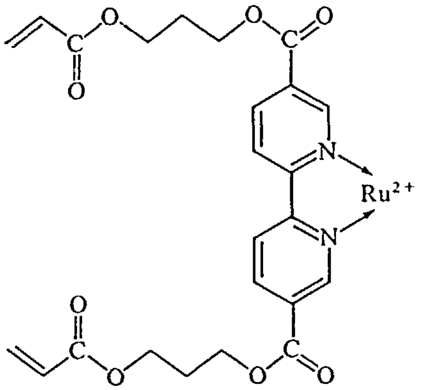
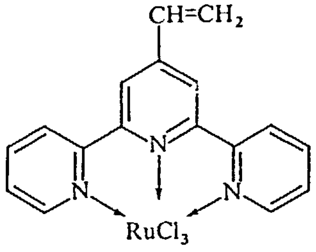
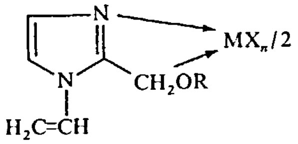
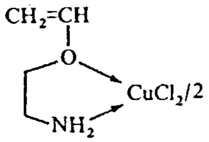
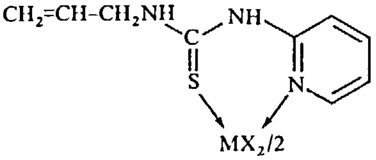
Monomer	Reaction	Refs.
	Ni(II), Co(II), and Cr(III) acrylates + Dipy	12
	allyltitaniumtrichloride + Dipy	13
	4-vinyl-4'-methyl-2,2'-dipyridyl + $Ni(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$	14
	5,5'-bis[(3-acrylyl-1-propoxy)carbonyl]-2,2'-dipyridyl + $Ru(Dipy)_2Cl_2$	15
cis-$[Ru(Phen)_2(4\text{-}VP)_2] \cdot (PF_6)_2$	$Ru(Phen)_2Cl_2 \cdot 2H_2O$ + 4-VP + NH_4PF_6	3
	4'-terpyridine + $RuCl_3$	9

TABLE I (*continued*)

Monomer	Reaction	Refs.
	MX_n (M = Cu, Ni, Co, Mn, Zn) + 1-vinyl-2-hydroxymethyl-(vinyloxymethyl)imidazole	10, 11
	$CuCl_2$ + vinyl ether of mono-ethanolamine	8
	MX_2(M = Cu, Ni, Co, Cd, Pd) + 1-allyl-3-(2′-pyridyl)-2-thiourea	16

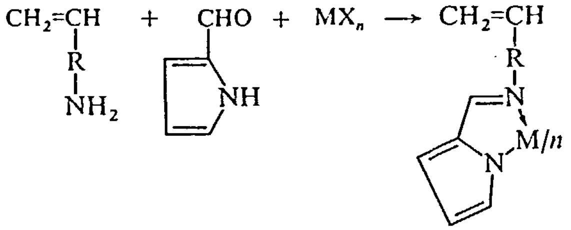
(ii) a covalent binding of metal chelates with monomers. This can be exemplified by the reaction of cobalt chelates with *p*-chlormethylstyrene, which leads to the formation of cobalt chelate monomers with a cobalt–carbon bond;[18]

(iii) the addition of acetylene monomers to the metal chelates. Thus, the reaction of phenylacetylene with dimethylglyoxime cobalt complex has been studied:[19,20]

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

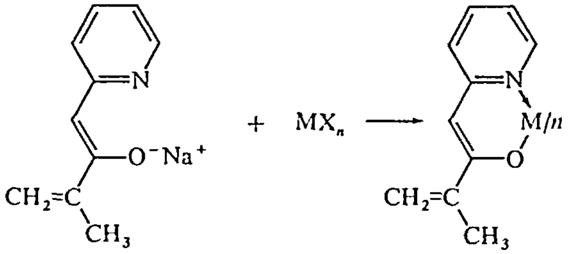
where DH_2 is dimethylglyoxime;

(iv) the methods of "assemblage" of MCM, for instance, according to the following scheme:[21,22]



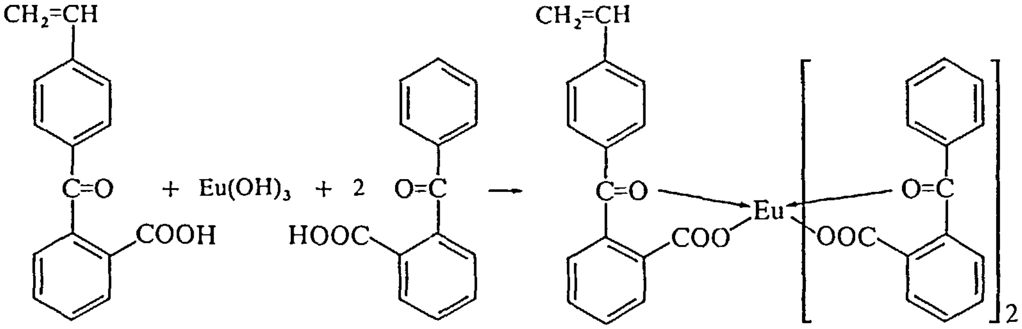
where R is $-C_6H_4-$ or $-CH_2-$, M is Cu(II) or Co(III), and n = 2, 3;

(v) exchange of metals. This method consists in mixing MX_n with chelate monomers, mainly incorporating alkaline and alkaline-earth metals:[23]

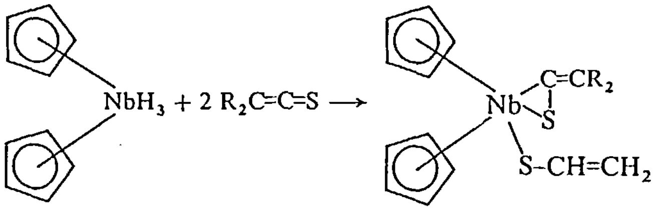


where M is Cu(II), Ni(II), Co(II), Fe(III), Cr(III), and n = 2, 3;

(vi) neutralization reaction. Thus, Eu(III) chelate monomer was synthesized by $Eu(OH)_3$ neutralization with the mixture of 4-vinylbenzoyl-2′-benzoic acid and 2-benzoylbenzoic acid in 1:2 molar ratio:[24]



(vii) the interaction of metal hydrides with thioketenes:[25]



The most typical representatives of intracomplex MCM and methods of their preparation are listed in Table II.

2.3. *Macrocyclic complexes*

The macrocycles, in particular porphyrins and phthalocyanines, are π-conjugated planar tetradentate ligands with high chelating ability. For construction of MCM based on these, different methods can be used. One of them is use of a clearly defined

TABLE II
Synthesis of intracomplex MCM

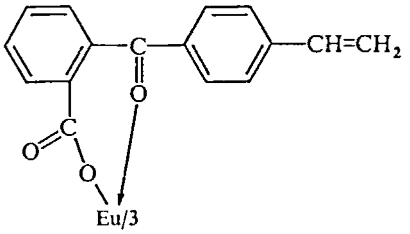
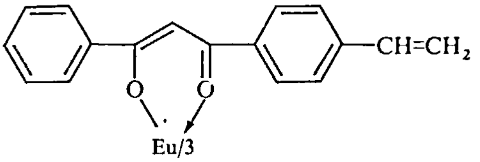
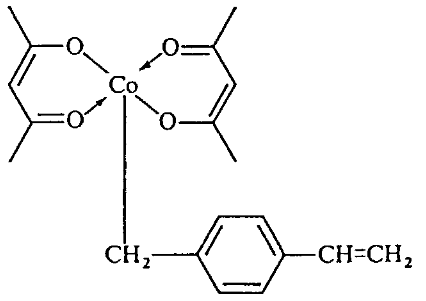
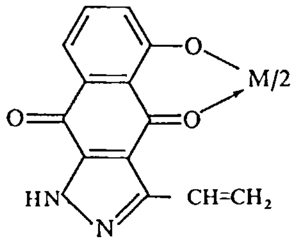
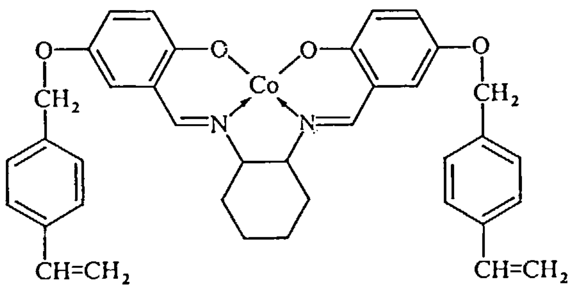
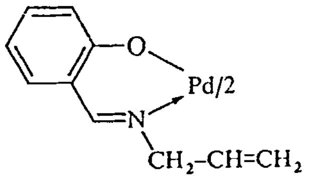
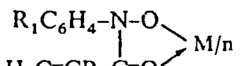
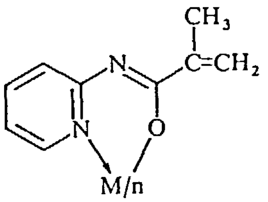
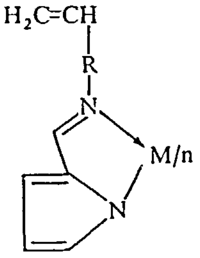
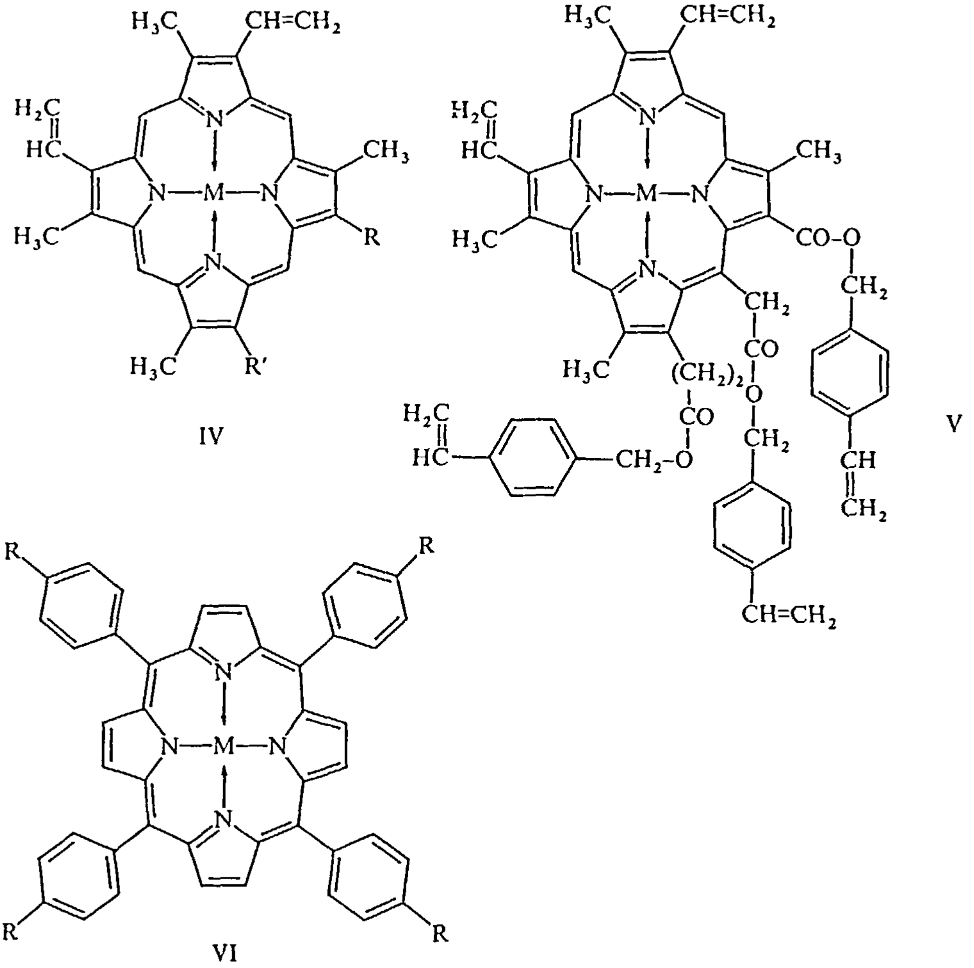
Monomer	Reaction	Refs.
	$Eu(OH)_3$ + 4-vinylbenzoyl-2'-benzoic acid + 2-benzoylbenzoic acid	24
	$EuCl_3$ + 1-(*p*-vinylphenyl)-3-phenyl-1,3-propanedion	17
	Cobalt acetylacetonate + chloromethylstyrene	18
	MSO_4 (M = Cu, Ni, Zn) + 3-vinylbenz/f/-indazole-5-hydroxy-4,9-dione	26
	$Co(CH_3COO)_2$ + N,N'-bis[4'-(*p*-vinylbenzyloxy)salicylaldehyde]-1,2-diaminocyclohexane	27

TABLE II (*continued*)

Monomer	Reaction	Refs.
	PdX_2 + N-allylsalicylaldimine	28
	MX_n (M is metal of first or second transition series + N-arylacryl (methacryl)hydroxamic acids	29-31
	MX_n (M = Cu, Ni, Co, Fe, Cr) + sodium salt of N-(2-pyridyl) methacrylamide	23
	MX_n (M = Cu, Co) + formylpyrrol + *p*-aminostyrene (allylamin)	21,22

ability of porphyrins and phthalocyanines to be additionally coordinated (extracoordinated) with a planar complex of ligands occupying the 5 and 6 positions in the inner coordination sphere.[32] Generally speaking, vinylpyridines, vinylimidazoles, etc. can be such ligands. The second method consists in the direct interaction of metal compounds with the macrocycles containing multiple bonds. Thus, appropriate MCM have been synthesized by the interaction of nickel acetate with vinylporphyrin.[33] Metal porphyrin complexes, where M is Co(II), Fe(III), Fe(II), Mg(II), Zn(II), Cu(II), Ni(II), etc., having one or two side vinyl groups, have also been prepared.[34-36] Their typical representatives are listed in Scheme 1.



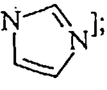
IV

V

VI

(Scheme 1)

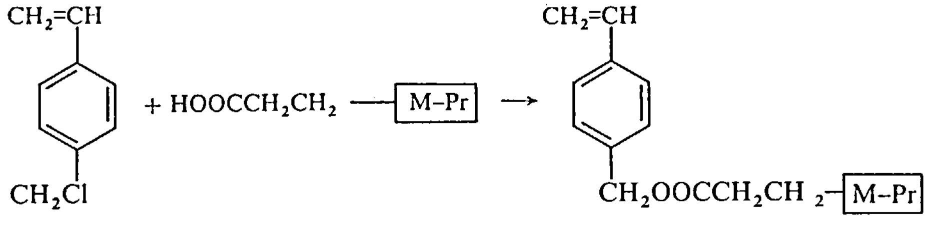
where IV is metal derivatives of protoporphyrin-IX [$R = R' = (CH_2)_2COOH$;M is Fe(III) or Fe(II)];dimethyl ester of protoporphyrin-IX [$R = R' = (CH_2)_2COOCH_3$]; vinylbenzyl ester of protoporphyrin-IX [$R = R' = (CH_2)_2COOCH_2C_6H_4CH{=}CH_2$]; N-(*p*-vinylbenzyl)-N'-(imidazolylpropyl)dipropylamidoprotoporphyrin-IX



$[R = (CH_2)_2CONHCH_2C_6H_4CH{=}CH_2,\ R' = (CH_2)_2CONH(CH_2)_3\text{-}N\text{(imidazole ring)}];$

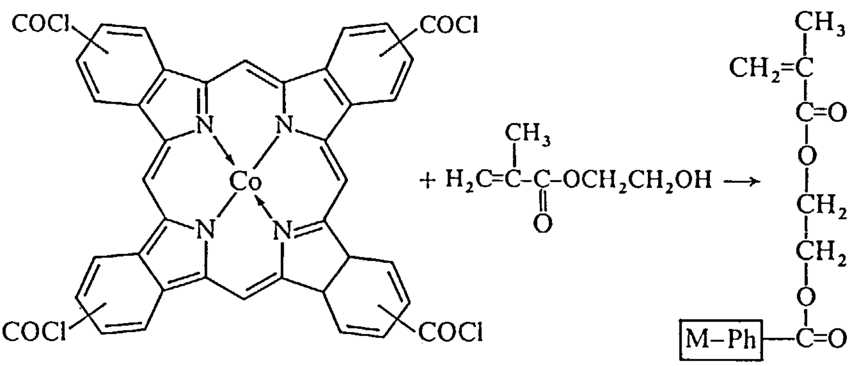
dimer of protoporphyrin-IX [$R = (CH_2)_2CONHCH_2$–, $R' = (CH_2)_2COOCH_2$-$C_6H_4CH{=}CH_2$]; V is metal derivatives of chlorine, VI is metal derivatives of tetra-(*p*-styryl)porphyrin ($R = CH_2{=}CH$–) or acrylamidotetraphenylporphyrin ($R = NHCOCH{=}CH_2$).

However, the most widely spread method used to prepare metal porphyrin monomers is the interaction of reactive peripheral groups of the metal porphyrin (chlorophyll, chlorine, etc.) with the monomer:[35–37]



where symbol $\boxed{\text{M-Pr}}$ denotes the metal porphyrin. Carboxyl, amino and sulfo groups are most commonly used as such peripheral groups. The analogical metal monomers can be synthesized by the reaction of acrylic acid chloride with tetra-*p*-aminophenylporphyrinate of manganese(II).[37]

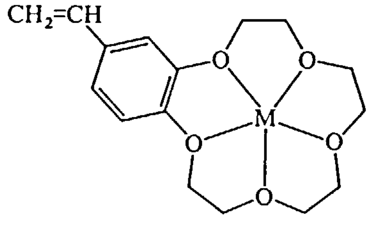
Approaches for the preparation of the metal phthalocyanine monomers have been considered. Thus, recently the synthesis of the monomer with covalent binding cobalt phthalocyanine has been described:[38]

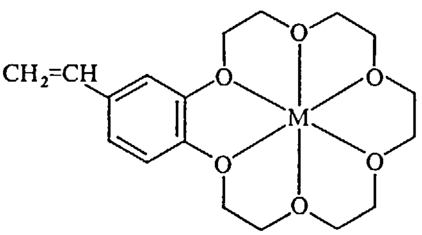


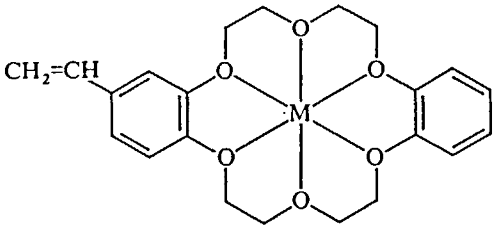
where symbol $\boxed{\text{M-Ph}}$ denotes the metal phthalocyanine.

It should be noted that the method of "assemblage" of macrocyclic MCM can not be ignored, however the experimental data as regards this are absent.

The metal complexes based on crown ethers with exocyclic multiple bonds could be the potential MCM of macrocyclic type. In this case the cavity of crown ether can be considered as a polydentate chelating mode. Although up until now data concerning such complexes have been lacking, the need to analyze these problems is demonstrated by intense investigations in this field. Thus, the hypothetical model of such MCM for 4′-vinylmonobenzo-15-crown-5, 4′-vinylmonobenzo-18-crown-6 as well as 4′-vinyldibenzo-18-crown-6, the synthesis of which has been developed in detail,[39] can be presented as follows:







where M is ion of alkaline or alkaline-earth metal.

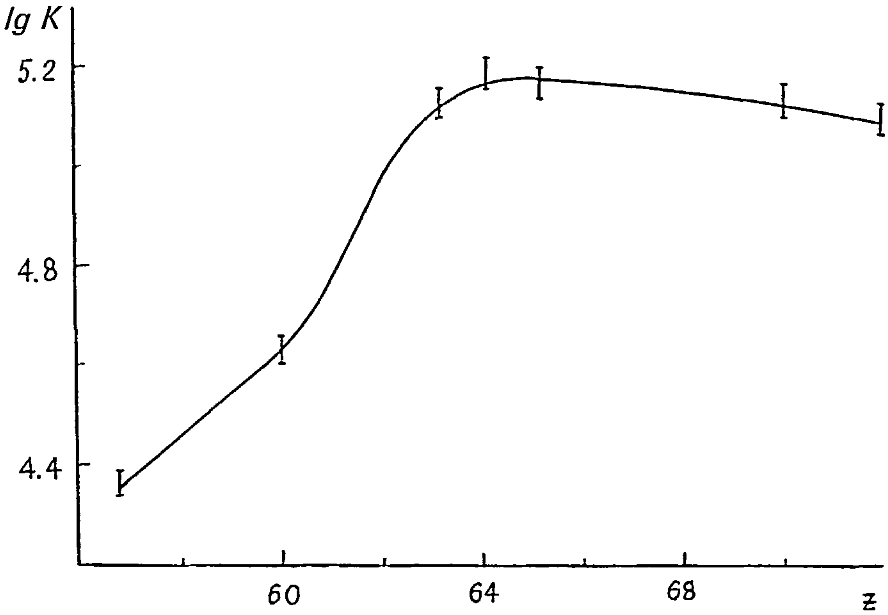
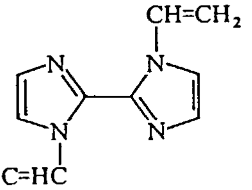


FIGURE 1 Change of stability constant for rare-earth element complexes with vinylidenediphosphone acid (z is ordinal number of element).

2.4. *Structure of metal chelate monomers*

Among some of the most important problems connected to the structure of MMC are the multiple bond effect on the spatial structure of complexes and electronic structure of the metal as well as metal effect on reactivity of the multiple bond. In most cases the ligand arrangement around the metal ions is MCM and their saturated analogues is very similar. This especially is related to macrocyclic type MCM.[33-38] The stability constant of rare-earth element complexes with vinylidenediphosphone acid $CH_2=C(PO_3H_2)_2$ is maximum for the elements of the middle rare-earth element series (Fig. 1).[40] The analogical relationship was discovered earlier in saturated diphosphonates.[41,42] However, the substitution of vinyl group in MCM by ethyl group leads to an increase of complex stability.[11] Besides, the introduction of vinyl groups to the ligand molecule can hinder formation of metal chelate. Thus, for example, in contrast to 2,2'-dipyridyl and 2,2'-diimidazolyl the steric repulsion of vinyl groups in 1,1′-divinyl-2,2′-diimidazolyl (VII) hinders the transition of the ligand from S-*trans*- into S-*cis*-conformation and, hence, the formation of metal chelate.[43]



VII

A comparative analysis of splitting parameters for the complexes of nickel(II), cobalt(II), chromium(III) acrylates and acetates with Dipy and Phen shows a decrease of Dq value in going from MCM to their saturated analogues (Table III).[12] It is known[44] that

$$Dq \sim 1/a^6,$$

therefore the decrease of the splitting parameters proves an increase of metal–ligand distance (a) under transition from MCM to the analogous saturated complexes. An increase in nepheloxetic parameter β in this row shows a decrease of covalency degree of metal–ligand bond, resulting from an increase in the effective positive charge on the metal atom moving from MCM to their saturated analogues. It should be noted that the absorption frequency of the C=C bond is lowered during the reaction from metal acrylates[45] to their complexes with Dipy and Phen[12] due to shifting of electron density from the multiple bond on the metal atom. However, this absorption band remains independent of the nature of the transition metal, as with the initial metal acrylates.

TABLE III
Electronic transitions and splitting parameters of complexes of cobalt(II) acrylate (1,2) and acetate (1′,2′) with Dipy and Phen, respectively.[a]

	Transitions (cm^{-1})			Parameters		
Sample	$^4T_{1g}(F) \to {}^4T_{2g}$,	$\to {}^4A_{2g}$,	$\to 4T_{1g}(P)$	Dq(cm^{-1})	B′(cm^{-1})	β
1	10250	—	21500	1152	834	0.859
	10250	21770	21500			
2	10350	—	21800	1163	849	0.874
	10350	21980	21800			
1′	8970	—	21000	1018	883	0.909
	8970	19160	21000			
2′	8950	—	21000	1016	884	0.911
	8950	19110	21000			

[a] Experimental values are presented as the numerator, and calculated values are shown as the denominator

An interesting fact was discovered in the complex of cobalt(II) chloride with 1-vinyl-2-hydroxymethylimidazol by X-ray analysis.[46] In this compound the ligand shows the intra-complex ambidentate character: one molecule of the ligand is monodentate with N(3) donor atom and the second molecule of the ligand is bidentate with N(3) and oxygen donor atoms (Fig. 2).

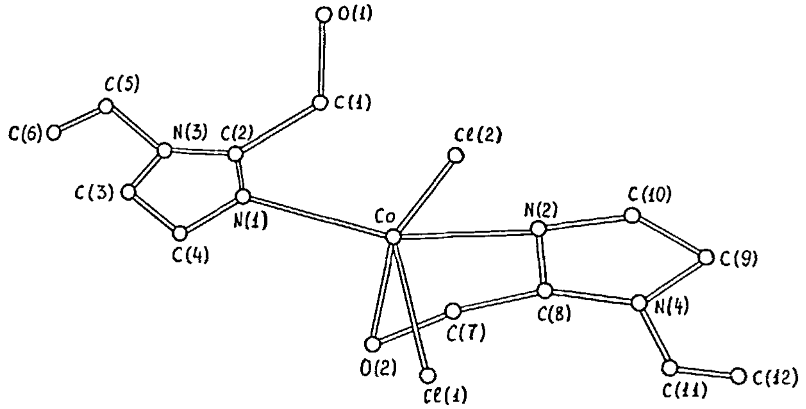


FIGURE 2 Structure of cobalt(II) chloride complex with 1-vinyl-2-hydroxymethylimidazol.

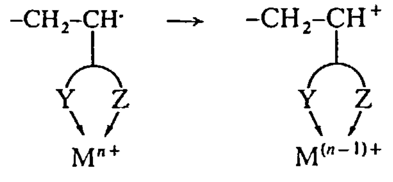
3. HOMOPOLYMERIZATION OF METAL CHELATE MONOMERS

Unfortunately, information on the radical polymerization of MCM is very limited. Thus, radical polymerization of dimethyl ester of hemin was carried out in 1977.[47] The possibility of polymerizing 4-VP complex bound to Ru(II) (cis-[Ru(Dipy)$_2$-(4-VP X]$^{n+}$ complexes, where n = 1, X = Cl; n = 2, X = CO or 4-VP) has been shown[7] but the properties of the polymers obtained have not been described. Under comparable conditions, the rate of radical polymerization of transition metal complexes with enaminoketones (EAK) decreases in the series:[48,49]

$$\text{EAK} > \text{Co(II)} > \text{Ni(II)} > \text{Cr(III)} > \text{Fe(III)} > \text{Cu(II)}$$

In other words, the rate of polymerization of MCM is lower than that of its "metal-free" analogue.[48-50] It should be noted that homopolymerization of MCM does not proceed readily and in most cases it is excluded altogether.

The effect of the nature of the metal on the kinetics of MCM polymerization has a specific chemical basis in each case. Thus, the almost ineffective polymerization of Cu(II) and Fe(III) chelate monomers is a consequence of intramolecular chain termination: a free electron localized at the growing chain end is transferred to a metal ion leading to its reduction and chain termination:



$$-CH_2-CH^{\cdot}(YZ)M^{n+} \longrightarrow -CH_2-CH^{+}(YZ)M^{(n-1)+}$$

This process is promoted by the low reduction potentials of the corresponding ions.

Radical polymerization of MCM with the same elementary steps as in the polymerization of conventional monomers is very popular. However, this data is very limited. This is primarily due to a variety of accompanying processes having mainly a non-radical character. The rate of radical polymerization of MCM is described by a kinetic equation which is first order with respect to initiator and MCM concentration:

$$W_p = k[\mathrm{MCM}][\mathrm{I}]$$

More detailed studies were devoted to the mechanism of electrochemical polymerization as applied to Fe(III), Ru(II) and Os(II) complexes containing chelating ligands (Dipy, Phen, etc.) and monofunctional monomers such as 4-VP, bis(4-pyridyl)-ethylene, trans-4-stilbazol or N-(4-pyridyl)acrylamide.[4,6] Electrochemical polymerization of MCM is a unique method of production of films, the repeating unit of which contains a redox centre. The first stage of electrochemical polymerization is shown to reside in the formation of a radical-anion, e.g., by the following scheme:

$$[\mathrm{Ru(II)(Dipy)_2(L)_2}]^{2+} + \bar{e} \rightleftarrows [\mathrm{Ru(II)(Dipy)(Dipy^{\cdot-})(L)_2}]^{+} + \bar{e} \rightleftarrows$$
$$\rightleftarrows [\mathrm{Ru(II)(Dipy^{\cdot-})_2(L)_2}]^{0},$$

where L is monofunctional monomer. The polymerization is induced by a one-electron reduction, based on the intramolecular redox equilibrium including a thermodynamically less favourable isomer in which the electron is located on L:

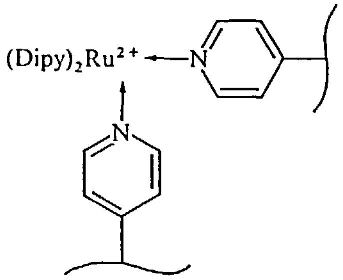
$$[\mathrm{Ru(II)(Dipy)(Dipy^{\cdot-})(L)_2}]^{+} \rightleftarrows [\mathrm{Ru(II)(Dipy)(Dipy^{0})(L)(L^{\cdot-})}]^{+}$$

4. COPOLYMERIZATION OF METAL CHELATE MONOMERS

The copolymerization of MCM with traditional monomers is a more popular process than their homopolymerization. This method has three important aspects. Firstly, there is a great number of MCM which are not capable of homopolymerization and which readily copolymerize with other monomers. Secondly, this approach allows known polymers to be modified and provided with appropriate properties. Thirdly, since the composition of the copolymers obtained depends on many factors, this helps to reveal the hidden effects of MCM reactivity.

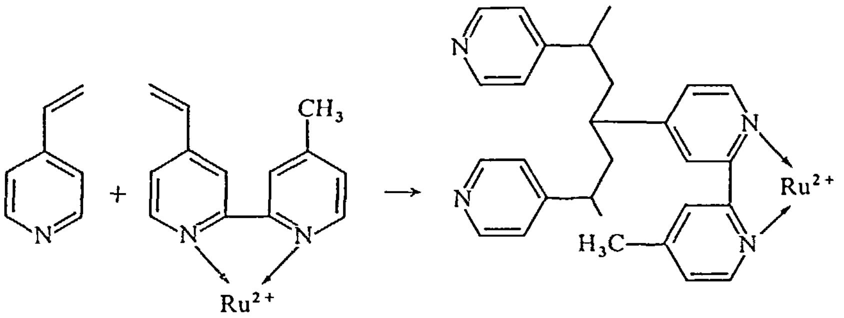
As a rule, MCM are the less active comonomers (M_2) in copolymerization with traditional vinyl monomers. Radical copolymerization has been studied in more detail. Composition and molecular weight of copolymers are influenced by the nature of the reaction medium, especially pH, ionic strength and solvent polarity. This permits the description of the character of interactions in the system: macroradical–counterion–monomer anion. In most cases, the copolymerization leads to products with M_2 units scattered over the chain. However, the contribution of complex formation between copolymerized monomers may also be significant. This leads also to the formation of intermolecular complexes, resulting in an alternating copolymer, irrespective of the composition of the monomer mixture.

Copolymers containing complex-bound compounds of rare-earth metals such as Eu(III) and Tb(III), were obtained by copolymerization of MCM of the type M(4-vinyl-4′-methyl-2,2′-dipyridyl)$_3$ with methyl methacrylate (MMA) in block or methanol.[51] Radical copolymerization was also affected in the case of complexes based on 4-VP and ruthenium compounds such as cis-[Ru(Dipy)$_2$(4-VP)Cl]ClO$_4$, cis-[Ru(Dipy)$_2$(4-VP)$_2$](ClO$_4$)$_2$ and cis-[Ru(Dipy)$_2$(4-VP)(CO)](PF$_6$)$_2$. Used as the comonomers were styrene (St), MMA and 4-VP. The reaction occurred in toluene or acetonitrile in the presence of the initiator azobisisobutyronitrile (AIBN). The copolymers of Ru(II) complexes containing a molecule of 4-VP turned out to be soluble in dichloromethane and methanol whereas the copolymerization product [Ru(Dipy)$_2$(4-VP)$_2$](ClO$_4$)$_2$ (comonomer is 4-VP, the initial ratio [4-VP]/[MCM] = 20) was insoluble in organic solvent due to the fact that the polymeric chains were cross-linked through the Ru atoms:[7]

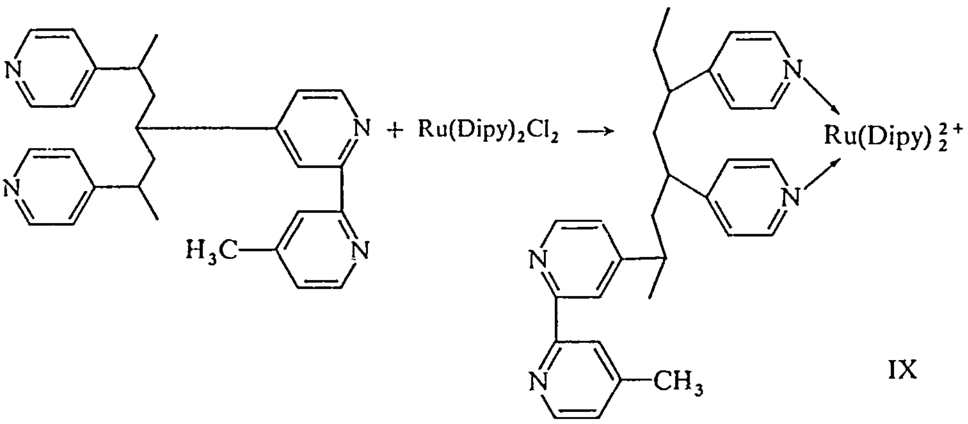


However, as the ratio was increased to 200, the effect of MX$_n$ became smaller so that a soluble product was obtained.

It should be noted that to obtain such metal polymers the parallel "route" is more often used, for example, the interaction of Ru(Dipy)$_2$Cl$_2$ with copolymer of 4-VP and 4-vinyl-4′-methyl-2,2′-dipyridyl.[52] However, the formed products are not identical. In particular, in the case of MCM copolymerization, the grouping [Ru(Dipy)$_2$]$^{2+}$ is co-ordinated via Dipy fragments (VIII), but in the case of the product of polymer analogous reaction this grouping is co-ordinated via pyridine ligands (IX).



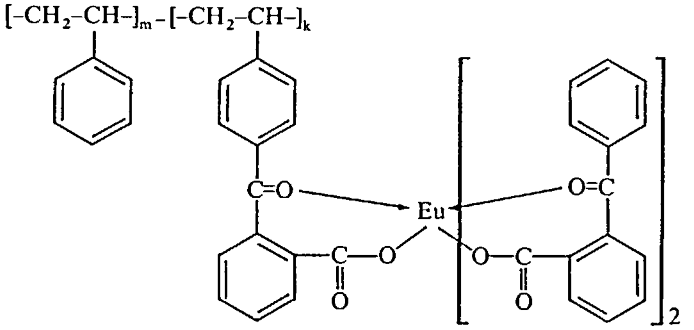
VIII



IX

It is important that migration of the grouping $[Ru(Dipy)_2]^{2+}$ is not occupied in the course of copolymerization.

It has been shown that cis-$[Ru(Dipy)_2(4\text{-}VP)X]^{n+}$ (n = 1, X = Cl; n = 2, X = CO or 4-VP) can polymerize with St or MMA,[7,53] although neither a mechanism of the process nor the properties of the resulting products have been described. There is no mechanism for the copolymerization of MCM–Eu[2-(4′-vinylbenzoyl)benzoate]-di(2-benzoyl benzoate) with St to give product X:



X

It is interesting that this metallopolymer is distinguished by strong fluorescence which is proportional to the metal content as distinct from complexes produced by the interaction of $EuCl_3$ with macroligands containing 2-carboxybenzoyl (XI) or 2-carboxynaphthoyl (XII) groups (Fig. 3).[24] A similar method was used to copolymerize MMA and MCM of Eu(III) with 1-(*p*-vinylphenyl)-3-phenyl-1,3-propanedione (methylenechloride, 60–65°C, initiator AIBN).[17]

Radical copolymerization of MCM obtained by interaction of $Co(CH_3COO)_2$ with N,N′-bis[4′-(*p*-vinylbenzyloxy)salicylaldehyde]-1,2-diaminocyclohexane with St and divinylbenzene (DVB) gave the product of ternary copolymerization with twenty St and DVB units per MCM unit.[27]

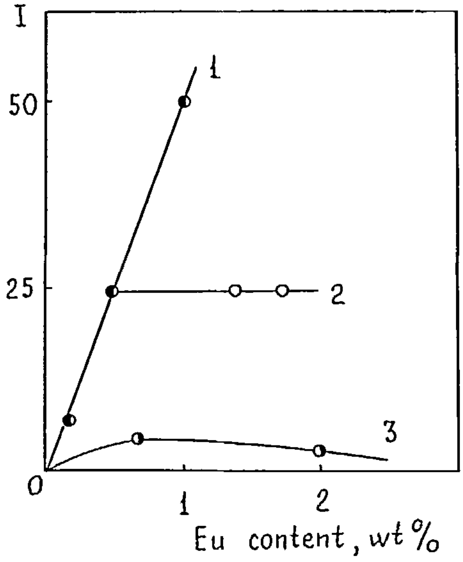


FIGURE 3 Relationship between fluorescence intensity (I) and Eu content in complexes X (1), XI (2), and XII (3).

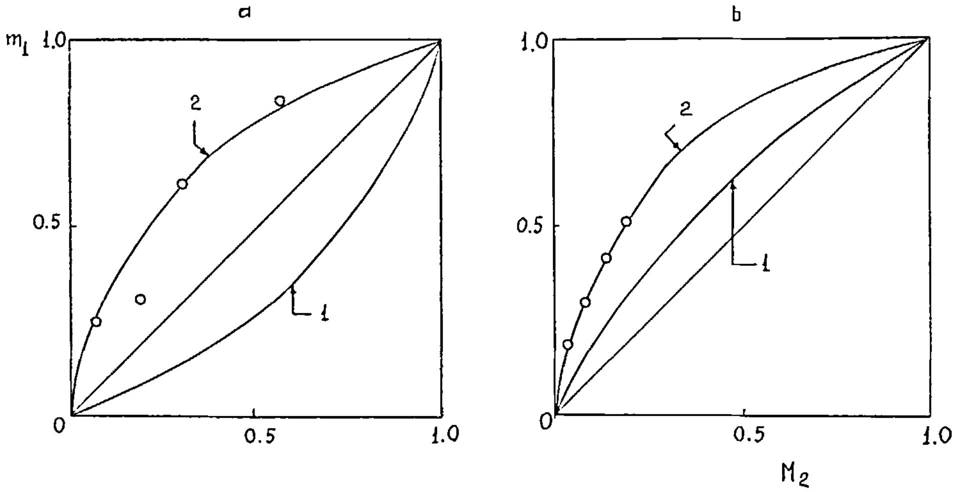


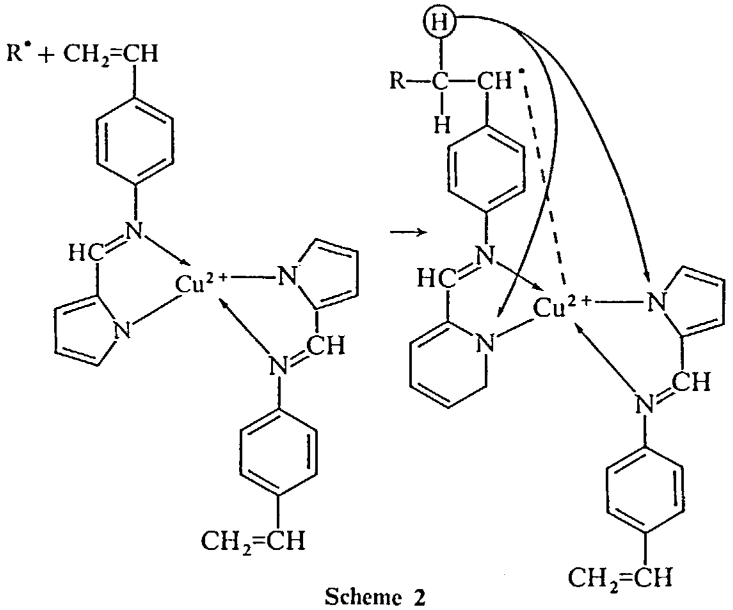
FIGURE 4 Composition diagrams for copolymerization of MCM (2) and their "metal-free" analogs (1) with AN (a) and St (b): a – cobalt(II) complex with PIP; b – copper(II) complex with PIS.

As distinct from these qualitative studies, a detailed consideration has been given[21,22] to the copolymerization involving St, acrylonitrile (AN), MMA or acrylic acid (monomer M_1) and MCM (monomer M_2) representing complexes of Cu(II) or Co(III) with pyrrolylmethyleneiminopropene (PIP) or pyrrolylmethyleneiminostyrene (PIS). As can be seen in Fig. 4, the molar fraction of monomer M_2 in the resulting copolymers is higher for the MCM than for its "metal-free" analogue. The reactivity of the comonomer increases as it accepts metal (Table IV), which is

TABLE IV
MCM copolymerization activity.

		Copolymerization constant	
M_1	M_2	M_1	M_2
AN	PIP	2.30	0.40
AN	$Co(PIP)_3$	0.86	8.60
St	PIS	0.50	1.80
St	$Cu(PIS)_2$	0.45	6.90

comparatively rare in the polymerization and copolymerization of metal-containing monomers.[54] Moreover, the copolymerization involves no more than one or two groups out of the three coordinated with Co(III), one multiple bond remains in the copolymer. In the case of a Cu(II) chelate the process involves two vinyl groups. However, the initiation of this MCM polymerization proceeds in a complicated way (Scheme 2). The primary radical first attacks the vinyl group of the monomer and then the free electron from this group is transferred to the central metal ion. This is encouraged by the presence of a conjugation chain (long coplanar π-electronic system) and chain propagation does not start until the complete reduction of Cu(II) to Cu(I). Simultaneously proton β-elimination of the vinyl group, which is attacked by the primary radical, and its addition to pyrrol nitrogen atom occur.



Scheme 2

Generally speaking, such a mechanism is confirmed by mono-molecular chain termination, low polymer molecular weight ([η] = 0.041 in tetrahydrofuran at 30°C), and weak polymerization inhibition of complexes with completely filled metal d-orbitals. Finally, it has been shown by direct method (Fig. 5), that the rate of the interaction of stable radical diphenylpicrilhydrazine (DPPH) with copper complexes with conjugated ligands is higher than that with unconjugated ones.

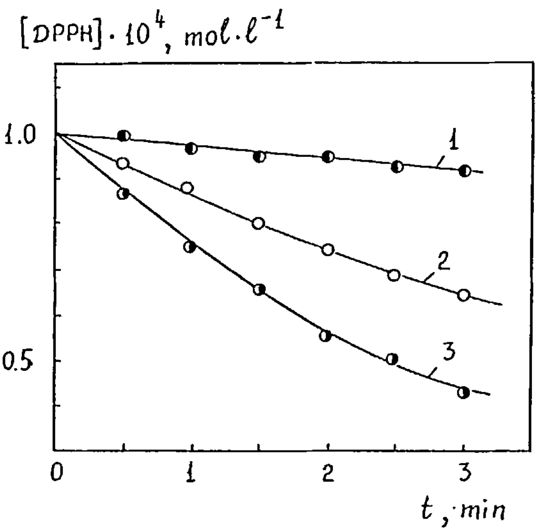
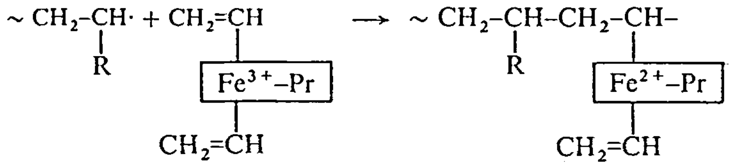


FIGURE 5 Kinetics of redox-reaction of DPPH with copper(II) compounds ($[Cu^{2+}] = 1 \cdot 10^{-4}$ $mol \cdot l^{-1}$, tetrahydrofuran, 35°C): 1 – $CuCl_2$, 2 – $Cu(PIP)_2$, 3 – $Cu(PIS)_2$.

Apparently, MCM, in which the multiple bond is not conjugated with metal ion, can turn out interesting comonomers.

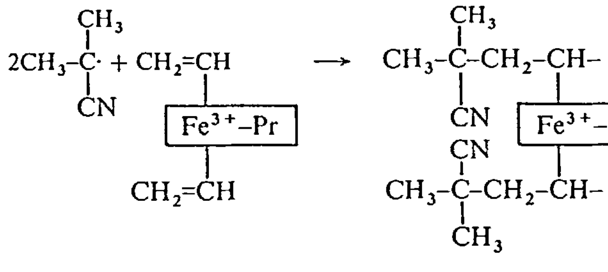
The data about copolymerization of macrocyclic MCM are very limited. Thus attempts to copolymerize hemin with such monomers as vinylpyrrolidone and vinylimidazole were unsuccessful.[55] The comonomers are classed into two types, viz., π-conjugated and nonconjugated. Conjugated monomers (St, MMA, etc.) with a high value of Q parameter (resonance stabilization of monomer in the course of copolymerization) copolymerize with macrocyclic MCM as follows:



$$\sim CH_2\text{-}\underset{R}{CH}\cdot + \underset{\underset{CH_2=CH}{\boxed{Fe^{3+}\text{-}Pr}}}{CH_2=CH} \longrightarrow \sim CH_2\text{-}\underset{R}{CH}\text{-}CH_2\text{-}\underset{\underset{CH_2=CH}{\boxed{Fe^{2+}\text{-}Pr}}}{CH}\text{-}$$

Spectroscopic evidence suggests[55] that Fe(III) reduces to Fe(II) in the course of copolymerization.

Nonconjugated monomers with a low value of Q parameter do not copolymerize with macrocyclic MCM because of the radical being added to the hemin to give stable adducts:



$$2CH_3\text{-}\overset{CH_3}{\underset{CN}{C}}\cdot + \underset{\underset{CH_2=CH}{\boxed{Fe^{3+}\text{-}Pr}}}{CH_2=CH} \longrightarrow \begin{array}{l} CH_3\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_2\text{-}\underset{\boxed{Fe^{3+}\text{-}Pr}}{CH}\text{-} \\ CH_3\text{-}\overset{CN}{\underset{CH_3}{C}}\text{-}CH_2\text{-}CH\text{-} \end{array}$$

It is interesting that nonconjugated monomers can copolymerize with hemin in the presence of a conjugated (third) comonomer, e.g., resulting in the appearance of a ternary hemin–vinylimidazole–styrene copolymer.[47,55,56]

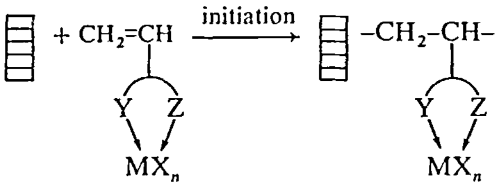
Copolymerization of a heme with vinylpyrrolidone under ^{60}Co irradiation (irradiation dose 1.5–3.0 kJ/kg) or with hydroxymethacrylate in buffer solution (Na_2CO_3–$NaHCO_3$, pH = 10) has been described.[57] Tetra(*p*-vinyl)benzyl esters of a dinuclear Mg(II)-chlorophyll complex copolymerize by the cationic mechanism (BF_3 complex with ether) with α-methylstyrene. Copolymerization of vinylporphyrin Co(II), Fe(II) and Ni(II) monomers, containing one or two side vinyl groups, with acrylamide and N,N′-methylenebisacrylamide gives a three-dimensional structure with a parallel immobilization of a metallomonomer within the polymeric gel.[33,34] The parameters of such a cross-linked structure are readily controlled by the comonomer ratio.

The soluble metalloporphyrin-containing polymers are formed by the copolymerization of MMA or 4-VP with macrocyclic MCM presenting the interaction product of acrylic acid chloride with tetra-*p*-aminophenylporphyrinate acetate manganese.[37] It should be also noted that copolymers are obtained by the radical copolymerization of acryloyl derivatives of cobalt phthalocyanine with 9-vinylcarbazole.[38]

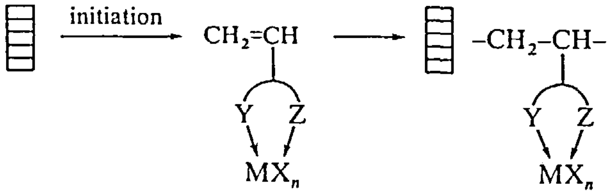
It can be supposed that intramolecular electron transfer processes, which complicate the stages of initiation and growth of chains, occur also in MCM including π-conjugated porphyrin and phthalocyanine macrocycles (in the case of Cu^{2+}, Fe^{3+}, etc.).

5. GRAFT POLYMERIZATION OF METAL CHELATE MONOMERS

Graft polymerization of MCM may be considered an ordinary radical polymerization but with the difference that the initiating particles are immobilized on the polymer support surface :



The initiation of graft polymerization is carried out by chemical and radiative methods. However, in these cases the formation of homopolymer as by-product is observed. Using high-energy irradiations (of the ^{60}Co isotope, electron accelerator, glow discharge plasma) for postgraft polymerization initiation is very beneficial. Schematically, this process can be presented as follows:



Unfortunately, the data on MCM graft polymerization are extremely limited, and practically all of them have been published during the last decade. The main kinetic principles of graft polymerization of MCM are, in many ways, similar to those of homopolymerization of the respective MCM. Thus, for example, the reactivity of acrylates and their complexes with Dipy and Phen in graft polymerization increases in the order Cr < Ni < Co. However, the absorption band at ca. 1640 cm^{-1} in the IR spectra of immobilized complexes indicates the presence of some unpolymerized vinyl groups of the MCM. Apparently, in the graft polymerization of MCM containing two or three vinyl groups participation of some groups is excluded.[58,59]

It should be noted that the close similarity of the IR spectra and magnetic properties of the immobilized complexes and MCM (Table V) indicates that the ligand arrangement of metal ions in both cases is very similar.[59] However, the absorption bands in the IR spectra of the immobilized complexes are broader, a characteristic of these macromolecular complexes.[60]

TABLE V

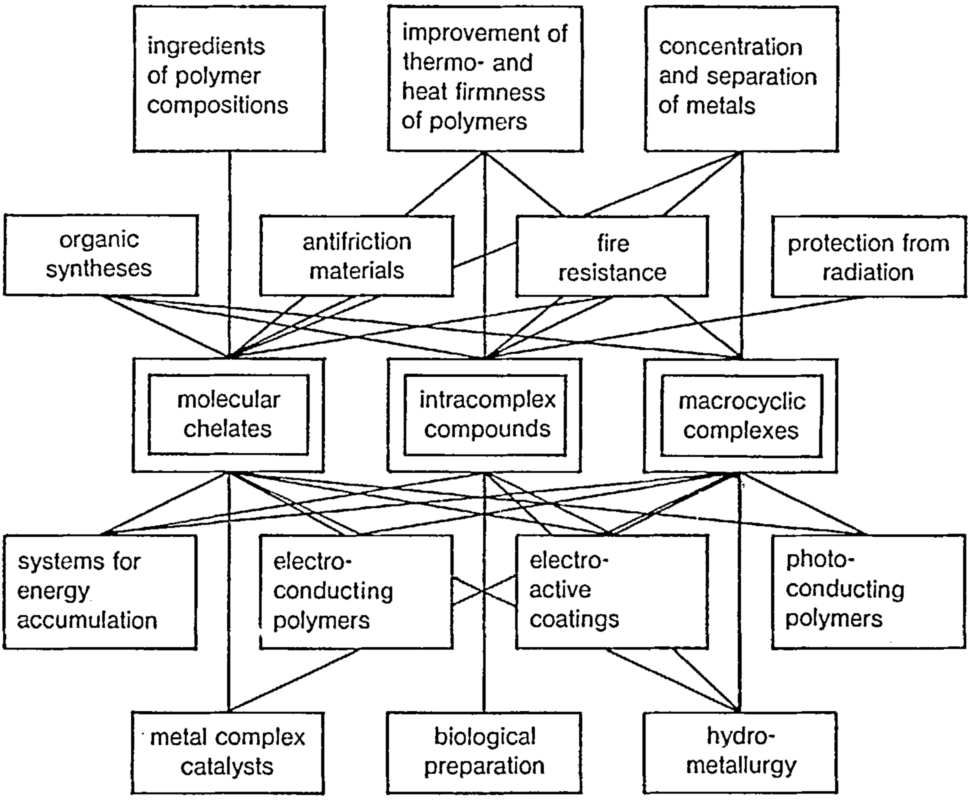
Spectral and magnetic data for nickel(II), cobalt(II), chromium(III) acrylate complexes with Dipy (1–3) and Phen (4–6), and their grafted analogs (1′–6′).

Sample	IR spectrum (fundamental wavenumbers) (cm^{-1})			μ_{eff} (BM) [T (K)]
	ν(C=C)	ν(heterocycle)	$\nu(\mathrm{COO}^-)$	
1	1635	1605	1565	3.16 (290)
2	1637	1600	1565	3.17 (290)
3	1637	1610	1560	4.53 (290)
4	1635	1605	1565	4.75 (290)
5	1635	1605	1586	4.33 (287)
6	1637	1605	1580	4.73 (287)
1′	1639	1606	1560	2.96 (290)
2′	1640	1600	1560	2.95 (290)
3′	1638	1608	1560	4.75 (290)
4′	1639	1608	1565	4.87 (290)
5′	1639	1610	1580	4.40 (287)
6′	1640	1610	1575	4.70 (287)

A method of preirradiation in air (^{60}Co γ-irradiation with a dose $D = 200$ kJ/kg and a dose power $I = 1$ J/kg·s) has been used to effect the graft polymerization of Pd(II) chelate monomers with diketone and enaminoketone onto a polyethylene powder.[61] The kinetic curve for the yield of the grafted copolymer is shown in Fig. 6. It is evident that the graft polymerization rate reaches a maximum during the first 1 h, after which it falls. Interestingly, the grafting rate is independent of MCM concentration within 1–10 wt%. This is likely to be due to the fact that the process takes place in the adsorbed monomer layer.

6. APPLICATIONS OF METAL CHELATE MONOMERS AND MACROMOLECULAR METAL CHELATES BASED ON THEM

Metal chelate monomers and macromolecular metal chelates based on them find various, sometimes fairly unexpected, applications. The appropriate information is largely contained in the patent documentation. The major fields of MCM and MMC applications are presented in Scheme 3.



Scheme 3

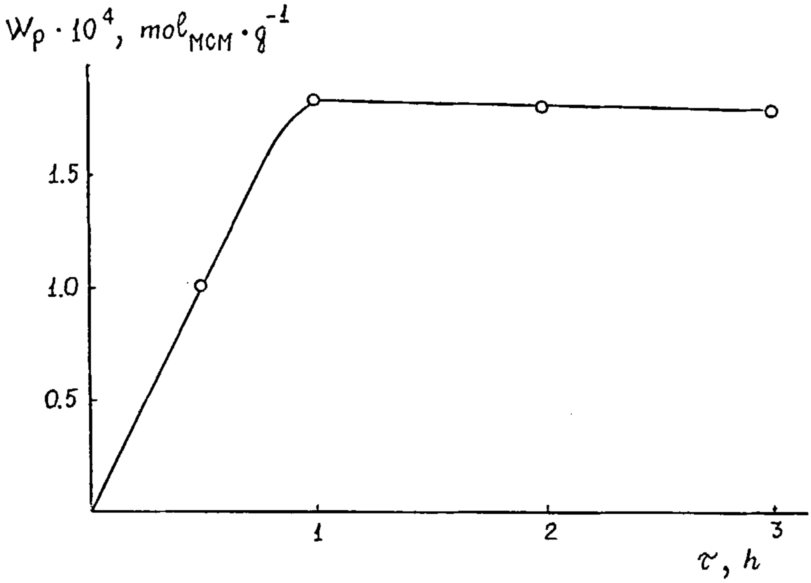


FIGURE 6 Dependence of the yield of the grafted copolymers of Pd(II) enaminoketonate with polyethylene powder on time.

6.1. *Upgrading operating and physico-mechanical polymer properties*

All MCM-based polymers are usually stable up to 473–523 K. Even a small amount of these monomers in copolymers with conventional monomers gives rise to a tough cross-linked polymer with enhanced thermal stability and resistance to organic solvents. These properties are used, particularly in the case of titaniun-containing polymers, in the production of various coatings, frequently with enamel-like surfaces. To effect the cross-linking of polyethylene in order to increase its thermal aging and cracking resistance, use is made of zinc bis(amino-ethyleneamido-maleinate)tetrahydrate obtained from zinc maleinate and ethylenediamine.[62,63]

The products of reductive electrochemical polymerization of Fe(II), Ru(II) and Os(II) vinylderivatives containing Dipy groups show photo conductivity (λ_{max} = 420–520 nm).[64] It should be noted that metal ions in metallopolymers, as a rule, have the same photophysical properties, as those in appropriate low molecular weight compounds. Thus, Eu(III) and Tb(III) monomer complexes with 4-vinyl-4′-methyl-2,2′-dipyridyl as well as their copolymers with MMA transfer in the excited state with λ_{max} = 335 nm and in the range λ_{max} = 500–600 nm, is characteristic for these ions.[17] Interestingly, the polymer products show higher fluorescence in comparison with MCM. It is possible that the substances of this type can be used in laser equipment.

Metal containing polymers based on $[Ru(Dipy)_2(4\text{-}VP)_2]^{2+}$ and $[Ru(Dipy)_2(4\text{-}VP)Cl]^+$ are capable of luminescence in methanol or dilute acids at room temperature.[7] Thus, in methanol the excitation of metal ions in poly$[Ru(Dipy)_2(4\text{-}VP)_2]^{2+}$ and $[Ru(Dipy)_2(4\text{-}VP)Cl]^+$ are capable of luminescence in methanol or dilute acids at room temperature.[7] Thus, in methanol the excitation of metal ions in poly$[Ru(Dipy)_2(4\text{-}VP)Cl]^+$ at 455 nm leads to the broad emission with maximum at 615 nm.

Electroactive polymeric coatings are obtained by reductive electrochemical polymerization of MCM representing vinylpyridine derivatives of Fe(III), Ru(II), and Os(II) complexes with chelating agents.[4] They are unique in that the redox centres are located in each polymeric unit. The redox conductivity permits continued growth of the polymer film since the outer boundary of the film can act as an electron-transfer mediator at the film-solution interface.

6.2. *Catalytic activity*

MCM are homogeneous and pseudo-homogeneous catalysts in a variety of processes (polymerization, hydrogenization, oxidation, etc.). MMC based on MCM relate to the immobilized catalysts, which couple a high activity and selectivity of homogeneous and a workability of heterogeneous catalytic systems.[65] It should be noted that chelation is the simplest way to overcome the main disadvantage of immobilized metallocomplex catalysts, i.e., the relatively low stability of the metal-polymer bond in the course of the reaction being catalyzed. Moreover, synthesis of such MMC is one-stage, i.e., by polymerization and copolymerization of MCM. Finally, the advantages of these catalysts are the possibility of simpler identification of metal complex structure (valent and electronic metal stage, its ligand arrangement, geometrical structure, etc.) as well as controlled distribution of structural uniform metal complexes along the polymeric chain.

Thus, soluble metalloporphyrin-containing polymers obtained by copolymerization of MMA or 4-VP with macrocyclic MCM presenting the interaction product of acrylic acid chloride with tetra-*p*-aminophenylporphyrinate acetate manganese are capable of catalyzing olefin oxidation by molecular oxygen.[37] A copolymer of acrylamide with N,N′-methylenebisacrylamide and a Ni(II) vinylporphyrin complex has been used for creating an effective redox system (in conjunction with H_2O_2) to initiate acrylamide polymerization in an aqueous environment.[34]

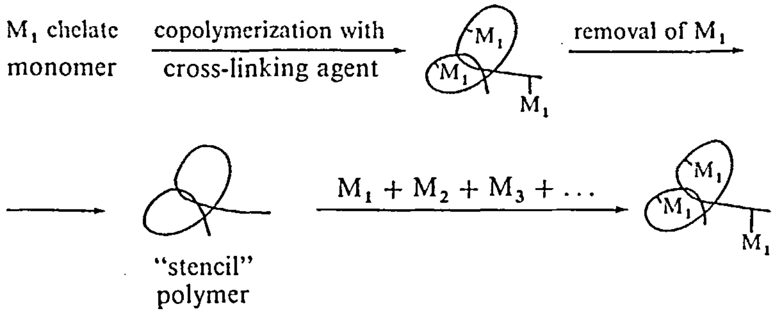
As could be expected, the grafted metal chelate polymers are even more effective catalysts. Among them, the polyethylene-grafted palladium(II) chelate monomers with diketone and enaminoketone are the most advantageous for nitrochlorobenzenes hydrogenization.[61]

6.3. *Template effect in macromolecular metal chelates*

As applied to metallopolymeric systems, the template effect consists of the "recognition" and binding of the transition metal ions which were used as templates or "stencils" in the synthesis of metallopolymeric chelates.[66–69]

In ordinary chelate polymers the selectivity of binding ions of definite metals is, as a rule, absent. It is defined only by constants of the formation of corresponding complexes and reaction conditions such as the nature of solvent and chelate node, pH of a solution, etc.

The phenomenon of "adjustment" is observed in the formation of MMC by copolymerization of MCM with cross-linking agents. In this case, after removal of the ions, one can observe a significant rise in the absorption capacity and rate as well as selectivity on the "adjusted" polymers. The mechanism of this phenomenon can be described as follows. The bond length and angle between the central metal ion and the coordinated ligand is strictly controlled by their nature. After the coordination structure (type of polyhedron) of the complex has been somehow fixed and the metal ion is removed geometrically, i.e., with the ready stereostructure remaining intact, the polymeric ligands left behind may have "pockets" specially tailored to the same metal ions (templates) that have been removed from the polymeric matrix (Scheme 4).



Scheme 4

Thus, if a copolymer of 4-vinyl-4′-methyl-2,2′-dipyridyl, St and DVB from solutions of these salts with equal concentrations of Ni(II) and Cu(II) binds more strongly to Cu(II) (due to a greater constant of formation of this complex), the same copolymer obtained in the presence of Ni(II) displays a template effect (Fig. 7).[70]

Polymeric chelates obtained by copolymerization of dithiophosphate complexes such as bis-di(4-vinylphenyl)dithiophosphinate of Ni(II), Co(II) or Cr(III) with St and ethylene glycol dimethacrylate after removal of metal therefore have a selectivity in addition to that of their "own" ion. The gain factor is 1.4 and 2.4 for Ni(II) and Co(II), respectively.[71]

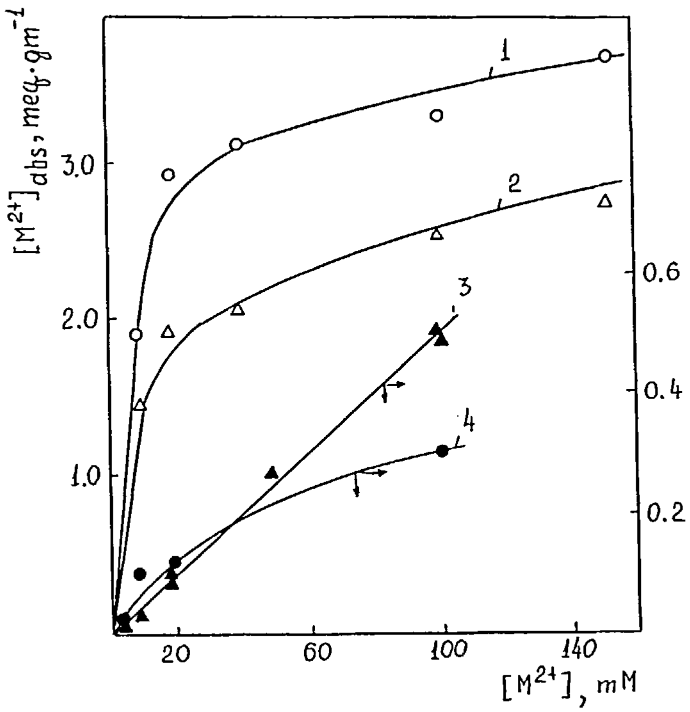


FIGURE 7 Absorption of Ni^{2+} (2, 3) and Cu^{2+} (1, 4) by Ni^{2+} template polymers (3, 4) (13.9% Dipy) compared with non-template polymer (1, 2) poly(vinyldipyridyl): acetate buffer, pH 4.6.

It should be noted that the selectivity and magnitude of the template effect depend on a variety of factors, e.g., spatial orientation and nature of chelating ligand, stability of the complexes formed, etc.

Mention should be made of a new type of "adjusted" polymer presenting the models of the "active" part of histidine (Fig. 8).[72] Cobalt(II) complexes with 4(5)-vinylimidazole and amino acid derivatives as substrate analogue were copolymerized with DVB. Then "template" molecules were removed by extraction and the "adjusted" polymer was used as a catalyst of hydrolysis of *p*-nitrophenyl ester of an amino acid.

The examples cited above for MCM and MMC applications can be enlarged. In the near future we can rely on further advances in this field.

7. MAJOR PROBLEMS IN THE CHEMISTRY OF METAL CHELATE MONOMERS

The above analysis of the major syntheses, polymerizations and copolymerizations of MCM points to a considerable progress in the solution to many problems relating to the MCM chemistry and extensive studies under way in this field. Among the most important problems awaiting further treatment in order to disclose the general principles of the MCM chemistry are listed below:

1) finding new methods for MCM preparation;
2) establishing ways for the activation of the multiple bonds of MCM, new techniques for the initiation of polymerization processes, detailed analysis of the effect of the type of metal on the individual stages of polymerization;
3) studies into the reactivity of double MCM bonds in other conversions involving these bonds (hydration, isomerization, oxidation, ozonolysis, hydroformylation, hydroxylation, etc.);
4) features of the copolymerization of MCM between each other and with conventional monomers;
5) examination of the structure of metallopolymeric chains, changes experienced by metals as they are incorporated into the polymeric matrix as well as cooperative interactions between the metal ions;
6) problems of stereoregulation and supramolecular organization of MMC as well as their topochemistry;
7) catalytic problems revealing the features of the chain structure of metal chelates.

The final solution of these problems will require joint effort on the part of specialists in the fields of coordination chemistry, high molecular weight compounds, organic synthesis, catalysis, etc.

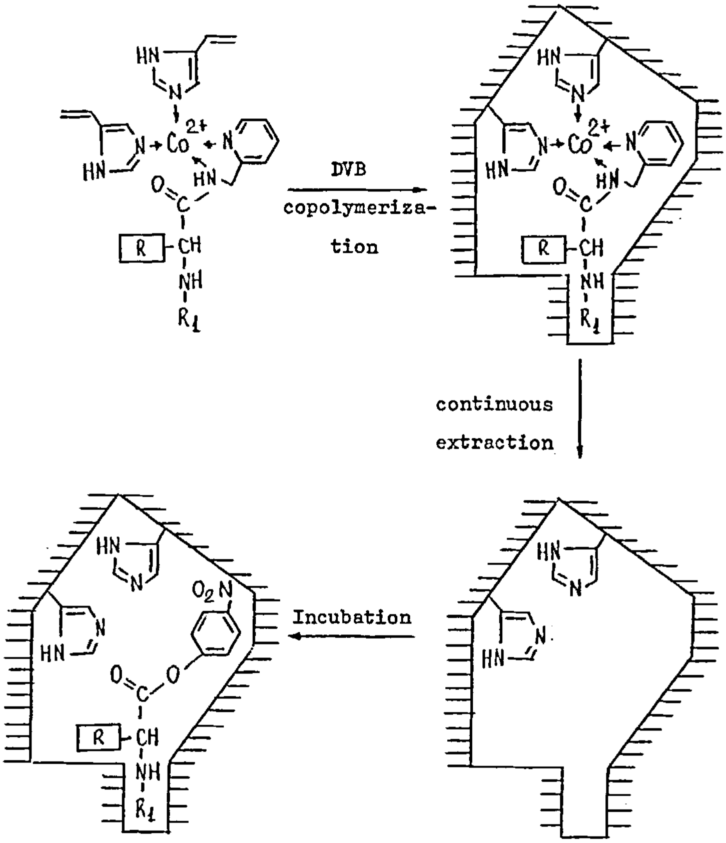


FIGURE 8 Scheme of template effect in the polymers presenting the models of the "active" part of histidine.

LIST OF ABBREVIATIONS AND SYMBOLS

a	metal-ligand distance
AN	acrylonitrile
AIBN	azobisisobutyronitrile
B′	Racah parameter
Dipy	2,2′-dipyridyl
Dq	splitting parameter
DVB	divinylbenzene
MCM	metal chelate monomer
MMA	methylmethacrylate
MMC	macromolecular metal chelate
M-Pr	metalloporphyrin
M-Ph	metallophthalocyanine
MX_n	metal compound
PIP	pyrrolylmethyliminopropene
PIS	pyrrolylmethyliminostyrene
Phen	1,10-phenanthroline
St	styrene
4-VP	4-vinylpyridine

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