Reviews

Problems of unit variability in metal-containing polymers

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The main types of unit variability in metal-containing polymers, including those typical of traditional polymers and those peculiar only to polymers with metal-containing groups, are surveyed and classified. The methods for controlling unit variability and the possibility of taking it into account and using it for practical purposes are analyzed. The main problems in this field and the prospects for their solution are considered.

Key words: unit variability, metal-containing monomers, metal-containing polymers, polymerization, copolymerization.
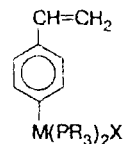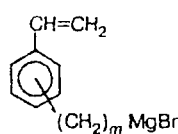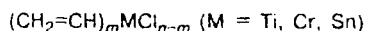
Introduction

The concept of unit variability[1] is used for all types of high-molecular-weight compounds. It allows deeper insight into the relationship between their structure and properties. As applied to specific objects such as metal-containing polymers, this concept can be further developed and substantially enriched because the composition and structure of metal-containing groups can vary over wide limits.
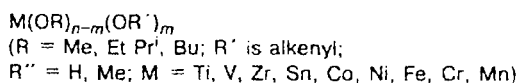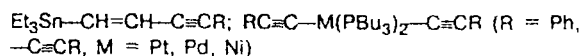
Metal-containing polymers can be produced by all known methods used to synthesize high-molecular-weight compounds, namely, polymerization (most often, radical[2,3]) or polycondensation of the corresponding monomers and polymeranalogous transformations.[4] Polymerization and copolymerization of metal-containing monomers (MCM) are of interest for the preparation of structurally homogeneous products with specified properties.[5] The main problem on this route is the synthesis of the corresponding monomers. Depending on the nature of the linkage between the metal with valence n and the ligands containing a multiple bond, MCM can be classified into several types,[6,7] which are presented below.
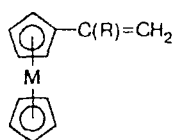
σ-MCM

$(CH_2{=}CH)_m MCl_{n-m}$ (M = Ti, Cr, Sn)

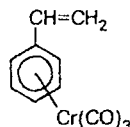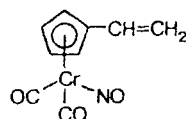R = Et, Bu; M = Pt, Pd

$Et_3Sn{-}CH{=}CH{-}C{\equiv}CR$; $RC{\equiv}C{-}M(PBu_3)_2{-}C{\equiv}CR$ (R = Ph, $-C{\equiv}CR$, M = Pt, Pd, Ni)

$M(OR)_{n-m}(OR')_m$
(R = Me, Et Pr^i, Bu; R' is alkenyl;
R'' = H, Me; M = Ti, V, Zr, Sn, Co, Ni, Fe, Cr, Mn)

π-MCM

R = H, Me; M = Fe, Os, Ru

Donor-acceptor (*nv*) type MCM

$MX_n(CH_2=CH)_m$

$MX_n(CH_2=CH)_m$

M = Pt, Pd, Rh, Co, Ni

$MX_n(CH_2=C(R))_m$
C≡N

$MX_n(CH_2=C(R))_m$
C≡O NH₂... (see structure)

$MX_n(CH_2=C(R))_m$
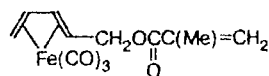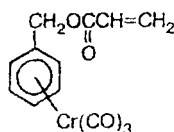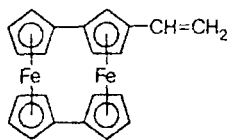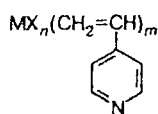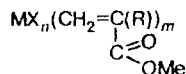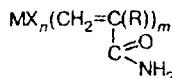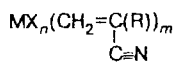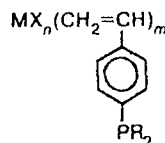
R = H, Me; M = Ti, V, Co, Ni, Cu, Zn, Sn, Mn, Fe, Cr, Y, Ba

Ionic type MCM

$M(OOCC(R)=CH_2)_n$ (R = H, Me; M = Ti, V, Zr, Sn, Co, Ni, Fe, Cr, Mn, *etc.*)

$(C_5H_5)_2M(OOCC(R)=CH_2)_2$ (R = H, Me; M = Ti, V, Zr)

M = Co, Ni, Fe, Mn, Cu

$CH_2=CHCOOCH_2CH_2OCO$...
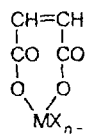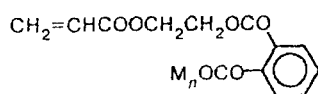
M = Zn, Mg, Fe, Cu

Cluster type MCM
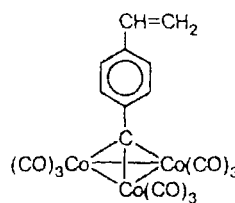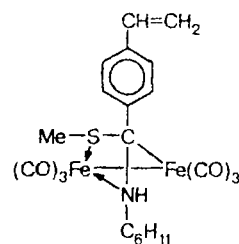
$Rh_6(CO)_{15}(4-VinPy)$ $Rh_6(CO)_{14}(4-VinPy)_2$
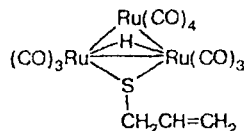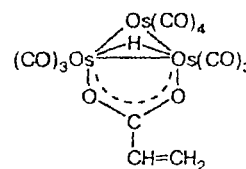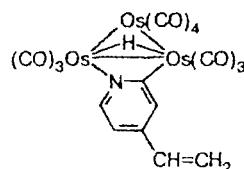
Chelate type MCM
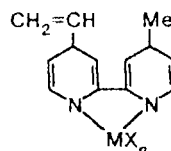
M = Ti, Co, Ru, Os, Zn, Cu, Ni
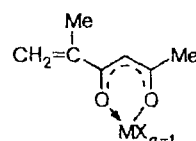
M = Eu, Cu, Ni, VO, Co, Mn, Fe
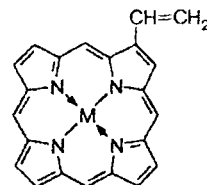
M = Fe, Zn, Cu, Co, Mg

In the general case, MCM are metal complexes with specific ligands, whose most important property is the ability to polymerize.[8] In these monomers, metals do not act as chain-forming centers (they are not included in the backbone) but serve as peculiar pending groups.

The reactivities of MCM differ markedly; some of them polymerize even during their synthesis, whereas

others are unable to polymerize or polymerize with difficulty even under fairly drastic conditions (high temperature, pressure, and concentration of an initiator or a catalyst). The limitations imposed on the polymerization of most of the known MCM are associated with their solubility, possible dissociation, change in their composition in solution, *etc.*

When analyzing polymerization of MCM, it is reasonable to assume that the composition of the polymer formed corresponds to that of the initial monomer. In reality, this is not always true. In the formation of these polymers, some units appear, whose structure and geometry differ from those of the main type of units. As a consequence, the chemical and structural homogeneity of the macromolecular chain is disturbed ("defectiveness"); thus, real molecules cannot actually be represented as sequences of identical repeating units, because diverse anomalous types of addition (unit variability) should also be taken into account. These problems are fairly important for elucidation of the relationship between the compositions, structures, and properties of the products formed upon MCM (co)polymerization; they often determine or restrict particular applications of these polymers.

Metal-containing polymers can contain two types of abnormal units: those characteristic of traditional high-molecular-weight compounds (violation of stereoregularity, residual multiple bonds, structurization and cyclization during polymerization, *etc.*) and specific ones. The latter include partial elimination of metal-containing groups, disturbance of the electronic structure of the units (changes in the valence state and nuclearity of the metal ion, the ligand environment, the shape of metal complex polyhedron (especially for polyvalent transition metals), the distribution of metal-containing groups along the polymer chain, extra coordination, *etc.*, during the formation of metal-containing polymers). In some cases, these factors are fundamentally important.

Since no systematic classification of the types of unit variability in the objects in question can be found in the literature, we shall analyze the general state of the problem and emphasize those aspects of it that present not only theoretical but also practical interest.

Unit variability due to elimination of a metal-containing group during polymerization

The unit variability caused by elimination of a metal-containing group during polymerization is one of the most important types of structural defectiveness in metallopolymeric chains. Attempts to polymerize many MCM have failed due to the elimination[9] of metal hydride and the formation of polymers devoid of the metal.
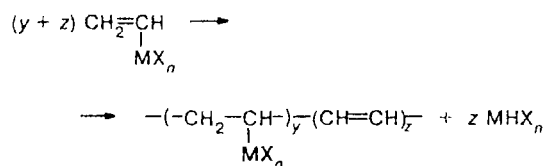
As a rule, introduction of a vinyl group into the ligand environment of a metal complex decreases its reactivity, apparently due to its additional conjugation with the metal d-electrons. In the case of MCM with

$$(y + z)\; CH_2{=}CH \longrightarrow$$
$$\qquad\qquad\quad | $$
$$\qquad\qquad\; MX_n$$

$$\longrightarrow\; -(-CH_2{-}CH{-})_{\overline{y}}(CH{=}CH)_{\overline{z}}\; +\; z\,MHX_n$$
$$\qquad\qquad\quad\; | $$
$$\qquad\qquad\; MX_n$$

other types of polymerizable groups (styryl, allyl, (meth)acrylate, *etc.*), the probability of these processes is low.

Chemical transformations of MCM in aqueous and polar solvents are accompanied by their ionization and dissociation; this also can result in the formation of products devoid of the metal. This is especially so in the case of transition metal carboxylates, which are strong electrolytes in water. In aqueous or water-organic media at pH > 7, salts of unsaturated carboxylic acids are almost completely dissociated (the molar electrical conductivity at infinite dilution λ_0 = 146—154 cm Ohm^{-1} mol^{-1}); hence, instead of MCM, other species, for example, acrylate and methacrylate ions in the case of metal acrylates and methacrylates, act as the monomers.[10] Similarly, in the acrylonitrile—sodium prop-2-ene-sulfonate system, which undergoes copolymerization in DMSO—H_2O mixtures at various pH values (45 °C, AIBN as the initiator), the relative reactivities of the comonomers change in different media due to the increase in the solvation capacity of water. Actually, copolymerization in these systems involves three types of monomers: $CH_2{=}CH{-}CH_2SO_3...Na$ (in DMSO), $CH_2{=}CH{-}CH_2SO_3^-$ (in aqueous DMSO), and $CH_2{=}CHCH_2SO_3H$ (in DMSO at pH = 1.5).

Aqueous solutions of Cu^{2+}, Co^{2+}, and Ni^{2+} acrylates are medium-strength electrolytes; the concentration plot of the molar electrical conductivity is described satisfactorily by the Kolrausch equation.[11] For 0.05 *M* aqueous solutions of calcium acrylate (Acr) and methacrylate[12] at 25 °C, the specific electrical conductivities K = 5.16 · 10^{-5} and 2.787 · 10^{-5} Ohm^{-1} mol^{-1} and the degrees of dissociation α = 0.46 and 0.2, respectively. The degrees of dissociation of Zn, Pb, and Ba acrylates ($M(Acr)_2$) in methanol are sufficient for the $M(Acr)^+$ cations formed to react with radical initiators (alkylcobalt chelates with tridentate Schiff's bases) giving free alkyl radicals, which induce[13] radical polymerization of these MCM even at low (5—10 °C) temperatures. For other types of MCM (*nv-*, π-types, see above), metal elimination processes are less typical, and in some cases (chelate type), these processes do not occur at all.

Thermal polymerization of MCM* is also often accompanied by the elimination of metal-containing groups.

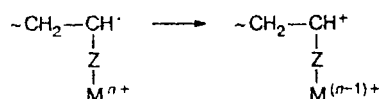* Thermal polymerization of MCM (with transition metal acrylates as examples) is of interest in at least two aspects.[14] First, the structure of these salts contains many dislocations, which facilitate solid-state polymerization. Second, thermal decomposition and polymerization transformations are the stages of a potential method for the synthesis of polymer-immobilized highly dispersed nano-sized metal particles.

Thus in the case of copper acrylate,[15] the relatively weak Cu—O bond cleaves to give the $CH_2=CH—COO^.$ radical, whose interaction with the matrix can serve as a channel leading to the formation of units containing no metal. At 190—240 °C, thermal decomposition is accompanied by polymerization in the solid phase. The polymers can incorporate metal-containing fragments formed upon elimination of either CO_2 or $Cu(COO)_2$ groups depending on the temperature of the solid-phase recombination-polymerization process.[15]

It is significant that dissolution of obtained metal polymers can also be accompanied by dissociation, especially in polar solvents. Thus in aqueous solutions (especially at pH $\geq$ 7), alkali and alkaline earth metal polyacrylates dissociate almost entirely (dissociation can be suppressed by adding nonpolymerizable salts, for example, 0.15 M KCl). This is often accompanied by destruction of the polymers to give products with lower molecular weights containing no metals.

Unit variability due to different valence states of transition metal ions

This is also a fairly widespread type of unit variability. By analogy with macromolecular complexes, it may be expected that homo- and copolymerization of metal-containing monomers would prevent or retard redox processes with participation of metal ions. Numerous experimental data confirm the fact that the polymeric matrix stabilizes complexes of metals in low oxidation states (for example,[16] Pd^+). Moreover, the stability of the Cu^+ state during polymerization of copper acrylate (including its thermal polymerization) enables the use[17] of this method for the preparation of coordination compounds of Cu^+. The polymeric framework plays the stabilizing role, whereas metal ions localized in the surface layer are oxidized[18] to Cu^{2+}. However, polymerization of monomers containing metal ions in high oxidation states is often accompanied by their reduction, for example, $V^{5+} \rightarrow V^{4+} \rightarrow V^{3+}$, $Fe^{3+} \rightarrow Fe^{2+}$, $Mo^{5+} \rightarrow Mo^{4+}$, etc. This may be due to diverse reasons. Thus polymerization of Cu^{2+} and Fe^{3+} acrylates is accompanied by intramolecular chain termination;[19] apparently, this is due to the relatively low standard reduction potentials of these metal ions ($E_0(Cu^{2+} \rightarrow Cu^+)$ = 0.15, $E_0(Fe^{3+} \rightarrow Fe^{2+})$ = 0.77 V).

$$\begin{array}{ccc} \sim CH_2-CH^. & \longrightarrow & \sim CH_2-CH^+ \\ | & & | \\ Z & & Z \\ | & & | \\ M^{n+} & & M^{(n-1)+} \end{array}$$

In systems of this type, electron transfer occurs *via* a complex route and is accompanied by reduction of Cu^{2+} to Cu^+. Monomolecular chain termination, resulting in reduction, has also been observed during graft post-polymerization of these monomers and acrylamide cop-

per complexes[20,21] to γ-irradiated polyethylene (PE).* It is assumed[18] that the set of eigen states of a structural fragment of dimeric copper dimethacrylate allows delocalization of the excited π-electron of the C=C bond to the COO^- group during the initiation of graft post-polymerization; this is accompanied by the reduction of copper and partial dissociation of the monomer:

$$(Cu^{2+})_2L_4 \longrightarrow 2 Cu^+L + 2 L^.$$
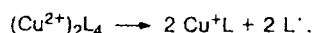
An estimate of the proportions of different valence forms of copper in copper polyacrylates shows[23] that the content of Cu^{2+} does not exceed 60%, and Cu^0 is absent. Most probably, autocatalytic $Cu^{2+} \rightarrow Cu^+$ reduction occurs. The role and the subsequent transformations of the ligands eliminated during the reduction are not entirely clear, although some of the possible routes will be analyzed below. It stands to reason that the geometry of complexes also changes upon reduction of metal ions; for example, square-planar Cu^{2+} complexes add an additional ligand and are thus converted into square-pyramidal complexes, whereas Cu^+ complexes are normally tetrahedral.

It has been suggested[24] that the chemical reaction that accompanies electron transfer in the electrochemical polymerization of copper methacryloylacetonate $Cu(MAA)_2$ involves replacement of the anionic MAA^- ligand by solvent molecules (MeCN) and affords the neutral complex $(MMA)^-Cu^+(MeCN)_2$, which is oxidized at $E = -0.22$ V.

Reduction processes also occur quite often in the step of synthesis of the corresponding monomers; certainly, this should be taken into account if the aim is to prepare a structurally homogeneous product. Thus in the $Fe(OH)_3$—maleic acid system in water, instead of the expected Fe^{3+} maleinate, a mixture of Fe^{3+} maleinate and Fe^{2+} hydrogen maleinate is formed. According to the Mössbauer spectroscopy,[25] the ratio of these products is 9 : 1. Dissolution of finely dispersed metallic Fe in an aqueous solution of maleic acid under inert atmosphere gave only Fe^{2+} hydrogen maleinate. Special methods for the synthesis of monomers containing transition metal ions in low oxidation states (Fe^{2+}, Cu^+, Cr^{2+}, V^{3+}, etc.) have been developed.[17]

The tendency of vanadium in high oxidation states to undergo reducion is well known and is due to its low redox potential. Apparently, this process is accelerated in the presence of radical species (I˙); therefore, initiation of polymerization occurs in parallel with the reduction of vanadium in mixed orthovanadates with elimination of alkoxyl radicals according to the following scheme[26]

$$VO(OR)_n(OR')_{3-n} + I^. \longrightarrow$$
$$\longrightarrow VO(OR)_m(OR')_{3-(m+n)} + n ^.OR \text{ (or } n ^.OR').$$

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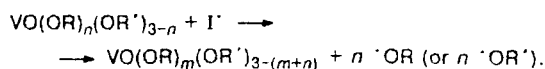
* However, no reduction of Cu^{2+} to Cu^+ was observed[22] during γ-initiated (beam-induced) copolymerization of copper bis-2-acetoacetoxyethyl methacrylate with various comonomers.

Elimination of a polymerizable fragment and its incorporation in the polymeric chain (this process has been called[26] *in situ* copolymerization with the monomer (ligand)) can also lead to unit variability. In addition, radical fragments can initiate polymerization, recombine, detach a hydrogen atom from coordinated ligands, *etc.*

ESR study of the products of transformation of mixed-ligand orthovanadates containing a polymerizable group able has shown[27] that diamagnetic V^{5+} is partially reduced during polymerization to paramagnetic V^{4+}. Although it is difficult to characterize strictly these processes, rough estimates of the V^{4+} content in the resulting homopolymers give a value of ~1 mol.% of the total vanadium content. In copolymers with styrene, this value is much higher and reaches 14—16 mol.%, and in copolymers with acrylonitrile it is even higher, 35—44 mol.%. Data of ESR and polarographic studies[28] of the products of thermolysis of model Ti^{4+} complexes in the presence of a radical polymerization initiator (AIBN) show that Ti^{4+} is reduced to Ti^{3+} (~5%); the reasons for this are obscure.

Oxidation of a metal during polymerization is relatively rare; the most typical example is vinylferrocene (see Ref. 2 and references therein). The ferrocenium cation, generated upon the transfer of an electron from the Fe atom to the terminal radical, rearranges to give a high-spin Fe^{3+} $3d^5$-complex. This process is facilitated by the ferrocene conjugation system. Evidently, the polymerization features of this MCM are unique, because effects of this type have not been observed for other π-type MCM. At the same time, polymerization of praseodymium(III) maleinate induced by H_2O_2 deserves attention; the reaction is accompanied by partial oxidation, $Pr^{3+} \rightarrow Pr^{4+}$; a complex of the resulting ion catalyzes polymerization.[29] An oxidative method has also been used[30] in the synthesis of triphenylantimony and triphenylbismuth diacrylates; in the presence of *tert*-butyl peroxide or hydrogen peroxide and acrylic acid, Ph_3M is oxidized to M^{5+}.

Thus, knowing the character of redox processes in systems with metal-containing monomers able to polymerize makes it possible, at least, to predict these processes and take them into account.

Unit variability due to the presence of stable isotopes of metals

This type of unit variability is fairly well known for traditional polymers; it is associated with stable isotopes of polymer-forming elements (^{13}C, ^2H, ^{18}O, ^{15}N, *etc.*). For metal-containing polymers, it is caused by the presence of stable isotopes of metals. In some cases, metals are specially enriched in definite isotopes during the synthesis of MCM, for example, enrichment in ^{57}Fe is used for γ-resonance studies[26] of the products of polymerization of Fe^{2+} acrylates. In some cases, stable
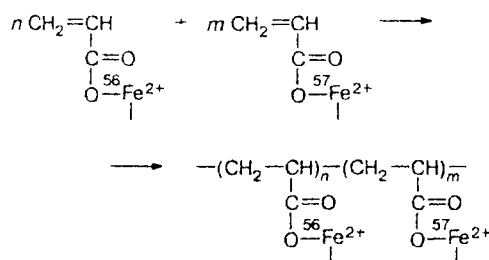
isotopes of other metals, for example, tin and vanadium, are also used.

Anomalies in metallopolymeric chains caused by the diversity of chemical binding of a metal to polymerizable ligands

This type of unit variability can be demonstrated most clearly by considering metal salts of unsaturated carboxylic acids. The polydentate properties of the carboxylate group $RCOO^-$ are well known.[31] In reactions of M^{2+}, it can act as a mono-, bi-, tri-, or tetradentate ligand even when the multiple bond does not participate in complexation. Mono- and bidentate types of metal binding are the most typical.
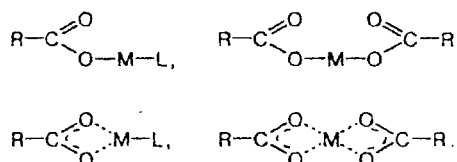
The metal—ligand bonds in metal acrylates were found[32] to be mostly ionic (the degree of covalence is 0.13—0.16). It is of interest that on going from acrylates to their saturated analogs (acetates), the metal—ligand bonds become longer and less covalent. During syntheses of metal acrylates and methacrylates, for example, the Cu^{2+} salts, molecules of the initial acid and solvating solvents (alcohols, acetone, DMF, *etc.*) can also be included in the complexes (*e.g.*, $Cu_2(CH_2CHCOO)_4 \cdot 2CH_2CHCOOH$ or $Cu_2(CH_2C(Me)COO)_4 \cdot 3CH_2C(Me)COOH$). When these components are removed, these MCM are converted into chain coordination polymers $[Cu_2(CH_2C(Me)COO)_4]_n$ consisting of dimeric repeating units, some of which can contain these ligands.

The situation becomes even more complicated in the case of unsaturated dicarboxylic acids, which are tetradentate ligands, capable of forming both neutral (cobalt maleinate $CoC_4H_2O_4 \cdot nH_2O$) and acid (for example, cobalt fumarate $Co(OCOCH=CHCOOH)_2$) salts.[25] Acid salts are normally monomeric, while neutral salts are normally chain or three-dimensional polymers (coordination polymers) in which the multiple bond does not participate in coordination.[33] IR spectra

imply that the bridging structure of the carboxylate groups is retained upon polymerization (at least, upon polymerization of copper diacrylate[23]), because the $v_{as}(COO^-)$ and $v_s(COO^-)$ absorption bands, located at 1575 and 1440 cm^{-1} in the spectrum of the initial complex, shift to 1550 and 1410 cm^{-1} in the spectrum of the polymerization product, while the difference between their frequencies ($v_{as}(COO^-)$ − $v_s(COO^-)$ ≈ 130 cm^{-1}), typical of bridging COO^- groups, remains virtually unchanged.
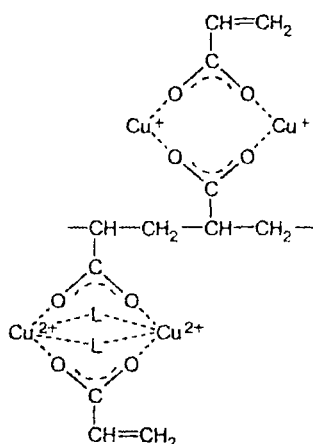
In polymers (especially in network polymers based on metal diacrylates[18]), the geometry of bridging groups is distorted due to the presence of internal strain. Polymerization of the polynuclear Cr$_3$O monomer (see below) is accompanied most likely by the formation of monodentate carboxylate groups upon destruction of the bridging bonds.[34] Frequencies corresponding to bridging and non-bridging bidentate carboxylate groups do not tend to merge.[35]

In the case of thermal polymerization, the number of modes of metal binding to carboxylate groups usually sharply increases, because it is accompanied by recombination-polymerization processes. Both the monomer itself (for example,[15] in the case of Cu^{2+} diacrylate) and the transient polymer can undergo thermolysis. At higher temperatures, the role of the latter route increases; terminal metal carboxylate groups are much more susceptible to decarboxylation than the internal groups.

The situation is much more complex in those cases where the polymerizing ligand contains several metal binding sites. Thus in metal chelates based on N-(2-pyridyl)methacrylamide, the metal is coordinated to oxygen of the carbonyl group and nitrogen of the heterocycle.[36]
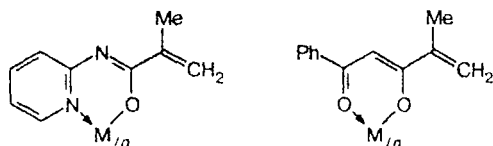

It follows from analysis of the Rack parameter and the degree of covalence (0.375) that the bond in these complexes is largely covalent, pointing to substantial shielding of the d-shell from the nucleus and to a decreased effective positive charge on the metal. This is also true for metal chelates based on methacryloylacetophenone.[37] The electronic spectra of macrochelates, transition metal polymethacryloylacetonates, attest[38] to some decrease in the orbital contribution to the metal—ligand bond in the polymer with respect to that in the monomer.

The potential unit variability of this type can also be manifested in metal-containing polymers based on metal—acrylamide (AAm) complexes. Since it is impossible to obtain a crystal of this polymer, the polymer structure is roughly modeled by the monomer structure. Acrylamide can form complexes through both the oxygen and the nitrogen atoms. The complex Co(NO$_3$)$_2$ · 4AAm · 2H$_2$O was studied by X-ray diffraction analysis,[39] which showed that the octahedral complex cations, [Co(AAm)$_4$(H$_2$O)$_2$]$^{2+}$, and the NO$_3^-$ anions are joined by a three-dimensional system of hydrogen bonds. The octahedral environment of Co^{2+} is formed by the oxygen atoms of the four AAm molecules and the two water molecules; thus, in these MCM, AAm is coordinated through the O atoms of the amide groups. The scatter of the Co—O distances from 2.065 to 2.114 Å reflects nonequivalence of the ligands. It is important (at least, for subsequent polymerization transformations), that cations containing longer double bonds be arranged in a chain along a particular axis. Evidently, it is these double bonds that would be the most reactive under appropriate conditions. This assumption is also confirmed[40,41] by the possibility of thermally initiated frontal polymerization of acrylamide complexes of transition metals. The cobalt environment apparently consists of only O atoms, because Co complexes containing nitrogen atoms in the inner coordination sphere are typically tetrahedral (T_d), which can be readily identified by the electronic absorption spectra (specific for octahedral chromophores). The d—d-transitions observed in cobalt acrylate[42] have low intensity; with allowance for the selection rules, this indicates an octahedral structure. Naturally, complexes with other metals and also polymers based on them can have a different structure.

A frequently encountered type of structural anomaly in polymers (predetermined at the stage of their synthesis) is artificial unit variability, *i.e.*, different arrangements of the multiple bonds in the ligand molecules (see Ref. 2 and the references therein). This type of unit variability is observed, for example, in vinyl-substituted heterocycles, *viz.*, isomeric vinylpyridines (VP), vinylimidazoles, vinyltetrazoles, *etc.* Since the degree of activation of an exocyclic C=C bond depends on its position in the ring, the rate of polymerization of, for example, zinc complexes of vinylpyridines decreases in the series 4-VP > 2-VP > 2-methyl-5-VP. This reflects the overall influence of many factors, including the

steric accessibility of the double bond. Moreover, the results can be different even for similar ligands. For example, $M(4\text{-}VP)_4X_2$ and $M(2\text{-}VP)_4X_2$ complexes ($M = Co^{2+}$, Ni^{2+}, $X = Cl^-$) are octahedral, whereas $Co(4\text{-}VP)_2Cl_2$ and $Co(2\text{-}VP)_2Cl_2$ exist either in the blue tetrahedral (α) form or in the pink octahedral (β) form.* These forms differ in the distance between the $C=C$ bonds, which is 4.47 Å in the α-form and 3.65 Å in the β-form. This difference has a substantial effect on the ability of these MCM to polymerize; only crystals of the tetrahedral α-$Co(4\text{-}VP)_2Cl_2$ undergo thermal polymerization on heating in air or under nitrogen at 103—130 °C, whereas the highly dense octahedral modification does not polymerize in the solid phase upon any type of initiation. Nevertheless, polymers based on $Co(2\text{-}VP)_2Cl_2$ were obtained, but they were block copolymers formed by complexes with a smaller coordination number of the metal and released ligands, *i.e.*, unit variability was caused by ligand elimination *in situ*. Note another example of this type: polymerization of VP in methanol—pyridine media initiated by the complex $(4\text{-}VP)_2Cu(OCOCH_3)_2$. Initiation was effected by the transfer of an electron from the monomer to the copper ion in the complex.
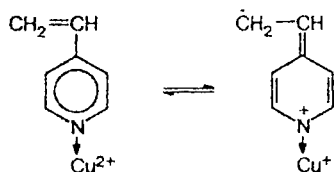

The principal difference between this mechanism and the repeatedly mentioned redox process with participation of Cu^{2+} is that the electron transfer involves a π-electron of the double bond rather than the free radical electron. This accounts for the double bond opening as the extreme case of its activation. Reactivation of the initiator is attained by oxidation of Cu^+ to Cu^{2+} in air, because the end units can contain Cu^+, which is also a source of unit variability.

As noted above, the coordination number of the metal can change during polymerization of MCM due to abstraction of some of the ligands; this can result not only in mixed-unit chains but also in a changed rate of polymerization. This is difficult to follow; however, some examples are documented. Thus the rate of homopolymerization of vinylimidazole (VIA) complexes depends on the coordination number of the metal,[43,44] which is determined by the number of attached VIA molecules: $Mn(VIA)_4Cl_2 > Mn(VIA)_2Cl_2 > VIA$.

* Note that the magnetic moments of octahedral and tetrahedral Ni^{2+} and Co^{2+} are significantly different: the μ_{eff} values, equal to 3.15 and 4.52 μ_B, respectively, point to the high-spin state of these ions in the octahedral ligand fields.

Unit variability due to (qualitatively and quantitatively) different ligand environments of the metal

This is also a relatively widely distributed type of anomaly. Thus it was found by IR and ^1H NMR spectroscopy[45] that in $Ti(OBu)_4$—unsaturated alcohol systems, the following equilibrium exists:

$$Ti(OBu)_4 + n\ R'OH \rightleftharpoons Ti(OBu)_{4-n}(OR')_n,$$
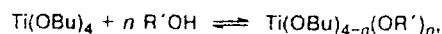
where $R'OH$ is the monomethacrylate of ethylene glycol (2-hydroxyethyl methacrylate, MEG), furfuryl alcohol, propargyl alcohol, 2-methylhex-5-en-3-yn-2-ol ($CH_2=CHC\equiv CC(Me)_2OH$), *etc.* The Ti—O—Bu bond in Ti^{4+} alkoxides is rather labile, which is confirmed by fast (on the NMR time scale) radical exchange.

Polymerization of some MCM of this type can be accompanied by the formation of mixed-unit chains as a result of their disproportionation during the process. This is especially typical of vanadium-containing monomers; thus all three isopropoxy radicals in isopropyl orthovanadate $VO(OPr^i)_3$ can be substituted successively during the reaction with MEG to give polymerizable vanadium-containing monomers, $VO(OPr^i)_{3-n}(OR')_n$.[27] On the one hand, the possibility of these reactions imposes rigid restrictions on the stoichiometry of the initial compounds during their synthesis and on the conditions of the synthesis, and, on the other hand, when conducting polymerization of these monomers, one should take into account unit variability in the polymer chains caused by different ligand environments of the metal. Some unsaturated alcohols (for example, $CH_2=CHC\equiv CC(Me)_2OH$) form vanadium-containing monomers susceptible to disproportionation:

$$2\ OV(OR)(OR')_2 \rightleftharpoons OV(OR)_2(OR') + OV(OR')_3.$$
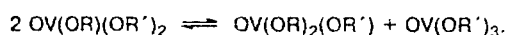
Therefore, monomers of this type (and correspondingly, the polymers based on them), except for only few specific alcohols, are mixtures of related vanadium-containing complexes. Of monomers of this class, compounds with identical ligands $VO(OR')_3$ are the most stable, apparently, since there is no possibility for disproportionation.

Mention should be made of the type of unit variability caused by the fact that many MCM (especially, organometallic ones) are susceptible to hydrolysis in the presence of even traces of H_2O (sometimes they react with traces of O_2). In some cases, the resulting compounds are also able to polymerize; this violates the structural homogeneity in the polymers. Hydrolysis of acetone solutions of copper(II) acrylate[46] and methacrylate[47] was specially studied.

Even more complicated processes occur in the case of ligands that isomerize during the formation and polymerization of MCM. For example, methacryloylacetone (5-methylhex-5-ene-2,4-dione), which is the initial

Scheme 1

Keto form
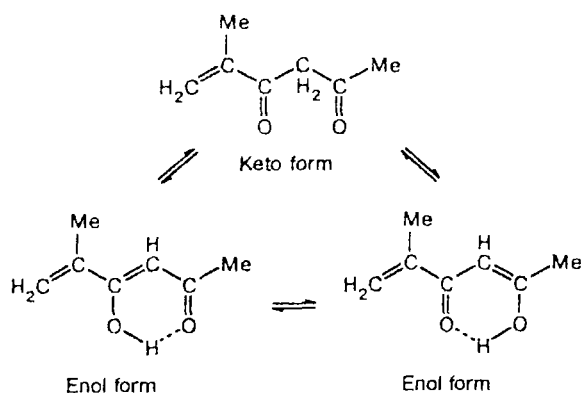
Enol form   Enol form

monomer for the synthesis of dicarbonyl type chelates, is susceptible to keto-enol tautomerism[48] (Scheme 1). The reaction of this ligand with metal ions, e.g., with copper ions, involves the enol form of methacryloylacetone (i.e., the ligand acts as an OH acid), whose fraction, according to pH-titration data, is quite large (~30% w/w). The formation of MCM by these ligands with doubly charged metal ions occurs in two steps and can generally be represented in the following way:

$$M^{2+} + L^- \xrightarrow{k_1} ML^+ + L^- \xrightarrow{k_2} ML_2.$$

It is obvious that polymerization transformations of tautomers or monomers containing different numbers of ligands would result in the corresponding unit variability. The constants for successive addition (k_1, k_2) were used[48,49] to calculate the stability constants and to optimize the synthesis of metal methacryloylacetonates. The greatest mole fraction of ML^+ is observed at pH = 5.4—5.8, and the formation of the neutral chelate ML_2 is completed at pH = 8. It is of interest that polymers prepared by the electrochemical method[24] contain a higher fraction of the keto-form units than those synthesized by conventional radical polymerization.

When the vinylic group of the ligand also participates in complexation, the number of possible types of anomalous units markedly inc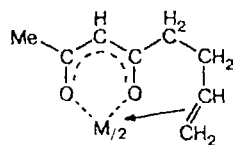reases. Thus for oct-7-ene-2,4-dione, the possibility of tridentate coordination due to additional binding of the double bond has been shown.[50]

The tridentate ligand occupies three adjacent vertices of the coordination polyhedron; the stability of complexes based on it would differ markedly from that in the case of bidentate coordination. As a rule, π-coordination hampers (and often totally prevents) polymerization processes, al-

though numerous π-complexes between comonomers were found to exist during copolymerization.[51]

Polymerization of MCM can be accompanied by interaction of the monomer with the initiator (catalyst), which also results in generation of anomalous units in the chains, although these reactions have scarcely been studied. It is only known that alkoxy derivatives of many metals efficiently react with peroxide initiators (see Ref. 2 and the references therein). Thus benzoyl peroxide (BP) readily reacts with alkyl titanates to give the titanium acylates $(BuO)_3Ti-O-Ti(OBu)_2OCOPh \cdot PhCOOBu$ and with allyltrimethyltin to give allyl benzoate and trimethyltin benzoate in a quantitative yield in relation to BP. Therefore, BP cannot induce polymerization of MCM of the $(BuO)_3TiOCOC(Me)=CH_2$ type. However, it polymerizes in the presence of AIBN, and at 80 °C, the degree of conversion can reach 60% in as soon as 20—30 min. In general, other transformations in the ligand groups can also occur during polymerization. The most important of these are exothermic effects observed during differential thermal analysis of MCM based on metal nitrates, which were attributed[52] to oxidation of acrylamide ligands, initiated most likely by decomposition of the nitrate groups of the complexes; apparently, these effects are also typical of polymers.

Extra-coordination as a type of anomaly (spatial and electronic structure of the polyhedron)

The relatively low stability of some MCM and polymers based of them can be due, among other reasons, to coordination unsaturation of the central atom, which facilitates a whole series of side processes. The coordination number of a metal can be increased by using[53] complex formation; for example, the structure of Ni^{2+}, Co^{2+}, and Cr^{3+} acrylates can be supplemented to an octahedral structure. Both specially introduced compounds and solvent molecules, most often water molecules, can act as the additional ligands. After polymerization, not all the addends chemically bound to the metal are removed from the product; this also serves as the source of anomalous units in the polymers. Since the structure of coordination units in the metal-containing polymer is difficult to study due to the set of various possible states, this type of unit variability is more convenient to study using metal-containing monomers.

Thus many metal acrylates often contain water of crystallization.[32] The $M...OH_2$ coordination bonds are the least stable; therefore, dehydration is the first step of thermal polymerization.[54] Metal chelates of the same metals and N-(2-pyridyl)methacrylamide also tend to coordinate additionally H_2O molecules to the axial positions to give octahedral structures.[36] Acrylamide complexes of metal nitrates (M = Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}) contain water of crystallization.[39] All of them are built as high-spin octahedra. In the case of chelate compounds of the β-diketonate type based on Ni, Co,

and Mn methacryloylacetonates, additional axial coordination of H_2O molecules is observed;[55] thus, the coordination unit is supplemented to an octahedron. Unlike acetylacetonates, which lose the water of crystallization in the 70—100 °C temperature range, methacryloylacetonates are dehydrated at higher temperatures[56] (110—160 °C); however, this is accompanied by thermal polymerization of the corresponding MCM. At higher temperatures, partial destruction and loss of the ligand molecules occur; the intermediate compound (which is considered above) retains the chelate structure. In polymeric methacryloylacetonates, the M—O bond in the chelate unit is apparently weakened, which results in lower temperatures of the onset of destruction of metal-containing polymers. As a rule, on going from a monomer to a polymer, the structure of the closest environment of the metal changes, for example, the Fe^{3+} environment with a local symmetry of the Fe—O bonds close to the cubic symmetry changes toward a more asymmetric structure.[57] At the same time, the rate of spin-lattice relaxation of Fe^{3+} ions decreases.

It is significant that the use of an additional ligand can also influence the rate of polymerization of the MCM formed. For example, for post-polymerization of allyl alcohol to γ-irradiated PE, it was found[58] that in the case of $CoCl_2 \cdot 6H_2O$, the rate of grafting is much lower than that in the presence of anhydrous $CoCl_2$, whereas in the presence of $Co(NO_3)_2 \cdot 6H_2O$, it is almost twice as high. Study of the properties of the product of spontaneous polymerization (at ~20 °C) of concentrated aqueous solutions of the acrylamide—$Cr(NO_3)_2 \cdot 9H_2O$ system showed[58] the formation of glassy polymers containing water. The crystal water evolved during polymerization either passes into a bound state or forms microinclusions of the electrolyte solution within the polymer bulk. Maybe, this is one of the rare cases where distribution of water in the polymer was strictly determined.

Of other solvents, alcohols are used most often for polymerization. Since the structure of nonsolvated Cu^{2+} acrylate is unknown, it may be expected that upon desolvation of its complex with ethanol, some of the bidentate carboxy groups become tridentate (see above); thus, they act simultaneously as the ligand and the solvation agent, which is absent. The increase in the dentate number of β-diketonate groups leads[14] to the distortion of the oxygen environment of Cu; in particular, the Cu—O distances and, hence, the C—O bond lengths change.

It should be noted that the spatial and electronic structure of MCM can change on going from the solid state to solution; in the case of liquid-phase polymerization, the structural change is fixed in the polymer. Diverse dissociation processes that accompany dissolution can result in anomalous units in the chains of the polymers obtained by solution polymerization. Thus in the case of cobalt chloride complex with AAm, the spatial structure changes from a tetragonally distorted

octahedron in the crystal to a tetrahedron in solution.[59] However, the coordination units of β-diketonates were found[55] to remain invariable on going from the crystalline state to chloroform solutions; complexes of nitrogen-containing vinyl heterocycles remain structurally invariable in the crystalline state and in methanolic and DMF solutions.[60]

However, complexes of cobalt and nickel chlorides with these ligands, ML_2Cl_2, are polymeric structures in which the metal ion lies in the plane of the chloride bridges, and the ligands occupy the axial positions. When these MCM are dissolved in, *e.g.*, methanol, the chloride bridges are cleaved and the arising vacancies are occupied by methanol molecules, which possess a stronger coordination field than chloride ions. DMF also ruptures the chloride chains and occupies part of the coordination sites that have liberated; both six- and four-coordinate complexes are formed. Elucidation of the structural organization of metal-polymer complexes and identification of various types of polyhedra, resulting in unit variability in metal-containing polymers, is a task that is still to be solved.

Additional coordination can also involve other components of the polymerizable system and can exert a substantial influence on the polymerization kinetics and the structures of the products formed. In particular, the formation of MCM complexes[28] with an initiator can both accelerate (generate the initiating species) and retard its decomposition, and it leads to a set of products that can, in particular, be incorporated in the formed polymer as its terminal groups. Thus the unusual kinetics (the order of the reaction with respect to the monomer is ~0.5) of radical polymerization of Ti^{4+}-containing monomers are due to the occurrence of parallel reactions[61] (Scheme 2).

Scheme 2
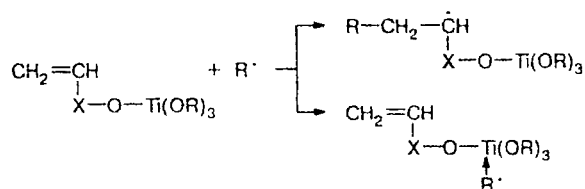
The Ti^{4+}-coordinated radicals thus formed can participate both in chain growth and (mainly) in chain termination. The metal ion acts as a sort of radical trap; in the complex formed, the radical becomes passivated with respect to the initiation of new chains. These complexes can be relatively stable.* As the first approximation, this situation is modeled by stable (for example, iminoxyl)

* It is assumed[62] that the single-electron $Ti^{IV} \leftarrow R \cdot$ bond in the complex radical can prove to be fairly strong; its energy is estimated to be half that of the σ-Ti—C two-electron bond.

radicals. In fact, the reaction of initiating radical species with the monomers of the η⁴-(hexatrienyl)tricarbonyliron[63] type is accompanied by the formation of stable radicals, which are inefficient for chain initiation.
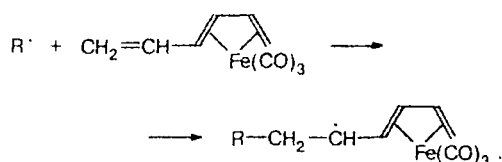
Copolymerization of MCM is even more complicated due to diverse complexation reactions between the monomers participating in the copolymerization; this accounts for both the unusual pattern of the "monomer mixture composition—copolymer composition" diagrams and the abnormal distribution of metal-containing sites along the chain. For example, in the V^{5+}-containing monomer—styrene system,[26] the coordination interactions of the weak Lewis acid (MCM) with the electron donor (styrene) yield mostly alternating copolymers. The tendency for unit alternation in the product points to a complex-radical mechanism of copolymerization.[51] In the ESR spectra of styrene copolymers with copper complexes of vinylporphyrins (see above), two types of signals for Cu^{2+} were detected;[64] apparently, one of these signals corresponds to an extracoordinated Cu^{2+} complex.

Exchange interactions
between metal ions incorporated in the chain

Many properties of metal-containing polymers depend appreciably on the character of localization of metal ions; this brings up the problem of describing the ways of arrangement of metal ions along the polymer chain. Different types of supermolecular associates can be formed: metal ions can either be separately arranged along the chain or form dimers, trimers, multiplets, block structures, ionic clusters, etc. (one of the main types of unit variability). If the ions weakly interact with the polymer, phase separation occurs and ionic clusters are formed. In other words, in addition to the units including metal atoms, the polymers can contain ionic domains containing no metal and separate fragments of metal ions located together.

We will present only the most typical examples. The ESR spectrum of the V^{4+} ions formed upon polymerization of V^{5+}-containing monomers is broadened due to exchange interactions and represents a broad singlet.[26] Such a polymer can be regarded as a cooperative system in which the V^{4+} ions are included in the matrix of the V^{5+} ions. In all probability, these associates are formed around the vanadium atoms that cross-link two polymer chains; this may increase the probability that other vanadium atoms would approach them. The absorption spectra of styrene copolymers with metal-containing

vinylporphyrin monomers is a superposition of the spectra of porphyrin units that are located close together and do not interact.[64] The differences in the chain conformations caused by the addition of porphyrin units through a pyrrole ring have been proved by spectroscopy.[65] A typical example of ionic clusters is the structure of lithium sorbate ($C_6H_7LiO_2$), which consists of separated organic and inorganic layers; in this two-dimensional network structure, lithium ions are located at both the corners and the edges of the lattice.[66] During polymerization, the orientation of these monomeric units is retained, at least, partially.

In Cu^{2+} and Fe^{3+} polyacrylates, exchange interactions occur,[28] which may be due to the specific bi- and trinuclear structure of these MCM. The composition diagrams for copolymers of styrene with cobalt or nickel acrylate[67] point to the tendency for the formation of alternating copolymers; alternating structures account for 42% of the total number of acrylate groups (calculated from the constants for relative reactivities of the comonomers). Metal ions are remote from one another. The Ti^{4+}—Ni^{2+} metal copolymers are ensembles of noninteracting (or even discrete, as regards electron localization) sites, although they are linked by the polymer chain.[68]
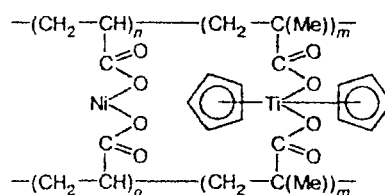
However, when these copolymers are synthesized under specific conditions (in particular, solid-state polymerization at high pressure combined with shear deformation), interchain interactions can appear. They are manifested as intense antiferromagnetic exchange, caused by conformational changes in macrochains.[68] The structure of complexes combined in clusters with antiferromagnetic interaction is formed during the polymerization. It has been suggested[69] that the Fe^{3+} and Zn^{2+} ions in copolymers that contain zinc and iron methacrylates, in addition to unsubstituted methacrylic acid, undergo long-range interaction, which is transferred along the polymer chain. This was explained by the relatively large inductive polarizability of the functional groups attached to Fe^{3+}. It can be considered formally that the presence of alternating and non-alternating units also results in unit variability in metallopolymers. Its influence on the properties of these polymers is now difficult to elucidate.

Change in the nuclearity of metal sites as
a type of unit variability

During polymerization transformations of MCM in the solid phase or in solution, the nuclearity of metal

complexes can either increase or decrease; under certain conditions, polynuclear, cluster, or even nano-size metal particles can be formed.[70] As has already been noted,[32] the binuclear structure of Cu^{2+} acrylate can be either destroyed or retained during polymerization.

Monomers of the general formula[35] $[M_3O(OCOCH=CH_2)_6]OH \cdot 3H_2O$ ($M = Fe^{3+}$, Cr^{3+}) are built as trinuclear clusters in which the metal atoms form a regular triangle with the oxygen atom in the center, while the carboxy groups form bridges between the metal atoms.
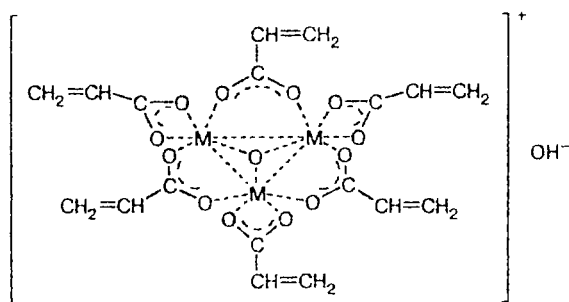
It is not completely clear whether the M_3O clusters retain their individuality during polymerization (when the spatial network of the polymer is formed) or they decompose with elimination of H_2O and $CH_2=CHCOO$ groups (nor in what particular step it occurs). However, it is known that after polymerization the structure of the local environment of the M^{3+} ion can both remain unchanged[49] ($M = Cr^{3+}$) and change substantially ($M = Fe^{3+}$); the partial loss of the water of crystallization of the monomer decreases the coordination number of the iron ions, i.e., the symmetry of their local environment decreases. However, this does not imply destruction of the cluster structure during polymerization, although the data of mass spectroscopy lead to the conclusion[34,35,57] that dissociation of the M—O bonds is energetically nonequivalent. Thus, polymers based on this type of monomers can contain several types of anomalous units, viz., those caused by the change in nuclearity of the metal complex or its ligand environment, and those due to the formation of branched polymers with retention of the M_3O framework during polymerization.

Apparently, similar structures can also be found in acrylates and methacrylates of other transition metals in high oxidation states and polymers based on them, for example,[71] zirconium methacrylate $Zr_4[OCOC(Me)=CH_2]_{10}O_2X_2 \cdot nH_2O$ ($X = HO^-$, $CH_2=C(Me)COO^-$; $n = 2, 4$). Moreover, even acrylates of some transition metals in low oxidation states (e.g.,[17] V^{3+}) are built in the same way (V_3O); this is also true for unsaturated dicarboxylic acids and their polymers.[25,33] Naturally, it becomes immeasurably more difficult to determine the fine structures of these metallopolymers and to take account of all the types of mixed units in them. The problem is somewhat simpler in the case of cluster-containing monomers obtained
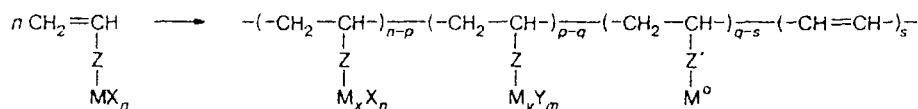
upon interaction of ligands, capable of polymerization transformations, with individual clusters. For example, the reaction occurring in the carbonyl cluster $Rh_6(CO)_{16}$—4-VP system in the presence of trimethylamine N-oxide under mild conditions affords[72] the monosubstituted derivative $Rh_6(CO)_{15}(4\text{-}VP)$ (the major product) and disubstituted compound, $Rh_6(CO)_{14}(4\text{-}VP)_2$, in a relatively low yield. They can be separated and isolated in a pure state by chromatography. The vinyl group in these MCM lies in the plane of the pyridine fragment and does not interact with the rhodium cluster. In the case of $Rh_4(CO)_{12}$ and 4-VP, non-selective polysubstitution of the CO groups occurs, resulting in a number of products formed in relatively low yields. Thus, the problem involved in the synthesis (and subsequent polymerization) of MCM of this type is to introduce selectively specific ligands with retention of the noncoordinated double bond. Since the IR spectra in the region of vibrations of the cluster carbonyl groups provide a great deal of information, these spectra are used for elucidation of the nuclearity of metal-containing sites in polymers. Yet another specific feature, namely, the formation of a cluster with the ortho-metallated 4-VP ligand, was noted in a study of the triosmium carbonyl cluster with 4-VP;[73] replacement of a CO group in it by PPh_3 made it possible to prepare the phosphine derivative of this MCM.
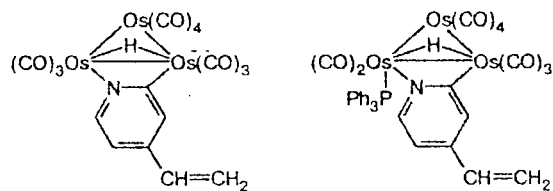
Heating $(\mu\text{-}H)Os_3(\mu\text{-}OH)(CO)_{10}$ with excess acrylic acid in benzene gives a new cluster complex with bridging bidentate coordination of the acid to two osmium atoms;[73] this complex is capable of polymerizing. Since the Os_3 cage is highly stable during polymerization transformations, only anomalous units caused by different ligand environments can be detected in the products. The same is true for the product of the reaction of $Os_3(CO)_{12}$ with allylamine, which exists as two isomers[73,74] due to the hindered rotation around the C—N bond, the complex $(\mu\text{-}H)Os_3(\mu\text{-}O=CNHCH_2CH=CH_2)(CO)_{10}$. However, most often these reactions are accompanied by coordination of the double bond (tricobaltalkylidene complexes $Co_3(\mu_3\text{-}CR)(CO)_{9-x}(PPh_2CH=CH_2)_x$, where $x = 1, 2, 3$, are examples[75]). A similar product, $Rh_6(CO)_{14}(\mu,\eta^2\text{-}PPh_2CH_2CH=CH_2$, was isolated upon the reaction of $Rh_6(CO)_{16}$ with allyldiphenylphosphine; in this case, π-coordination of the unsaturated ligand with the cluster core is also observed.[76]

Although homopolymerization of cluster-containing monomers occurs with difficulty (as a rule, low-molecular-weight oligomers are formed), their copolymeriza-

Scheme 3

$$n\,CH_2\!=\!CH \longrightarrow -(-CH_2\!-\!CH-)_{\overline{n-p}}(-CH_2\!-\!CH-)_{\overline{p-q}}(-CH_2\!-\!CH-)_{\overline{q-s}}(-CH\!=\!CH-)_{\overline{s}}$$

with the substituents Z / MX_n ; Z / M_xX_n ; Z / M_yY_m ; Z' / M^o

(*x* and *y* are the valences of the metal, Y and Z´ are the products of transformation of X and Z)

tion with vinylic monomers occurs with high yields. Physicochemical studies show that Os_3- and Ru_3-containing monomers do not undergo substantial transformations that could complicate copolymerization with styrene or acrylonitrile and do not react with AIBN. However, when a cluster-containing monomer adds to a growing polymer chain with its structure remaining almost unchanged, it restricts the chain growth.[77] Nevertheless, broadening of some bands in the IR spectra of copolymers (especially, in the case of Rh_6) can be interpreted as being due to anomalous units present in their chains and formed upon decarbonylation of some of the units, increase or decrease in their nuclearity, *etc.* Detailed analysis of these processes and identification of their role (for example, in the catalysis by these cluster polymers) requires further research.

Thus, unit variability in metallopolymers can be represented in a simplified form by the following diagram, which takes into account the change in the metal valence state, ligand environment, and nuclearity, as well as elimination of a metal-containing group (Scheme 3).

Stereoregularity of metallopolymeric chains

This type of unit variability, unlike those considered above, is frequently encountered in traditional polymers. Although the difference between the activation energies of iso- and syndio-addition during radical polymerization is small (<1 kcal mol^{-1}), in the case of MCM there exist prerequisites for the formation of stereoregular polymers. They are based, first of all, on the assumption that quadrupoles or ion pairs can affect the direction from which the monomer approaches the active center and the way of opening of the monomer double bond (orientation effect of the coordination bond of the cation, electrostatic interaction between the ionized growing radical and the polar metal-containing group in MCM, *etc.*). Thus due to the presence of an ionized group in transition metal acrylates, in each chain-lengthening event, the growing center changes its stereochemistry to the opposite one; this should result in alternating configurations of the MCM units in the chain, *i.e.*, in the formation of a syndiotactic polymer. Moreover, even small (up to 2 mol.%) amounts of transition metal acrylates added to the MMA (methyl methacrylate)—MAA (methacrylic acid) system during copolymerization not only influence the relative reactivity constants of the comonomers but also change the microtacticity of the copolymers.[78]

It is of interest that stereoregularity of metal-containing polymers changes markedly as a function of the MCM composition (see Ref. 2 and the references therein). Thus polymerization of $Zn(MMA)_2Cl_2$ gives a polymer with a higher degree of syndiotacticity (60%) than polymerization of $Zn(MMA)Cl_2$ (48%), whereas in the case of $Sn(MMA)Cl_4$ and $Sn(MMA)_2Cl_4$, the opposite relationship is observed (77 and 63%, respectively).

As for conventional monomers, a decrease in the polymerization temperature increases the content of the structurally ordered fraction in metal polyacrylates;[13] in the case of a Co^{2+} salt, the content of the syndiotactic fraction was[79] 60% (polymerization of acrylic acid under the same conditions gives only 25—30% of this fraction). Upon low-temperature (5—10 °C) radical polymerization of barium diacrylate, the content of the syndiotactic fraction reaches[13] 74%; in the case of zinc diacrylate, this content is 80%.

The process of polymerization of bifunctional monomers (diacrylates) can be divided into two steps (Scheme 4). The first step yields a linear comb-shaped polymer, the degree of whose stereoregularity depends on the nature of the metal ion. The second step results in a spatial network polymer. In this step, chain growth mostly involves the C=C bonds in the side chains of the macroradicals. The chain growth occurs under conditions of severe steric hindrance and with an increasing level of internal (shrinkage) stresses; this results in the formation of an atactic structure.

Up to now, we did not pay much attention to this type of unit variability in the "daughter" chains formed during matrix polymerization of MCM. This is due to the fact that the "parent" polymeric chain (the matrix) brings about structural and chemical control of the growth of the "daughter" chains formed from the MCM molecules adsorbed on the matrix: the orientation and nonvalence interactions in the MCM sorbed by the matrix units cause stereoregulation in the "daughter" chain growth events. Recently, the mechanism of these processes (the structural matrix effect) was studied in relation to the polymerization of sodium acrylate[80] and sodium methacrylate[81] on poly(allylamine hydrochloride). The ideal route of matrix polymerization follows the "zipper" mechanism: each growing chain propagates along a single matrix chain. At low degrees of conversion, this is really so, but during more extensive polymerization, deviations resulting in a peculiar unit variability appear. The growing radical, which reaches the end of the matrix chain, can capture a monomer from the bulk or react with a monomer adsorbed on

another chain. As a consequence, a network structure is formed.

Scheme 4
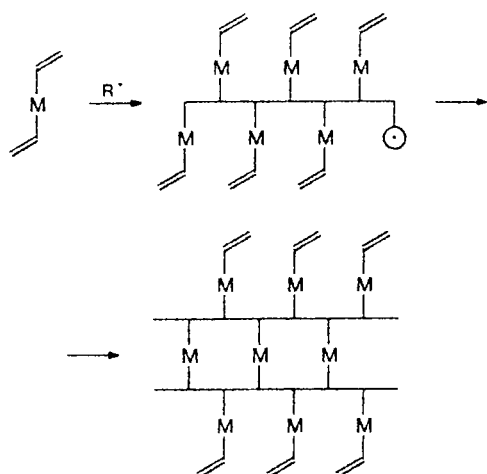
Unit variability due to optical activity in the pendent groups

This type of unit variability has scarcely been studied, although the presence of these units in metal polymer chains is important, for example, for asymmetric catalysis.[82] Apparently, the first study along this line was the synthesis of an optically active metal-containing monomer, a palladium complex with *R*- and *S*-1-(4-vinylphenyl)ethylamine,[16] $PdCl_2(CH_2=CHC_6H_4{}^*CH(NH_2)CH_3)_2$. Copolymers of these MCM with styrene and divinylbenzene proved to be chiral catalysts of reduction of acetamidocinnamic acid azlactone and products of its solvolysis. At least one more variant of this type of unit variability exists; it is caused by different ligand environments of the metal. This can be attained by introducing a group, for example, an alcoholic group, containing an asymmetric carbon atom into the ligand environment of MCM:[83]

$$Ti(OR)_4 + R'OH + R^*OH \ \rightleftharpoons$$
$$\rightleftharpoons Ti(OR)_2(OR')(OR^*) + 2\,ROH,$$
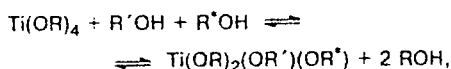
where $R^* = -O^*CH(CH_3)CH_2CH_3$ or l-menthol, (+)-ephedrine, (+)-cinchonidine, *etc.* residues, $R = -CH_2CH_3$; $R' = -CH_2CH_2OOCC(CH_3)=CH_2$. The difficulties associated with the transesterification of alkoxy derivatives of Ti^{4+} or V^{5+} even in binary systems have already been noted. In ternary systems, these difficulties immeasurably grow; however, in some cases, individual compounds still can be synthesized and characterized. This refers mainly to mixed compounds in which $R' = -CH_2CH_2OOCC(CH_3)=CH_2$ and $R^* = $ l-menthol resi-

due. The product is optically active, despite the fact that homo- and copolymerization of these MCM is accompanied by racemization.

Unsaturation and structurization of metallopolymers

These phenomena can occur for different reasons: incomplete involvement of the multiple bonds in polymerization, specific features of chain restriction and chain transfer reactions, *etc.*

Metal-containing copolymers of Co or Ni acrylates with styrene containing up to 20 mol.% of acrylate units are readily soluble in DMF and methanol, indicating that the process involves mostly one of the double bonds;[67] the same can hold for their graft polymerization.[20] During polymerization of transition metal methacryloylacetonates, the structure of the coordination units does not change; however, the double bonds not participating in the polymerization can either form cross-linked structures or remain free.[38]
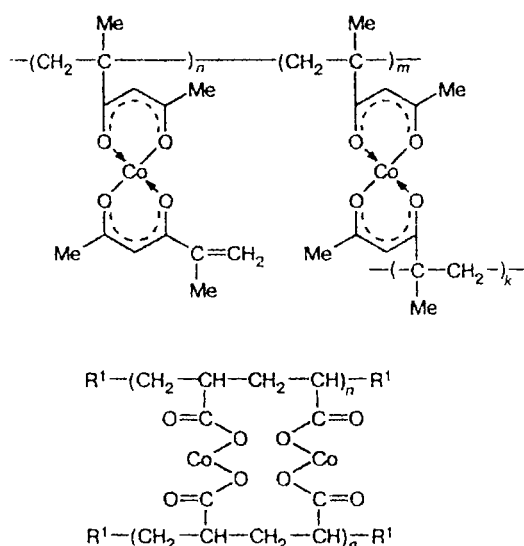
Similarly, the polymer formed upon thermal polymerization of Co^{2+} acrylate can be both linear and cross-linked, depending on the temperature.[15] The fraction of unreacted double bonds in copolymers of transition metal diacrylates with traditional vinylic monomers increases in the order Zn^{2+} (4—35%) $< Co^{2+}$ (14—39%) $< Ni^{2+}$ (22—49%), which correlates with the ability of these acrylates to undergo homopolymerization (in the hypothetical case where only one acrylate group reacts, the degree of unsaturation is 50%). Copolymerization of Co^{3+} complexes in which Schiff's bases with vinylic groups act as the ligands involves either one or two groups of the three groups coordinated to Co^{3+}, whereas in the Cu^{2+} chelate both vinylic groups participate in polymerization.

Scheme 5

~R· + CH$_2$=CH   CH$_2$=CH   →   ~R—CH$_2$—ĊH   CH$_2$=CH   →   ~R—CH$_2$—CH—CH$_2$—ĊH
| | | | | |
OC   CO   OC   CO   OC   CO
| | | | | |
O——M——O   O——M——O   O——M——O
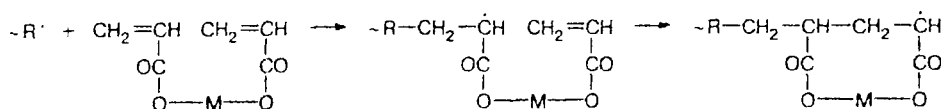
Cyclization during polymerization

As a rule, MCM based on polyvalent metals are bi- or trifunctional monomers with nonconjugated double bonds. The mechanism of formation of cyclic units is apparently close to that of polymerization of nonconjugated diene monomers (for example, 1,5- or 1,6-dienes), acrylic or methacrylic anhydride, *etc.* This is reduced to the alternation of inter- and intramolecular chain growth events (Scheme 5).

Apparently, the important role of metal ions is to ensure orientation of polymerizing units and close arrangement of their double bonds. The possibility of these processes is indicated by the known facts of higher efficiency of cycloaddition compared to ordinary addition: the radical formed upon cleavage of one of the double bonds normally reacts with the second double bond in the same monomer. It is significant that cycloaddition is realized even in those cases where the activities of the double bonds in the monomer are markedly different, for example, in the cyclopolymerization of allyl methacrylate.

It has been shown by a number of methods (measurement of the polymer solubility, comparison of the degree of polymerization and the number of double bonds in the polymer)[26] that radical polymerization of the trisubstituted vanadium-containing monomer VO(O(CH$_2$)$_2$OC(O)C(CH$_3$)=CH$_2$)$_3$ follows the cyclopolymerization mechanism (Scheme 6).

Scheme 6

R· +

→

Z = —O(CH$_2$)$_2$OC(O)—
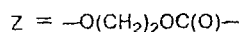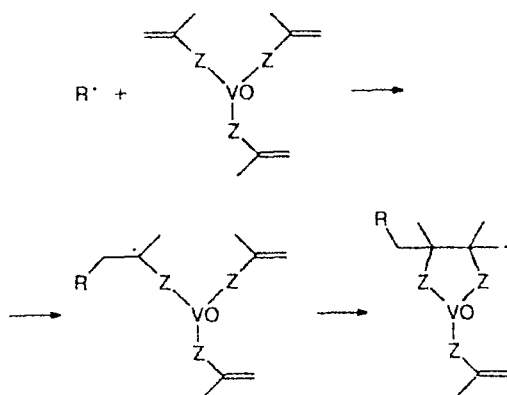
These processes also occur in systems that undergo copolymerization, especially if one of the monomers

chemically changes during the reaction (for example, copolymerization of sodium styrenesulfonate with sodium chloroacrylate, accompanied by partial dehalogenation of the monomer, involves intramolecular cyclization leading to the appearance of lactone units in the copolymer).

Some practical applications of unit variability of metal-containing polymers

The data presented here indicate that various types of unit variability in metallopolymeric chains can arise during polymerization of MCM; some of them serve as specific levers for controlling the composition and properties of the metallopolymers formed, whereas others are only hypothetical. The main point is the necessity of choosing conditions under which the metal-containing group is introduced into a polymer.

Note that polymerization of MCM containing different metal isotopes has already found practical use; in particular, it is used for effective separation of the ^{235}U and ^{238}U isotopes based on the different rates of polymerization of their acrylates, UO$_2$(OCOCH=CH$_2$)$_2$, in magnetic fields.[84]

Polymers whose monomeric units contain metal ions in different oxidation states are of interest for a number of reasons. Thus homopolymerization of 3-vinyl-bis-fulvalenediiron is an efficient way of producing conductive polymers;[85] this process is accompanied by oxidation of some of the Fe^{2+} ions to Fe^{3+} ions with simultaneous formation of charge transfer complexes with the oxidant, tetracyanoquinodimethane (TCCDM).

The formally mixed-valence (Fe^{2+}, Fe^{3+}) polymeric complex thus obtained is a delocalized system with a single type of iron ions, which possesses one of the highest electrical conductivities of those observed for organic polymers, (6—10) · 10^{-3} Ohm^{-1} cm^{-1}.

The unit variability caused by different spatial and electronic structures of metal-containing groups in polymers can also significantly influence their properties. We will present one typical example. Copolymers of Cr^{3+} alkyl vinyl sulfoxide complexes with MMA exhibit thermochromism;[86] their color changes from emerald-green (20—30 °C) to violet (40 °C). Evidently, on chang-

ing the temperature, the complex configuration changes, due to the behavior of the polymeric matrix in which the complex is fixed. As the temperature decreases, the matrix becomes more rigid, and this distorts the configuration of the polymeric complex, whereas at higher temperatures, the influence of the matrix is weaker, and the complex returns to its initial shape. Since reactions of polymers are not quantitative, all sorts of intermediate states of the complexes coexist in metal polymers.
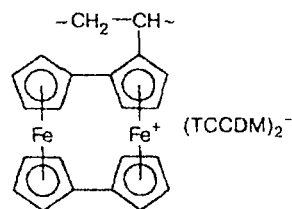
Note that extra-coordination processes are also important for controlling the properties of metallopolymers. Thus, mechanical and operation parameters of many metal polymers are determined by the ability of the metals to form ionic or coordination cross-links (additional inter-chain interaction), to exhibit cohesion and adhesion properties, etc. Formally, unit variability in these cases is determined by the presence of metals with different coordination numbers in the chain. The incorporation of cluster-containing Os_3-monomers into a polystyrene or polyacrylonitrile chain results in mutual thermal stabilization of both polymers and the clusters incorporated in the chains.[87] It is noteworthy that these effects are observed only in those cases where the cluster monomers are chemically bound to the polymeric chain. The influence of the chain may be manifested as the transfer of energy from the rotation-vibration degrees of freedom of the cluster to the forward degrees of freedom of the polymer chain segments at elevated temperatures, which increases thermal stability of both the cluster group and the polymer.

We have analyzed above the unit variability caused by the unsaturated character of metallopolymers and by their structurization. Many properties of metallopolymers are enhanced upon the formation of cross-linked structures, which is attained, for example, by additional thermal polymerization with participation of the residual double bonds aimed at producing cross-linked polymers with high strength and plasticity and high softening temperatures. Unsaturation in metallopolymers can also influence their color. In fact, the pink reaction mixture consisting of MMA, MAA, and Co^{2+} methacrylate becomes green when the number of C=C bonds decreases by 15%.[78] Transition metal acrylates can participate in cross-linking of polymeric chains themselves, which results in unit variability; in particular, this occurs during photochemical structurization of gelatin.[42] On exposure to the monochromatic radiation from a helium-neon laser, the amino and hydroxy groups of gelatin (hydroxyproline and lysine or arginine residues) react with activated double bonds. The high sensitivity of copper-acrylate-based layers is due to the fact that the position of its absorption maximum corresponds to the laser radiation wavelength (633 nm); these layers absorb light more efficiently.

Apparently, chain cross-linking can also occur by other mechanisms, for example, due to coordination interactions of the metal ions of MCM with functional groups of polymers.

* * *

The analysis of unit variability in metallopolymer chains presented here may give the impression that polymerization of MCM is accompanied by a lot of side processes. The fact noted in the Introduction that the unique character of the products of polymerization of these monomers is due to the structural uniformity of the macro complexes formed might appear problematic. Actually this is not so.

Many of the side reactions considered (as well as those remaining beyond the scope of this analysis) can be prevented, and some other reactions can be substantially suppressed. Numerous approaches exist for this purpose; the most convenient is low-temperature polymerization including that initiated by radiation (when the use of chemical initiators is complicated by their reactions with MCM); the radiation-induced polymerization can be carried out in any phase state of the monomer over a broad temperature range (including the post-radiation variant). Both in the review and in the original publications cited, attention was focused on some non-traditional methods of initiation of the MCM polymerization (low-temperature, frontal, spontaneous, etc.). In each particular case, a researcher has the opportunity to choose the optimum variant. If the unit variability cannot be ruled out, it can be taken into account in almost all cases (sometimes, quantitatively).

Depending on the fraction of anomalous units, metal-containing polymers can be divided into several types. According to the IUPAC nomenclature,[88] when the content of these units is low, the polymers can be classified as regular macromolecules, which mostly consist of identical repeating units linked to one another in the same way. When the contribution of unit variability is relatively large, they are called irregular macromolecules.

A lot of problems need to be solved in order to understand the reasons and the mechanism of formation of anomalous units from MCM, to elucidate their role, and to use this phenomenon for practical purposes to modify the polymer properties directly during polymerization. This refers, first of all, to copolymerization of MCM with both traditional monomers and other MCM. At present, little is known about the constants of relative reactivity of MCM (except, perhaps, for those for organotin and ferrocene monomers). It was found that[89] for the monomers CH_2=CHX, the parameter e (the measure of the polarity of the substituent X at the double bond in the Alfrey Price Q—e scheme) is correlated with the Hammett (σ_x) constant of this substituent. The e values of vinylic monomers range from −1 to +1.5, while those for MCM are normally large negative values; for metal acrylates, they vary from −1.96 to −2.65. This means that the metal-containing group is an electron-donating substituent (like p-NMe$_2$ or p-OMe in the aromatic ring), i.e., the electron density is markedly shifted toward the C=C bond.

Copolymerization of MCM with each other is less studied. Thermal transformations and solid-state copolymerization (with co-precipitated Fe^{3+} and Co^{2+} acrylates as an example) lead to the conclusion[90] that the Fe- and Co-containing fragments influence each other during these processes. This is manifested as initiation of polymerization routes as a result of partial thermal destruction of the Fe-containing monomer and as the decreased thermal stability of Co-containing fragments in the resulting polymer.

The situation is even more complicated when copolymerization involves three or more monomers and when production of uniform materials with a strictly defined ratio of the components is required in a multi-component system. Examples of thermal polymerization are those occurring in styrene—acrylonitrile—zinc acrylate[91] (chromium acrylate or copper acrylate[92]) systems.

A very rare case is copolymerization of several MCM with one another; the resulting polymers can contain mixed units of various types. This is especially true for the development of HTSC ceramics based on a preliminarily synthesized polymer. One of the methods is copolymerization of MCM, for example, acrylates (and, perhaps, maleinates[93]) or acrylamide complexes of Y^{3+}, Ba^{2+}, or Cu^{2+}, and synthesis of superconducting bismuth cuprates (such as $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4-\delta}$ ($n = 1-3$)) by copolymerization of the corresponding metal-containing monomers. Thermolysis of these polymeric precursors affords a finely dispersed mixture of metal oxides (for example, Y123 ceramics); this enables relatively easy production[94] of single-phase HTSC ceramics with a superconduction transition point of -163 °C. When there are some disturbances in the alternation of the corresponding units in these thermocopolymers (for example, they contain long blocks of units incorporating the same metal), it becomes difficult to prepare a single-phase material. Note that the products of solid-state polymerization of lithium acrylate, methacrylate, crotonate, fumarate, maleinate, and sorbate possess[66,95] high-temperature (250 °C) ionic conductivity ($10^{-4}-10^{-7}$ Ohm cm^{-1}, activation energy ~2 eV).

Development of a theoretical substantiation for the orienting influence of coordination bonds formed by a transition metal with functional groups of a monomer or with a polymer radical would ensure the possibility of efficiently regulating the stereochemistry of radical polymerization.

Since there the corresponding database is absent, we did not dwell in this review on the manifestation of different types of unit variability in one metal-containing polymer (for example, that caused by the different valence state of the transition metal ions in some units, and the diversity of their chemical binding in some other units, *etc.*) or on their multiple character on going to copolymers.

Finally, it should be especially noted that MCM are metal complexes with specific ligands and polymerization is only one of their functions. Generally, these compounds can participate in all the reactions typical of compounds with double bonds. Thus it was found under model conditions[96] that upon hydrogenation, metal acrylates are converted into the corresponding propionates. However, it is unclear whether the double bonds are hydrogenated simultaneously or involved in the catalyic process successively. This also refers to the residual double bonds in mixed-unit metallopolymers. Metallopolymers with this type of unit variability can also undergo other polymeranalogous transformations (reactions that do not affect the backbone), *viz.*, alkyl hydroperoxide-induced epoxidation, carbonylation, hydrosilylation, hydroformylation, *etc.* Realization of these reactions would give fairly valuable products. Since no data on this topic can be found in the literature, we plan to consider these problems in subsequent publications of this series.

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