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Metal-containing Monomers: Advances in Polymerisation and Copolymerisation

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The main advances in and problems of polymerisation, copolymerisation, as well as graft polymerisation of metal-containing monomers (MCM) are analysed. These are classified in terms of the type of bond between the metal and the organic component of the molecule into three principal groups, namely MCM with σ-, $n\nu$-, and π-bonded metal, are analysed. Attention is concentrated on the influence of the nature of the metal (both transition and non-transition) on the polymerisation process and on the properties of the products. A systematic account is given of the principal data for the polycondensation of metal-containing compounds. The applications of the metal polymer synthesised are considered.
The bibliography includes 215 references.

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I. INTRODUCTION

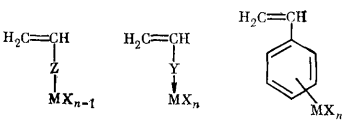
Metal-containing polymers have found extensive applications in recent years in the preparation of various coatings with special properties, catalysts, as thermoplastic constructional materials, etc. At the same time clearly inadequate attention has been devoted to problems of the synthesis of metal-containing monomers (MCM) and the characteristic features of their polymerisation, copolymerisation, and graft polymerisation. Only ferrocene and certain other metallocene compounds are perhaps exceptions in this respect[1]. Although the first publications of the radical polymerisation of vinylferrocene date back to as early as 1955,[2] subsequently attention was concentrated on coordination polymers[3]; studies on the polymerisation of MCM developed more slowly, primarily owing to the difficulty of the synthesis of such MCM and also the specific features of their polymerisation and copolymerisation. The presence of metal atoms in molecules of this class leads to the formation of coordinate bonds in the polymerisation process and a redistribution of electron density at the growing centre, which has a significant influence on the polymerisation mechanism.

In recent years there has been an appreciable growth of interest in the polymerisation of MCM. Three international specialist symposia, devoted to the polymerisation of MCM and the study of the properties of organometallic polymers, have already been held in the USA.[4,5] Much attention has been devoted to these problems in the USSR in the investigations of Nesmeyanov and co-workers[6], Korshak and co-workers[7,8], Kabanov and co-workers[9], and certain others[10,38].

In the present review an attempt has been made to summarise the available data on the characteristic features of the polymerisation of MCM, to analyse the present state of the problem of the influence of the nature of the metal on the character of the polymerisation of such monomers, to discuss the advantages and disadvantages of the methods employed, and also to outline the most rational ways of developing this field. Attention has been concentrated on the MCM based on transition metals. As regards MCM based on non-transition metals, mention will be made of studies in which hypotheses have been developed or quantitative data are presented concerning the influence of the nature of the metal on the polymerisation or copolymerisation mechanism.

II. CLASSIFICATION AND PRINCIPAL SYNTHESES OF METAL-CONTAINING MONOMERS

In the literature there is at yet no clear-cut system of classification and nomenclature for MCM. In principle, one can employ for them the classification for traditional monomers based on the type of chain formed, the nature of multiple bonds, etc. as well as the classification based on the consideration of MCM as salts or other derivatives of the corresponding metal. However, such approaches do not reflect the specific features of the MCM and the corresponding terminology is cumbersome. From our point of view, the classification of MCM based on the type of bond between the metal and the organic component of the molecule is most convenient and yields the maximum amount of information about their structure. In terms of this principle, MCM can be divided into three main types: MCM with a covalently bonded (σ-bonded), coordinated ($n\nu$-bonded), and π-bonded metal atom, which can be illustrated by the most characteristic examples:



Here M is the metal atom, X the ligand, and Z and Y are functional groups. The first two types of MCM are characteristic of both non-transition and transition metals and the third is characteristic only of MCM incorporating Group VIA, VIIA, and VIII metals. We may note that only those π-bonded MCM in which there is a multiple bond not coordinated to the metal, in contrast to the usual fairly numerous π-complexes[11], possess the capacity for polymerisation. Metallocenes with a covalent bond between the transition metal atom and the unsaturated group have been classified as σ-bonded MCM. The type of bond has a marked influence

both on the stability of MCM and on their behaviour in polymerisation and copolymerisation processes.

The character of the polymerisation not only of organometallic monomers—compounds containing a metal–carbon bond (which is characteristic mainly of MCM of the third type)—but also a wider group of MCM incorporating metal–oxygen, metal–nitrogen, metal–phosphorus, etc. bonds is analysed in this review. The characteristic features of the polymerisation and copolymerisation of monomers incorporating both non-transition and transition metals are examined in succession for the MCM of the first and second types; as a rule, the order in which they are considered corresponds to the position of the given elements in the Periodic System.

The commonest methods of synthesis of MCM with a σ-bond involve the interaction of metal hydroxides or oxides with unsaturated acids, treatment of transition metal compounds with unsaturated alcohols, acids, and amines (see, for example, Feld and Cowe[12]), transesterification of metalloesters with an unsaturated alcohol or acid, reactions of MX_n with enolisable aldehydes or ketones, etc. Organometallic monomers are synthesised by methods involving the use of Grignard reagents containing multiple bonds in the hydrocarbon residue. We may note that methods of synthesis of MCM with a σ-bond have now been developed for almost all metals. Their stability depends both on the nature of the metal and on the structure of the MCM, procedures for the stabilisation of such compounds being known[174]. On the other hand, in contrast to MCM incorporating groups of the vinyl, allyl, and acetylene types, there are almost no literature data on MCM incorporating a metal σ-bonded to diene or allene groups.

The synthesis of MCM with a coordinate bond is based on the formation of donor–acceptor complexes of the compounds MX_n with monomers containing, apart from a multiple bond, also groups or atoms with an unshared electron pair. In terms of the nature of the coordinate bond, such MCM can be divided into compounds with nitrogen-containing ligands (vinylpyridines, vinylcarbazole, vinylimidazole, vinylbenzimidazole, vinylbenzotriazole, allyl- and diallyl-amines, acrylonitrile, etc.), oxygen-containing ligands (methyl methacrylate, methyl acrylate, vinyl acetate, methyl vinyl ketone, vinylpyrrolidone, allyl alcohol, etc.), phosphorus-containing ligands (dialkyl- and diphenyl-styrylphosphines, vinylphosphonic acids, esters, etc.), and sulphur-containing ligands (diallyl sulphide, etc.). The range of the coordination interaction energies is fairly wide and is determined by the nature of the reacting components[13]. The study of the characteristics of the formation of such MCM showed that their composition and structure do not as a rule differ from those of coordination compounds with the usual ligands. Although the donor–acceptor interaction leads to a redistribution of the electron densities of all the bonds of the monomer, a multiple bond does not usually undergo significant changes.

As regards the synthesis of MCM incorporating a π-bonded transition metal, two main methods have come to be widely used: (a) the introduction (via a series of consecutive reactions) of a vinyl, allyl, or acrylate group into the cyclopentadienyl or benzene ring; (b) the addition of MX_n to traditional monomers (for example, to styrene and its derivatives). In terms of the number of groups capable of polymerisation, the π-bonded MCM obtained can be both monosubstituted and disubstituted[4,14].

Among the non-traditional methods for the synthesis of MCM developed successfully at the present time, we may mention interesting syntheses of π-bonded MCM using the "bare" atom procedure[15]—the MCM are formed on interaction of vapours consisting of transition metal atoms at low temperatures with vinyl monomers. π-Bonded organometallic monomers, incorporating low-valence transition metal atoms, have been obtained[16] by the reductive substitution of MX_n in the presence of non-metallated monomers (for example, dienes). Metal-containing monomers of the *nv*- and π-types can be obtained, in principle, by a method based on the oxidative dissolution of the metals in the presence of the corresponding monomers[17]. The procedures indicated have extensive potential synthetic possibilities and their realisation will apparently make it possible to obtain a whole series of hitherto unknown MCM.

One may expect the appearance of new types of MCM, for example, those containing cyclic groups of the type of epoxy-groups, which are known at the present time for ferrocene derivatives[18] and organotin compounds[19]. The possibility of synthesising MCM with a polyfunctional type of bonding of the metal as well as polymetallic MCM appears to be promising.

Much less attention has been devoted to problems of the structure of MCM and problems of the stabilisation and destabilisation of their multiple bonds than to the synthetic aspects; however, the reactivities of multiple bonds and the methods for their activation are of outstanding interest for the polymerisation and copolymerisation of MCM.

III. HOMOPOLYMERISATION OF METAL-CONTAINING MONOMERS

MCM are polymerised (except in special cases) under the influence of a wide variety of initiators and are as a rule characterised by the same elementary steps as the polymerisation of traditional monomers. The differences are quantitative rather than qualitative. On the other hand, in an MCM–initiator system (the type of initiation can be various—radical or ionic or can involve the use of metal-complex Ziegler–Natta catalysts), the monomer can undergo reactions which are undesirable from the standpoint of the polymerisation process and can also influence significantly the active polymerisation centre.

1. Polymerisation of MCM with a σ-Bond

There are at present no publications devoted to the homopolymerisation and copolymerisation of MCM in which the vinyl group is linked directly to the metal, although such studies would be of great interest: they would be useful for the elucidation of problems concerning the influence of the metal atom on the vinyl centre, the stabilisation or destabilisation of the metal–carbon bond of the MCM in the polymer chain, etc. It may be that the difficulties are due to the elimination of a metal hydride in the polymerisation process[1]:

$$X_{n-1}M{-}CH{=}CH_2 \xrightarrow{\text{initiation}} \rightarrow\!\!- (-CH_2{-}\underset{\displaystyle MX_{n-1}}{\underset{|}{CH}}-)_t-\!\!\rightarrow X_{n-1}MH + -(-CH{=}CH-)_t-\!\!\rightarrow .$$

On the other hand, as will be shown below, MCM with polymerisable groups of other types (allyl, acrylate, etc.) proved to be capable of polymerisation and the metal atom was retained in the resulting polymer.

(a) Homopolymerisation of MCM Incorporating a Non-transition Metal

The comparatively early studies of the homopolymerisation and copolymerisation of MCM containing alkali and alkaline earth metals, in aqueous solutions and certain other polar media, have been described in detail in a monograph[9]. The

influence of the nature of the metal atoms (even isotypical metals) on the tendency of MCM towards homopolymerisation[20-22] can be illustrated in relation to the alkali metal salts of *N*-vinylsuccinamic acid: the lithium, sodium, and potassium salts do not polymerise in aqueous and methanol solutions in the absence of initiators up to 333–353 K, the formation of a polymer being observed only in the presence of an initiator (H_2O_2). On the other hand, the rubidium and caesium salts polymerise spontaneously already in the stage involving the synthesis of the MCM, which leads to the formation of mixtures of monomeric and polymeric salts. It is striking that the tendency of these MCM towards spontaneous polymerisation increases on passing from aqueous to methanol solutions. Overall, the salts of *N*-vinylsuccinamic acid can be arranged in the following sequence in terms of the rate of formation of the polymer: Cs > Rb > Na > K > Li.

The rate of polymerisation of potassium styrene-*p*-sulphonate, the molecular weight (MW) of the polymer, and the ratios $k_p/k_t^{1/2}$ increase with increase of the ionic strength of the solution; at the same time the activation energy for polymerisation falls (from 47.9 to 30.7 kJ mol^{-1}).[23] In the concentration range 0.12–0.3 M the initial rate of the process, the molecular weight of the polymer, and the ratios $k_p/k_t^{1/2}$ in the polymerisation of the calcium, strontium, and barium salts of styrene-*p*-sulphonic acid increase in the sequence of cations $Ca^{2+} < Sr^{2+} < Ba^{2+}$.[24] With increase in the ionic strength of the solution, the rate of polymerisation rises, but the influence of the nature of the cation diminishes, which enabled the authors[24] to explain this influence from the standpoint of the electrostatic interaction between the ionised monomers and the growing polymer radicals.

The monomers do not ionise in their solid-phase polymerisation, which is usually initiated by radiation or photochemistry. Thus, on γ-irradiation (at 196 K) of potassium and rubidium acrylates, triplet lines, typical for the majority of the irradiated vinyl monomers (at least when the latter dimerise) were observed in the EPR spectra[25]. The molecular mobility of the acrylate ion in the salts is correlated with the rate of their radiation-induced postpolymerisation and increases in the sequence Na < Li ≤ K < Rb.[26] The study of the radiation-initiated polymerisation of lithium, sodium, and potassium acrylates showed[27] that potassium acrylate is polymerised fastest: even at 273 K, it polymerises faster than the lithium salt at 374 K or the sodium salt at 393 K. The rate of polymerisation of potassium acrylate decreased rapidly during the process with increase of the degree of conversion (E_a = 70.1 kJ mol^{-1}); the degree of polymerisation was almost independent of the yield of the monomer and for potassium acrylate was higher by an order of magnitude than for the sodium and lithium salts.

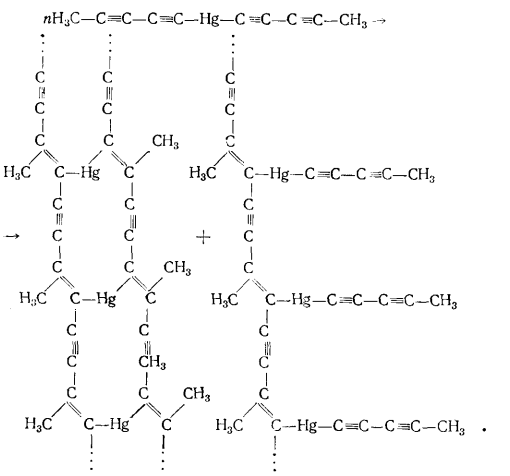
The photopolymerisation of potassium acrylate takes place effectively[28] (250–300 nm): the yield of the polymer reaches 40% at 346 K and the molecular weight diminishes from 4.7 × 10^5 to 2.2 × 10^5 with increase of the degree of conversion from 15.8 to 43.6%.

It has been noted[29] that the solid-phase radiation polymerisation of anhydrous barium methacrylate is not observed up to its decomposition temperature; the formation of only oligomeric products has been observed[30]. However, with increase of pressure, the rate of polymerisation increased (in contrast to traditional monomers such as acrylamide or methacrylamide). This has been attributed[31] to preferential polymerisation in ideal crystals. Since the rate of polymerisation is much higher when the salt hydrates are employed, it was concluded[32] that the abundance of dislocations should facilitate polymerisation. Another explanation has also been given[33]: the radicals produced by the radiolysis of the salt hydrates (water of crystallisation) contribute significantly to the formation of the free radicals initiating the solid-phase polymerisation. The yield of the polymer depends to a large extent on the degree of hydration of the salt: the maximum rate of the process is observed when calcium acrylate hemihydrate is used[32,34]. The initial rate and the limiting yield of the polymer increase in the sequence dihydrate < anhydrous salts < hemihydrate; the activation energies are 84, 38, and 4 kJ mol^{-1} respectively. The question of the influence of oxygen on this process has not so far been elucidated. According to some data[35], the rate of polymerisation is independent of the presence of oxygen (barium methacrylate dihydrate); according to other data[34], complete inhibition of the process is observed (the polymerisation of calcium acrylate dihydrate and hemihydrate as well as the anhydrous salt was investigated.) There is a possibility of postpolymerisation for calcium and barium acrylates and methacrylates[30].

In the photoinitiated (250–300 nm) polymerisation of calcium acrylate[36] the process proceeds at a constant rate up to high degrees of conversion.

The formation of coordination polymers is more characteristic of MCM containing a metal of the zinc subgroup. Studies of the polymerisation of mercury-containing monomers with a σ-bonded metal have been surveyed[38]. We shall consider only the polymerisation of one of the few MCM of the acetylenic type—bis-(1,3-pentadiynyl)mercury[37] (Scheme 1): on heating to 373–473 K, 100% conversion was rapidly attained; on ultraviolet irradiation at room temperature, the rate of polymerisation proved to be appreciably lower, because the monomer is surrounded by the polymer, which does not transmit ultraviolet light. The polymers obtained contained diacetylenic groups and exhibited different degrees of branching and cyclisation.

Scheme 1



Poly-yne polymers containing other metals (Ni, Pd, Pt) in the main chain are considered below (Section VII).

The formation of coordination polymers as well as a wide variety of condensation reactions leading to the appearance of high-molecular-weight products are more characteristic of Group III elements.

The homopolymerisation of MCM incorporating germanium, tin, and lead results as a rule in the formation of viscous oily or rubber-like products. Early studies on the polymerisation of MCM of this class have been surveyed in monographs[7,10]. Interesting results have been obtained in the investigation of the homopolymerisation of tributylstannyl methacrylate (TBSMA) in bulk (at 333 K) initiated by azobisisobutyronitrile (AIBN).[39,41]

The parameters $k_p/k_t^{1/2}$ and k_p have been estimated and compared with the corresponding parameters for methyl methacrylate (MMA): the ratios $k_p/k_t^{1/2}$ are 0.19–0.24 and 0.321, while the constants k_p (litre mol^{-1} s^{-1}) are 6.3×10^3–9.4×10^3 and 1×10^3 respectively. The fact that the rate constant for the propagation of the polymer chain is higher under comparable conditions for TBSMA than for MMA is noteworthy; this can be explained by the linear termination of the kinetic chains. Trimethylvinyltin and tributylvinyltin proved incapable of homopolymerisation[112].

The homopolymerisation of chlorodibutylstannyl acrylate is accompanied by the formation of a cross-linked polymer[42], which is probably caused by the disproportionation of the monomer, leading to dibutylstannyl dichloride and dibutylstannyl diacrylate (with polymerisation of the latter). A cross-linked polymer was also formed in the polymerisation of dimethylstannyl dimethacrylate. The polymer obtained from trimethylstannyl methacrylate was characterised by a comparatively high content of syndiotactic triads and was soluble in dimethylformamide (DMF) and methanol[43]. Triethylstannylmaleimide also polymerises via a radical mechanism[44] and, when initiating amounts of benzoyl peroxide are employed, there is no loss of the $Sn(C_2H_5)_3$ fragments from the polymer chain. At the same time a competitive interaction of the initiator with the initial monomer has been observed on increase of the concentration of benzoyl peroxide, accompanied by the cleavage of the Sn–N bond and the formation of triethyltin benzoate.

(b) Homopolymerisation of MCM Incorporating a σ-Bonded Transition Metal

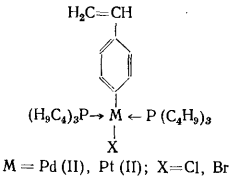
The polymerisation of polymers incorporating polyvalent transition metals is characterised by a whole series of features from the standpoint of both kinetics and the properties of the polymers formed. An even greater variety in polymerisation behaviour is characteristic of them, depending on the type and valence state of the transition metal and on the nature of the ligand groups. Thus, on being kept for several days, di-isopropoxydivinyloxytitanium polymerised spontaneously and became insoluble in heptane, while tetrastyryloxytitanium polymerises only on heating to 423 K and dihexadienyloxydi-isopropoxytitanium polymerises only on heating to 498 K.[45]

On heating in benzene in the presence of 0.1% of benzoyl peroxide, allyloxytitanocene chloride is converted into a trimer with a molecular weight of 770.[46] Polymers with a low degree of polymerisation have been isolated[47,48] on heating solutions of titanocene derivatives of methacrylic acid in DMF up to 353 K (in the presence of benzoyl peroxide as the initiator). Dimethacryloyloxy-titanocene then produced a cross-linked polymer.

It has been noted[49] that tributoxytitanium methacrylate does not polymerise in the presence of 2% of benzoyl peroxide on heating to 353–373 K. This is associated with the preferential interaction between benzoyl peroxide and alkyl orthotitanate with formation of titanium acylates[49,50]. On the other hand, in the presence of 2% AIBN, tributoxytitanium methacrylate polymerises (on heating to 423 K for 5 h), while dibutoxytitanium maleate polymerises spontaneously[51] with formation of a product having a molecular weight of 2230 (corresponding to seven monomeric units) and soluble in many organic solvents.

Among MCM with a σ-bond, containing other transition metals, copper and nickel acrylates[52] as well as zirconyl (ZrO^{2+}) methacrylate[53] proved to be capable of polymerisation. The solid-phase polymerisation of iron methacrylate takes place[54] under the influence of γ-radiation (dose rate 2.7 kJ $kg\ h^{-1}$, $T = 398$ K). Under the conditions indicated, a virtually quantitative yield of the polymer insoluble in methanol is attained after 12 h. Methacrylatopentamminecobalt(III) perchlorate polymerises with a high yield (pH 3, initiator—mixture of $K_2S_2O_8$ and $Na_2S_2O_3$).[55]

There is no information about the polymerisation of the few known σ-bonded MCM of the vanadium, chromium, and manganese subgroup metals. However, the radical polymerisation of *trans*-(4-vinylphenyl)bis(tributylphosphine)palladium chloride and bromide and the corresponding platinum compounds has been studied in comparatively high detail[56]:



M = Pd (II), Pt (II); X=Cl, Br

The polymerisation takes place under mild conditions (AIBN, 328–333 K) in benzene or toluene. White soluble polymers with molecular weights in the range 3600–10900 have been obtained, their yield depending on the polymerisation conditions. The attempts to polymerise the monomers with X = CN and C_6H_5 proved unsuccessful owing to their decomposition at the polymerisation temperature. On the other hand, their cationic polymerisation at a low temperature [in the presence of $B(C_4H_9)_3.O_2$ as the initiator] leads to the formation of polymers.

There are at present no data for the polymerisation of allene, diene, and acetylene σ-derivatives of transition metals.

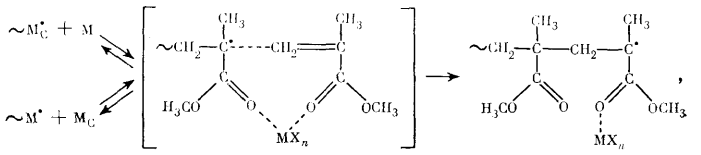
2. Polymerisation of MCM Bound in Complexes

A new branch of the field of polymerisation, based on controlling the reactions via the formation of complexes of the initial monomer with metal salts, has arisen[57,58]. In principle, the interaction between the molecules of the monomer and the complex-forming agent can influence radically all the stages of the polymerisation process. The monomer then becomes "chemically activated" fairly frequently. The chemical activation can be associated both the intramolecular and intermolecular effects. As a consequence of this, there is as a rule an appreciable increase of the rate of polymerisation. In the problem considered, it is possible to distinguish three main components, each of which has its own specific features:
(a) polymerisation of vinyl monomers bound in complexes;
(b) polymerisation of allyl monomers bound in complexes;
(c) polymerisation of heterocycles bound in complexes.

(a) Characteristic Features of the Polymerisation of Vinyl Monomers Bound in Complexes

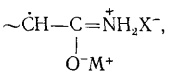
The influence of MX_n on polymerisation depends on the nature of the metal and the monomer, the method used to initiate polymerisation, and the ratio $[MX_n]/[\text{monomer}]$ in the system. $ZnCl_2$ is most frequently used as the complex-forming agent in the polymerisation of such MCM. Thus, is the polymerisation of MMA in the presence of $ZnCl_2$ or $AlCl_3$ (with initiation by AIBN at 323 K or by the photochemical decomposition of azo-compounds) in the presence of low contents of MX_n, the rate of the process increases linearly with the increase of the ratio $[MX_n]/[\text{MMA}]$ up to 0.2, after which there is some non-linear increase of the rate of polymerisation[59]. With increase of the ratio $[MX_n]/[\text{MMA}]$ under these conditions, k_p also increases, while k_t hardly changes; for $[MX_n]/[\text{MMA}] > 0.25$, k_p begins to diminish, while k_t falls sharply (by two orders of magnitude). An appreciable increase of the rate

of polymerisation of other vinyl monomers (4-vinylpyridine, 2-vinylpyridine, methylvinylpyridine, and acrylonitrile) has also been noted in the presence of $ZnCl_2$.[60] The complex-forming agent is regarded[59] as a "complementary species" involved in the formation of the transition complex (a coordination-radical mechanism of the propagation reaction obtains):



where M_c and M_c^* are the monomer and the growing radical bound in the complex respectively. One cannot exclude from consideration the possibility of the formation of organised aggregates of monomers bound in complexes (labile seeds) containing units with a suitable steric arrangement for polymerisation (an intermolecular effect)[61].

The importance of steric organisation is also confirmed by data for the solid-phase polymerisation of acrylamide and its *N*-alkyl derivatives bound in complexes with zinc halides. The polymerisation of the complexes is accompanied by an appreciable (by a factor of 1.5–2) increase of E_a.[104] This is attributed to the fact that the distance between the monomer molecules in the crystals of the pure monomer is much smaller than in the crystal of the complex. It is of interest that the polymeric complexes obtained have a linear structure, in contrast to the highly cross-linked polymers formed in the polymerisation of acrylamide derivatives not bound in complexes. The significant (by a factor of 3–5) increase of the rate of homopolymerisation of these monomers in the presence of lithium, calcium, and zinc salts is attributed to changes in the ratio $k_p/k_t^{1/2}$.[197] The increased activity of the radical incorporated in the complex has been explained[198] by the formation of the structure



characterised by an increase localisation of the unpaired electron at a carbon atom.

The homopolymerisation of vinyl monomers [particularly various vinylpyridines (VP)] bound in complexes with transition metal salts has been investigated in fair detail. Thus the complexes of cobalt and nickel chlorides were found to undergo solid-phase polymerisation[62]: $Co(4\text{-}VP)_2Cl_2$ polymerised on heating to 380–405 K and in the presence of AIBN the reaction was appreciably accelerated; $Co(4\text{-}VP)_4Cl_2$ and $Co(2\text{-}VP)_2Cl_2$ polymerise on photochemical initiation. The polymerisation of adducts of $CoCl_2$ with various vinylpyridines (DMF, AIBN, 323 K) has also been studied[263]. Their polymerisation behaviour proved to be qualitatively similar to that of the $ZnCl_2$ complexes[64]. On the other hand, the nickel complexes show less tendency towards polymerisation: $Ni(4\text{-}VP)_4Cl_2$ decomposes to $Ni(4\text{-}VP)_2Cl_2$, which polymerises at 353–403 K on the surface of the crystals, forming a small amount of the polymer[62]. On heating to 353 K, the complexes $Cu(2\text{-}VP)_2Cl_2$ and $Cu(2\text{-}VP)Cl_2$ decompose with dissolution in their own ligand without any polymerisation, while $Cu(4\text{-}VP)_2.Cl_2$ undergoes thermal polymerisation.

The interaction of tungsten, cobalt, and manganese carbonyls with 4-VP leads to the thermal polymerisation of the latter[65]. The possibility of the polymerisation of 4-VP bound in a complex with ruthenium(II) [of the complexes *cis*-$Ru(bipy)_2.(4\text{-}VP)X^{n+}$, where $n = 1$ and X = Cl or $n = 2$ and X = CO or 4-VP] has been demonstrated[66]; the properties of the resulting polymers were not described in the above communication.

When vinylpyridines are polymerised in the presence of MX_n, the polymerisation of 4-VP and methylvinylpyridine is accelerated, while that of 2-VP is sharply retarded[63,64]. The accelerating effect in the first two instances has been attributed to the increase of k_p owing to the heterogenisation of the polymeric system, while steric effects, resulting in the shielding of the vinyl group, play a significant role for 2-VP.

For other MCM, we may note the radical polymerisation of bis(1-vinylimidazole)-manganese dichloride in aqueous methanol[67]. It is striking that $MnCl_2$ is a more effective complex-forming agent than HCl and CH_3I: when HCl in the complex was replaced by $MnCl_2$, the rate of polymerisation increased by a factor of 4.5†. It has been suggested[69] that, as a consequence of the intense dynamic conjugation of the π-electron systems of the vinyl group and the heterocycle, the coordination of vinylimidazole with $MnCl_2$ results in an increase of the polarity of the double bond and of the polarity factor *e*. An increase of the ratio $k_p/k_t^{1/2}$ has also been noted in the polymerisation of coordinated vinylimidazole, which may be due to the decrease of k_t owing to the increase of the molecular mobility of the polymer chains bound in a complex.

The synthesis of the polymeric complexes can be greatly facilitated as a result of the free-radical polymerisation of 1-vinylazoles in the presence of the corresponding metal chloride added to the reaction mixture[68,70]. In this case the complex formation and polymerisation reactions take place simultaneously. The composition of the polymer unit usually corresponded under these conditions to the ratio of the initial components. Thus in an alcoholic solution it was possible to obtain polymers from the following systems: vinylimidazole–$MnCl_2$, vinylimidazole–$NiCl_2$, vinylbenzimidazole–$NiCl_2$; vinylbenzotriazole–$NiCl_2$. Comparison of the effects of the nature of the ligands showed that polymerisation takes place more efficiently when vinylimidazole is used as a monomer.

In an aqueous medium in the presence of copper, iron, nickel, cobalt, and manganese salts the polymerisation of MMA is accelerated[72]. It has been noted that the cation is of decisive importance in this effect, its activity varying in the sequence $Cu^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+} > Co^{2+}$, while the influence of the anion proved to be weaker. The results have been explained by the formation of the corresponding complexes. The homopolymerisation of complexes of palladium and nickel halides with vinylpyridine and phosphorus-containing monomers has been described[73].

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†On the other hand, it had been shown in an earlier study[68] that the complexes $M(vinylimidazole)_4Cl_2$ (M = Mn, Co, or Ni) show a smaller activity in free-radical polymerisation than the non-coordinated vinylimidazole; for example, under identical conditions (4% AIBN, 343 K, alcohol), the degree of conversion of vinylimidazole reached 75%, while those of its complexes with the manganese and nickel chlorides reached only 60 and 35% respectively. Furthermore, analogous complexes with iron and copper chlorides could not be converted into polymeric products at all; evidently in this case the radicals formed are inhibited. The yields of the polymeric complexes obtained from $Ni(vinylbenzimidazole)_2Cl_2$ and $Ni(vinylbenzotriazole)_2Cl_2$ were low.

(b) Polymerisation of Allyl Monomers Bound in a Complex

The approach based on the polymerisation of compounds bound in complexes has been used particularly successfully in the case of allyl monomers. The polymerisation of allyl monomers is known[74] to involve considerable difficulties associated with the effective degradive chain-transfer, which results in the formation of the relatively inactive allyl radicals:

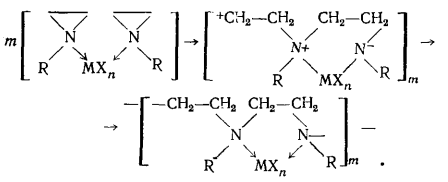
$$R^{\cdot} + H_2C{=}CH{-}CH_2X \rightarrow RH + H_2C{=}CH{-}C^{\cdot}HX \ .$$

On the other hand, the radical-initiated polymerisation of allyl monomers bound in complexes with metal salts proceeds at higher rates and with formation of polymers having high molecular weights. It has been suggested[75] that complex formation promotes the establishment of the steric conditions necessary for the reaction of the monomer and the radical, which are both ligands within the same coordination complex (intramolecular effect). Under these conditions, there is a possibility, firstly, of a decreased probability of the abstraction of a hydrogen atom by the growing radical and, secondly, the coordinated chain-transferring allyl radical formed in this instance may be capable of cleaving the double bond of the monomer (for example, as a consequence of the decrease of the rate of destruction of such species).

Various non-transition metal salts are used as complex-forming agents for allyl monomers[75-77]: LiCl, $LiNO_3$, Na_2SO_4, $MgCl_2$, $ZnCl_2$, and $ZnBr_2$. Among the few studies in which transition metal salts have been used as complex forming agents, we may mention one[78] on the radical polymerisation of allyl alcohol in the presence of chromium salts[78]. The rate of the process was found to decrease by a factor of 14.8 [$CrCl_3$, 348 K, $(NH_4)_2S_2O_8$]. The observed decrease of the reaction orders with respect to the initiator and the monomer (from 1.8 to 0.8 and from 0.5 to 0.4 respectively) has been attributed[78] to the involvement of the complex-forming agent in the elementary stages of the process and to the consequent increase of the probability of the transition from the degradative chain transfer to effective chain transfer.

(c) Polymerisation of Heterocycles Bound in a Complex

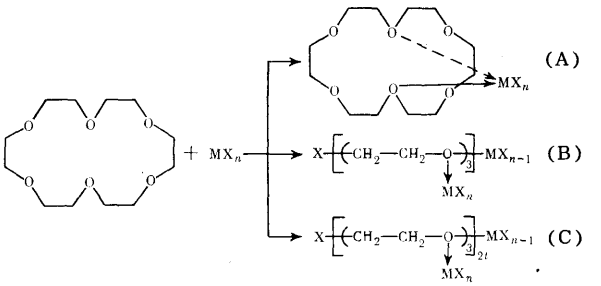
The redistribution of electron densities at the atoms and bonds in heterocycles as a consequence of complex formation, makes possible the occurrence of specific chemical reactions of the heterocycles in the coordination sphere of MX_n, which results in the formation of polymeric complex macromolecules. This can be demonstrated in relation to the $ZnCl_2$, $CdCl_2$, $PdCl_2$, $CoCl_2$, etc. complexes with ethyleneimine and and its derivatives[79-81]. Complex formation, the strain in the ethyleneimine ring increases by approximately 42 kJ mol^{-1}, which leads to a sharp decrease of the strength of the endocyclic bonds. Such complexes are capable of thermal polymerisation (both in bulk and in aprotic solvents) with opening of the heterocycle via a mechanism involving the heterolytic cleavage of the C–N bonds with formation of dipolar coordination ions:



The coordinate bonds are retained in the polymerisation process, which leads to the formation of polymeric chelate complexes. The characteristic features of such reactions are the presence in the initial complexes of at least two# heterocycles in the coordination sphere of the metal on the one hand, and the existence of "critical" temperatures for the dissociation of bonds in the heterocycles on the other.

The interaction of MX_n with macrocyclic crown-ethers takes place in an even more complex manner[82,83], involving the formation of three types of products (Scheme 2): (A)—the complexes of the *nv* type produced by the exocyclic coordination of an MX_n molecule with two oxygen atoms; (B)—products of the opening of the crown-ether ring; (C)—polymers which are probably formed via a cationic polymerisation mechanism (the degree of polymerisation reaches 3–4).

Scheme 2



The amounts of fractions (A), (B), and (C) in the products of the reaction of dibenzo-18-crown-6 with $TiCl_4$, VCl_4, and $MoCl_5$ are respectively (wt.%) 87.5, 4.5, and 8.0 for (A), 60.0, 20.0, and 20.0 for (B), and 64.0, 24.0, and 12.0 for (C). It may be that similar reactions take place also for other types of heterocycles bound in complexes.

Thus the polymerisation of MCM bound in complexes is one of the most thoroughly investigated branches of the chemistry of MCM and not only theoretical but also practical possibilities of this field have already been outlined: the regulation of the molecular weights of the polymers obtained (which is particularly important for monomers of the allyl type), the acceleration of the process, the increased degree of conversion of the monomers, and the opening and polymerisation of heterocycles. There is every reason to believe that this field will develop vigorously in the future.

3. Homopolymerisation of π-Bonded MCM

In this class of MCM, the homopolymerisation (using different initiation methods) of vinylferrocene has been most fully investigated[1,4,5]. The principal conclusions reached in the study of the polymerisation of this monomer reduce to the following. With radical initiation in the presence of AIBN there is intramolecular electron transfer from the iron atom to the radical centre with formation of an Fe(III)-containing terminal group, which is accompanied by intermolecular chain termination. The order of the polymerisation reaction with respect to the initiator is therefore unity and the molecular

#The reactions of complexes containing one heterocycle in the coordination sphere terminate with the formation of cyclic dimers (piperazine derivatives); complexes incorporating a heterocycle and a primary or a secondary amine are incapable of polymerisation.

weight of the polymer does not increase with decrease of the initiator concentration. This has been explained[4] by the high chain transfer constant ($k_{tr}/k_p = 8 \times 10^{-3}$ compared with 6×10^{-5} for the polymerisation of styrene at 333 K); the high value of k_{tr} leads to the branching of the polymer formed.

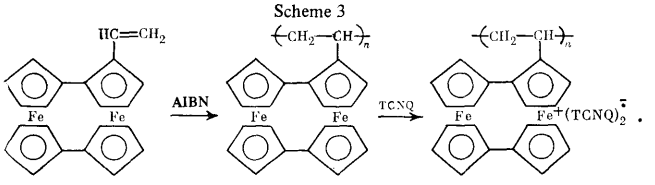
Vinylferrocene provides an example of the influence of the transition metal in the MCM molecule on the character of its polymerisation. Thus the introduction of separating bridges between the ferrocenyl and active vinyl groups (as, for example, in ferroceynyl methacrylate) leads to the usual chain termination mechanism for which the dependence of the rate on the initiator concentration corresponds to a reaction order of 0.5.

The radical polymerisation of vinylcyclopentadienyltricarbonylmanganese[84] (benzene, AIBN) results in the formation of a polymer with MW > 2500. Its thermal polymerisation in bulk (at 443 K) leads to the formation of a glassy polymer. The unusual kinetic features of the polymerisation of this monomer in benzonitrile have been noted: the rate of polymerisation is given by the equation $w_{pol} = k_p[M]^2[AIBN]$ but an explanation for this has not yet been found.

η^5-Vinylcyclopentadienyldicarbonylmolybdenum and the corresponding tungsten compound are capable of homopolymerisation[85]. It is of interest that η^5-vinylcyclopentadienyldicarbonylcobalt does not polymerise owing to the decomposition of the organometallic component of the molecule, while the analogous iridium monomer gives rise to a homopolymer containing up to 50 wt.% of the metal.

The reasons why styryltricarbonylchromium does not polymerise either via a radical mechanism or in the presence of LiC_4H_9 have not as yet been elucidated; at any rate they are not steric. The transition state is probably stabilised in this instance by the strong (contact or resonance) interaction of the active centre with the $Cr(CO)_3$ group. On the other hand, η^6-(benzyl acrylate)-tricarbonylchromium readily polymerises in tetrahydrofuran (THF) (AIBN, 328–343 K), forming polymers with different molecular weights[86]. The homopolymer obtained in ethyl acetate had a molecular weight of 1.5×10^4. Among the η^4-dienylmetal tricarbonyl MCM, only η^4-(hexa-2,4-dien-1-yl acrylate)tricarbonyliron polymerises effectively (AIBN, benzene).[87] The considerable role of the reaction involving chain transfer to the polymer (particularly at high monomer concentrations), which leads to the formation of a polymer with a branched structure and a broad molecular weight distribution and partly to the formation of a microgel, has been noted. Among other MCM incorporating π-bonded iron, we shall mention the radical polymerisation of 3-vinylfulvalene(fulvalene)di-iron (Scheme 3) (solution in benzene, 343 K 24 h, yield 18%).[88] A characteristic feature of the polymer formed, which has a molecular weight of 5000 (average degree of polymerisation 18), is that, following its oxidation by tetracyanoquinodimethane (TCNQ), it acquires an exceptionally high conductivity for organic polymers, amounting to $(6–9) \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$:

Scheme 3



More than 70% of the iron in the polymer is oxidised; the product consists of the mixed-valence salt $[Fe^{II}Fe^{III}][TCNQ]_2$. According to the results of physicochemical studies[88], the bisfulvalenedi-iron unit incorporating TCNQ constitute a delocalised system with only one type of iron atoms having a formal degree of oxidation of 2.5.

The homopolymerisation of η^5-(vinylcyclopentadienyl)-methyltricarbonyltungsten (AIBN, benzene, 333 K) has been investigated[89–91]. The operation of two different mechanisms of the polymerisation of this monomer was proposed initially: the traditional mechanism involving the vinyl bond and an unusual mechanism consisting in the initiation of the process by the $WCH_2^{\cdot}$ radical, formed via the intramolecular elimination of a hydrogen atom from the WCH_3 group. However, in a later study[85] the authors concluded that the traditional mechanism of vinyl polymerisation in fact operates. The process proceeds with difficulty up to molecular weights of 14000 with a high degree of consumption of the initiator, which corresponds to the kinetic process equation $w_{pol} = 1.13 \times 10^{-2}\ [AIBN]^{2.3}[M]^{0.8}$.[91] Such a high reaction order with respect to the initiator was not explained theoretically[91]. The calculated activation energy for chain propagation proved to be extremely high (338 kJ mol^{-1}).

A final conclusion concerning the influence of the metal atom on the elementary stages of the polymerisation of MCM apparently requires additional studies. The data available at the present time make it possible to conclude only that such influence is highly individual and depends on the type of bonding of the metal to the MCM, the nature of the metal itself, its ligand environment, and its valence state. As a rule, the MCM are highly active in chain transfer and termination reactions, although the mechanism of their action is still not clear. One can only conclude confidently that spatial separation of the multiple bond and the metal atom diminishes this effect. There are no direct data concerning the mutual influence of the metal atoms incorporated in the polymer chain.

There is virtually no information about the stereospecific polymerisation of MCM, although on general grounds it is not difficult to postulate that the metal atom is able to influence the orientation of the MCM molecule in the course of its addition to the growing chain and hence can influence the formation of stereoregular polymers.

IV. COPOLYMERISATION OF METAL-CONTAINING MONOMERS

A whole series of MCM incapable of homopolymerisation or polymerising with difficulty to oligomers are capable of copolymerising effectively with other monomers. One should note that there have been virtually no systematic studies of the radical polymerisation of MCM which would permit the calculation of the corresponding copolymerisation constants (r_1 and r_2) and the determination of the influence of the transition metal on their values and there have been no calculations of the parameters Q (a measure of the resonance stabilisation of the monomer during copolymerisation) and e (a measure of the polarity of the substituent at the double bond) in the Alfrey–Price mechanism. The only exceptions are the metallocene MCM [1,4] and the styryl-substituted palladium compound mentioned above[56].

1. Copolymerisation of σ-Bonded MCM Incorporating a Non-Transition Metal With Traditional Monomers

The rate of copolymerisation of MMA with alkali metal methacrylates (methanol, 333 K, AIBN) decreases with increase of the size of the cation[92]. It is striking that there is a clear-cut tendency towards the alternation of monomers in the MMA–lithium methacrylate copolymer: $r_1r_2 = 0.044$. An

alternating copolymer has also been obtained in the copolymerisation of acrylamide with sodium acrylate[93]. The composition of the copolymer obtained by the copolymerisation of the sodium salt of allenesulphonic acid with acrylonitrile in DMF was not described adequately[94]: apparently the parameters of the activity of the monomers varied with the initial molar ratio of the monomers.

The structure of such metal-containing polymers has been investigated. Thus it has been shown by Raman spectroscopy (absorption band in the range 166–170 cm^{-1}) [95,96] that, in the styrene–sodium methacrylate copolymer, the cations and anions are aggregated into clusters, particularly in the presence of a high metal content. Unfortunately the mechanism of their formation and the nature of the bonds in such aggregates have not so far been adequately studied.

The copolymerisation of alkaline earth metal acrylates with traditional vinyl monomers has been investigated in fair detail. Thus calcium, strontium, and barium acrylates have been copolymerised in aqueous solution with acrylamide and methacrylamide (mixture of $K_2S_2O_8$ and $Na_2S_2O_5$, 303 K).[97,98] The quantity r_2 varied in the sequence $Ba^{2+} < Ca^{2+} < Cr^{2+}$, while r_1 varied in the sequence $Ba^{2+} > Ca^{2+} \cong Sr^{2+}$. The overall rate of copolymerisation decreases with increase of the MCM concentration. Other conditions being equal, the rate of the process fell to a greater extent after the addition of barium acrylate than after the introduction of calcium and strontium acrylates. These facts have been attributed[97,98] to the electrostatic interaction between the growing macroradicals and the acrylate ions, which depends significantly on the interaction of the Ca^{2+}, Sr^{2+}, and Ba^{2+} cations with segments of the polyacrylamide chain in the macroradical (as for alkali metal acrylates). Similar results have been obtained also in the study of the emulsion copolymerisation of styrene with strontium acrylate initiated by $K_2S_2O_8$:[99] with increase of the MCM concentration to values exceeding 0.5%, the yield of the copolymer diminishes sharply. A reaction mechanism has been proposed in which account is taken of the growth of the macroradicals in different phases and the formation of the copolymer mainly as a result of the recombination of these macroradicals at the water–micelle interface is postulated.

The few studies of the catalytic copolymerisation of MCM merit special attention. For example, the copolymerisation of calcium acrylate with ethylene under the influence of the Ziegler–Natta catalytic systems $(RO)_2TiCl_2$–$Al(C_2H_5)_{1.5}Cl_{1.5}$, where R = n-C_4H_9, iso-C_4H_9, or iso-C_3H_7, has been investigated. For R = n-C_4H_9 or iso-C_4H_9, the yield of the copolymer did not change following an increase of the MCM concentration from 0.04 to 0.012 M, while for R = iso-C_3H_7 the yield fell appreciably. The reactivity of the calcium salt proved to be lower by a factor of two than that of the potassium salt. The calcium content in the copolymer depended on the structure of the alkoxy-group in $(RO)_2TiCl_2$ and increased in the sequence iso-C_3H_7O < iso-C_4H_9O < n-C_4H_9O. The observation of the influence of steric factors and allowance for this influence make it possible to diminish the effect of the polar monomer on the catalytic system in copolymerisation (this problem will be examined in greater detail below§).

The opposite examples, in which the rate of copolymerisation increased with increase of the MCM content in the reaction medium, are also known—for example[103] in systems comprising MMA, styrene, or 2-hydroxyethyl methacrylate, on the one hand, and the zinc or cadmium salt of ethylene methacrylate phthalate, on the other:

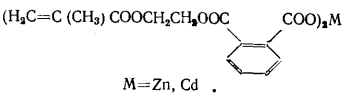


Table 1. The relative reactivity constants of tin-containing monomers M_1 in copolymerisation with traditional monomers M_2.

M_1	M_2	Conditions	r_1	r_2	$r_1 \cdot r_2$	Refs.
$(CH_3)_3Sn(CH=CH_2)$	St	AIBN, benzene, 323 K	0.001	44.8	0.0448	[112]
$(CH_3)_3Sn(CH=CH_2)$	MMA	ditto	0.03	25.1	0.753	[112]
$(C_4H_9)_3Sn(CH=CH_2)$	St	»	0 005	16.0	0.08	[112]
$(C_4H_9)_3Sn(CH=CH_2)$	MMA	»	0.03	27.9	0.837	[112]
$(CH_3)_3Sn(OOC(CH_3)=CH_2)$	St	AIBN, DMF, 333 K	0.53	1.57	0.832	[43]
$(CH_3)_3Sn(OOC(CH_3)=CH_2)$	MAN	ditto	0.20	0.0	0.0	[43]
$(CH_3)_3Sn(OOC(CH_3)=CH_2)$	MAN	BP, 333 K, *in oil*	0.220	0	0	[114]
$(C_2H_5)_3Sn(OOC(CH_3)=CH_2)$	MAN	ditto	0.122	0	0	[114]
$(C_3H_7)_3Sn(OOC(CH_3)=CH_2)$	MAN	»	0.081	0	0	[114]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	MAN	»	0.053	0	0	[114]
$(C_4H_9)_2Sn(OOC(CH_3)=CH_2)$	MA	AIBN, toluene, 343 K	1.738	0.657	1.142	[111]
$(C_4H_9)_2Sn(OOC(CH_3)=CH_2)$	EA	ditto	1.261	0.610	0.768	[111]
$(C_4H_9)_2Sn(OOC(CH_3)=CH_2)$	BA	»	0.851	0.575	0.489	[111]
$(C_4H_9)_2Sn(OOC(CH_3)=CH_2)$	AN	»	0.468	0.471	0.220	[111]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	MMA	»	0.79	1.0	0.79	[110]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	PMA	»	0.58	0.9	0.52	[110]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	BMA	»	0.65	0 68	0.442	[110]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	VPr	»	3.160	0.438	1.384	[107]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	VA	»	4.408	0.017	0.0749	[107]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	St	»	0.258	1.106	0.2848	[108]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	AMA	»	2.343	1.035	2.4258	[108]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	GA	»	1.356	0.367	0 4977	[109]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	GMA	»	0.754	0.794	0 5987	[109]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	MAA	»	4.230	0.381	1.6116	[109]
$(C_2H_5)_3Sn(OOCC(CH_3)=CH_2)$	MMA	AIBN, benzene, 333 K	0.705	0.37	0.261	[113]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	MMA	333 K	0 93	1.04	0.9672	[40]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	VA	333 K	0.76	0.028	0.0213	[40]
$(C_4H_9)_3Sn(OOC(CH_3)=CH_2)$	St	333 K	0.40	1.14	0.4560	[40]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	MA	AIBN, DMF, 323 K	0.03	0.82	0.0246	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	EA	ditto	0.08	0.75	0.0600	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	BA	»	0.15	0.70	0.1050	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	OA	»	0.23	0.66	0.1141	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	MA	aqueous emulsion, 345 K	0.51	1.97	1.0047	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	EA	ditto	0.41	0.89	0.3650	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	BA	»	0.42	0.73	0.3086	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	OA	»	0.49	0.67	0.3283	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	MMA	AIBN, toluene, 343 K	0.398	2.190	0.8714	[106]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	PMA	ditto	0.319	1.699	0.5410	[106]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	BM	»	0.196	1.659	0.3260	[106]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	AN	»	0.242	1.003	0.2421	[106]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	VPr	»	2.567	0.006	0.0154	[107]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	VA	»	0.517	0.610	0.3129	[107]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	St	»	0.213	1.910	0.4157	[108]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	AMA	»	0.195	2.257	0.4883	[108]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	GA	»	0.295	1.409	0.4157	[109]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	GMA	»	0.344	4.290	1.4758	[109]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	MAA	»	0.977	1.258	0.2291	[109]
$(C_4H_9)_2(Cl)Sn(OOCCH=CH_2)$	MA	AIBN, benzene, 333 K	0.08	0.81	0.065	[42]
$(C_4H_9)_2(Cl)Sn(OOCCH(C_6H_5)=CH)$	MA	ditto	0	2.0	0	[42]
$(CH_3)_2Sn(OOCC(CH_3)=CH_2)_2$	St	AIBN, DMF, 333 K	0.83	0.28	0.232	[46]

Notation: MAN = maleic anhydride, MA = methyl acrylate, EA = ethyl acrylate, BA = butyl acrylate, OA = octyl acrylate, AN = acrylonitrile, PMA = propyl methacrylate, BMA = butyl methacrylate, AMA = allyl methacrylate, GMA = glycidyl methacrylate, GA = glycidyl acrylate, N-MAA = *N*-hydroxymethylacrylamide, St = styrene, VPr = vinylpyrrolidinone, and VA = vinyl acetate.

§ We may note that catalytic systems based on alkoxy-derivatives of titanium combined with organoaluminium components generate free radicals under the influence of polar monomers (for example, MMA)[102]; the radicals can alter the polymerisation process.

In systems containing MMA, copolymerisation proceeds faster than in systems containing styrene: complete conversion is attained after several hours, but after 15–30% conversion gelling of the system takes place.

Table 2. The values of Q and e in the Alfrey–Price mechanism for the copolymerisation of Sn-monomers.

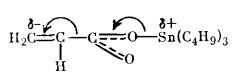
M_1	M_2	Q	e	Refs.
$(CH_3)_3Sn(CH=CH_2)$	St	0.005	0.962	[112]
$(CH_3)_3Sn(CH=CH_2)$	MMA	0.036	0.933	[112]
$(C_4H_9)_3Sn(CH=CH_2)$	St	0.017	0.822	[112]
$(C_4H_9)_3Sn(CH=CH_2)$	MMA	0.031	0.822	[112]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	alkyl acrylates	0.23	−0.5	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	alkyl acrylates*	0.23	−0.1	[105]
$(C_4H_9)_3Sn(OOCCH=CH_2)$	**	0.235	0.401	[109]
$(CH_3)_3Sn(OOCC(CH_3)=CH_2)$	St	0.45	−0.37	[43]
$(CH_3)_3Sn(OOCC(CH_3)=CH_2)$	MAN	0.31	−0.64	[114]
$(C_2H_5)_3Sn(OOCC(CH_3)=CH_2)$	MAN	0.27	−0.75	[114]
$(C_4H_7)_3Sn(OOCC(CH_3)=CH_2)$	MAN	0.23	−0.81	[114]
$(C_4H_9)_3Sn(OOCC(CH_3)=CH_2)$	MAN	0.18	−0.88	[114]
$(C_4H_9)_3Sn(OOCC(CH_3)=CH_2)$	**	0.852	0.197	[109]
$(CH_3)_2Sn(OOCC(CH_3)=CH_2)_2$	St	1.36	0.41	[43]

*Emulsion copolymerisation.
**Values obtained by averaging the data for glycidyl acrylate, glycidyl methacrylate, and *N*-hydroxymethylacrylamide.

The copolymerisation of tin-containing MCM, mainly trialkylstannyl acrylates, has been investigated in greatest detail, the copolymerisation constants for such monomers being summarised in Tables 1 and 2. The following features of the copolymerisation of tributylstannyl acrylate (TBSA) with alkyl acrylates have been discovered[105].

1. The rate of the process decreases with increase of the length of the alkyl chain of the alkyl acrylate and with the fraction of TBSA in the monomer mixture.

2. The alternation of units, confirmed by the S-shaped curves for the composition of the monomers and the values of r_1 and r_2 less than unity, is observed; such alternation is due to the negative polarisation of the double bond in the TBSA molecules and the positive polarisation in alkyl acrylates. The negative polarisation of the double bond in TBSA is due to the concentration of a considerable negative charge at the oxygen or tin atom, which is transferred inductively to the double bond, indicating a high polarity of the =–Sn bond:



3. The fraction of TBSA in azeotropic monomer mixtures increases with increase of the length of the alkyl chain of the alkyl acrylate owing to the decrease of activity in the series of alkyl acrylates.

It is of interest that TBSA and chlorodibutylstannyl acrylate have similar values of r_1 and r_2 in copolymerisation with methyl acrylate[42,105], which indicates the same influence of the C_4H_9 and Cl groups at the tin atom on the reactivity of the multiple bond.

The rate of copolymerisation of trialkylstannyl acrylates with maleic anhydride passes through a maximum for the equimolar composition of the monomer mixtures[19,71,114]. The constant $r_2 = 0$ for all the sytems, r_1 and Q decrease, and e_1 increases with increase of the length of the alkyl group in MCM. It has been suggested that the formation of the alternating copolymers is due to the interaction of the tin atom of the metal-containing monomer with the carbonyl group of maleic anhydride in the transition complex arising in the chain propagation reaction[19]. Under these conditions, the tendency of trialkylstannyl methacrylates to form complexes increases with increased length of the alkyl substituents at the tin atom, while the rate of their copolymerisation with maleic anhydride diminishes. It has been shown[44] that the copolymerisation of *N*-trialkylstannylmaleimide with styrene results in the formation of copolymers with a strict alternation of the monomeric units over a wide range of conversions and molar ratios of the monomers.

The following tin-containing terpolymers have also been synthesised: TBSA–vinyl acetate–vinylpyrrolidinone, TBSMA–vinyl acetate–vinylpyrrolidinone[107], TBSA–methyl methacrylate–acrylonitrile, TBSA–butyl methacrylate–acrylonitrile[111], TBSA–styrene–acrylonitrile, and TBSM–butyl methacrylate–acrylonitrile[108], the composition of the copolymers corresponding to the copolymerisation constants.

2. Copolymerisation of σ-Bonded MCM Based on Transition Metals

Tetramethylallyloxytitanium does not polymerise (either in the absence or presence of additives such as $SnCl_4$ and BF_4), but its copolymer with vinyl acetate has been obtained[115] (at room temperature without adding initiators), although the latter is incapable of homopolymerisation at room temperature. The same effect has been observed for the copolymerisation of trichlorotitanium acrylate with styrene (the reaction takes place explosively even in a dilute solution) or with isoprene[116]. The monomer itself is apparently a catalyst of cationic polymerisation in such cases. The copolymer of tetramethylallyloxytitanium with MMA has been obtained[115] in the presence of benzoyl peroxide at 338 K. The yellow solid polymer formed proved to be insoluble in solvents specific for poly(methyl methacrylate).

Tributoxytitanium methacrylate copolymerises (benzoyl peroxide, 363 K) with MA, while dibutoxytitanium dimethacrylate and dibutoxytitanium maleate copolymerise with styrene under the same conditions[51]. The possibility of the radical copolymerisation of a butenoxy-derivative of titanium with vinyl monomers has been noted[12]. The copolymerisation of allyloxytitanocene chloride[46] with styrene or MMA (monomer molar ratio 1:10, 0.5% of benzoyl peroxide, 373–393 K) leads to the formation of solid transparent orange copolymers with molecular weights of 22100 and 70000 respectively [the molecular weights of the polystyrene and poly(methyl methacrylate) obtained under the same conditions were 50000 and 90000 respectively]. These data confirm the conclusion that the MCM are highly active also in reactions involving the transfer of the growing chains. Infrared spectroscopic data indicate the retention of the titanocene structure in the copolymer[46]. The copolymerisation of methacryloyloxytitanocene chloride and also dimethacryloyloxytitanocene with the same monomers confirms these conclusions[48].

The copolymerisation of zirconyl methacrylate and acrylate[53] with styrene and various alkyl acrylates to form cross-linked copolymers insoluble in organic solvents and having a softening temperature higher than for the corresponding homopolymers, namely polystyrene and poly(alkyl acrylate), has also been reported[53]; however, quantitative data have not been published.

It has been noted[117] that the gelling of the ethylene glycol–chromium(III) methacrylate phthalate–styrene system (peroxide type initator, 328–373 K) beings already after 10–20%

conversion. Copolymers insoluble in the usual solvents were formed also in the radical copolymerisation of butoxy(methyl methacrylate)(ethylene glycol)titanium with styrene[118].

Data are available for the radical (comonomer–vinylpyrrolidinone, AIBN, solution in DMF, 323–353 K) and cationic (comonomer–α-methylstyrene, BF_3) copolymerisation of metalloporphyrin[119] and chlorophyll-containing[120] MCM.

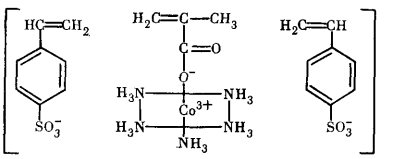
The copolymerisation of *trans*-(4-vinylphenyl)bis(tributylphosphine)palladium chloride (benzene, AIBN, 328 K) has been investigated in detail[56]. The parameters $r_1 = 1.49$ (styrene) and $r_2 = 0.45$ were calculated by the Fineman–Ross equation for low degrees of conversion, which led to $Q = 0.41$ and $e = -1.4$ for the Alfrey–Price mechanism (the corresponding values for styrene are 1.0 and −0.8). The value of e_1 shows that, on the basis of the equation for the correlation between e and the Hammett constant, the σ-bonded palladium gro:p in *p*-substituted styrene is highly electron donating, of the type of *p*-amino- or *p*-methoxy-group in an aromatic ring. It might have been expected that *trans*-(4-vinylphenyl)bis(tributylphosphine)palladium dichloride would manifest a high reactivity in cationic polymerisation owing to the negative value of e, but BF_3 etherate did not induce its polymerisation, which was explained[56] by the interaction of the palladium group with BF_3, leading to the inhibition of the homopolymerisation.

Table 3. The copolymerisation constants and the parameters Q and e for the copolymerisation of methacrylatopentaamminecobalt(III) perchlorate (I) and *cis*-dimethacrylatotetra-amminocobalt(III) perchlorate (II) with methacrylic acid (aqueous solution, 303 K, $K_2S_2O_8 + Na_2S_2O_3$ initiator).[55]

Monomer	pH	r_1	r_2	Q	e
(I)	3	0.02±0.02	3.8±0.4	0.17	−0.91
(II)	3	0.001±0.001	2.1±0.5	0.17	−1.8
(I)	7	0.8±0.3	0.15±0.1	1.4	+0.46

Interesting features were observed[55] in a study of the radical copolymerisation of methacrylatopentamminecobalt(III) perchlorate and *cis*-dimethylacrylatotetramminecobalt(III) perchlorate with methacrylic acid. Table 3 shows that the pH of the medium has a significant influence on the copolymerisation process. This is probably associated with the fact that 90% of methacrylic acid is ionised at pH 7 and only 3% is ionised at pH 3. Accordingly, in the former case a positively charged monomer copolymerises with the methacrylate anion, while in the latter the monomer polymerises with unionised methacrylic acid. The copolymers obtained are sparingly soluble in water but readily dissolve in solutions of acids. Bearing in mind that Q and e for methacrylic acid and the methacrylate ion are 2.0, +0.7 and 0.9, −1.0 respectively, the presence of the cobalt-containing group leads to a decrease of Q_1 for both monomers and also of e_1 for *cis*-dimethacrylatotetramminecobalt(III) perchlorate. It is striking that the copolymer obtained at pH 3 contained a much larger isotactic fraction.

The copolymerisation (pH 1, 323 K, inert atmosphere, $K_2S_2O_8$) of methacrylatopentamminecobalt(III) perchlorate with sodium styrene-*p*-sulphonate has also been investigated[121]. After 12–24 h, the yield of the copolymer reached 5–10%. This resulted in the formation of a polyampholyte insoluble in water, DMF, and DMSO, consisting of an alternating copolymer (A–B–A), in which the molar content of the sodium salt of styrenesulphonate was independent of the composition of the reaction mixture and amounted to 60–70%. The copolymer obtained is characterised by a repeating unit as a result of the polymerisation of a transition structure:



Evidently, because of their hydrophobic character, the formation of such structures via the ionic interaction between the monomers is more probable than the formation of pairs of ionised monomers with a counterion. Generally speaking, by virtue of the wide variation of the values of Q and e, MCM provide greater possibilities than the usual monomers for the synthesis of alternating copolymers, but this problem has not been adequately analysed for MCM based on transition metals owing to the lack of experimental data.

3. Copolymerisation of MCM Incorporating a Coordination-Saturated Metal

We shall examine two cases: when one or both copolymerising monomers form complexes with metal compounds. In the former case the copolymerisation of MMA with vinylidene chloride, 2,6-dichlorostyrene, *p*-chlorostyrene, and styrene (AIBN or ultraviolet irradiation, 323 K) in the presence of $ZnCl_2$ or $AlBr_3$ leads to the formation of alternating copolymers[59] as a consequence of the rapid increase of the effective rate constants for cross chain propagation under the influence of the complex-forming agent. According to other data[122], in the copolymerisation of styrene with methyl acrylate in the presence of $ZnCl_2$ (spontaneous process or photoinitiated), the composition of the copolymer depended on the monomer ratio; alternation was observed only when the molar content of methyl acrylate in the initial mixture was <0.8. This has been attributed to the formation of two types of complexes: $ZnCl_2$–methyl acrylate and $ZnCl_2$–methyl acrylate–styrene; accordingly, the alternating copolymer is a product of the homopolymerisation of the second complex, while in the presence of an excess of methyl acrylate in the monomer mixture the two types of complexes copolymerise. The spontaneous compolymerisation of 1,3-cyclopentadiene with acrylonitrile in the presence of $ZnCl_2$ led to the simultaneous formation of a copolymer having a predominantly 1,4-*cis*-structure and a small amount of a cyclic adduct[123].

The characteristics of the radical copolymerisation of allylbenzene with methyl acrylate, acrylonitrile, methacrylonitrile, and fumaronitrile in the presence of $ZnCl_2$, $ZnBr_2$, ZnI_2, $Zn(SCN)_2$, $AlCl_3$, or $SnCl_4$ (333 K, AIBN) have been investigated[124]. In the allylbenzene–MMA and allylbenzene–fumaronitrile systems in the absence of the above salts polymerisation did not occur, while in the presence of $ZnCl_2$ alternating copolymers were formed. The values of Q and e have been calculated for acrylonitrile and MMA bound in complexes with $ZnCl_2$.

Alternating copolymers have also been obtained in the copolymerisation of monomers each of which is capable of the formation of complexes with MX_n—for example, acrylic acid and acrylamide in the presence of $ZnCl_2$ (AIBN, 318 K, benzene)[124].

It is noteworthy that, in the copolymerisation of allyl monomers with vinyl monomers (M_1), the presence of MX_n hardly influences r_2.[59] On the other hand, in copolymerisation with monomers each of which is capable of forming a complex (allyl acetate or allyl alcohol with MMA; $ZnCl_2$, $AlBr_3$), the parameters r_1 and r_2 become appreciably closer to each other. However, as shown for the MMA–acrylonitrile and methyl acrylate–acrylonitrile pairs of monomers[36], when $SnCl_4$ is used as the complex-forming agent, the corresponding ester is more reactive regardless of the ratio of the reactivities of the initial monomers.

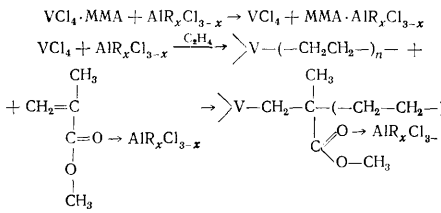
The copolymerisation of styrene (M_1) with vinylpyridines (DMF, AIBN, 323 K) in the presence of $CoCl_2.6H_2O$ [64] leads to a considerable (approximately threefold) increase of r_1, compared with the same process in the absence of an additive, and to just as large a decrease of r_2 (for both 4-VP and 2-VP and methylvinylpyridine). The authors[64] attribute these effects to the formation of the corresponding complexes.

The copolymers of *cis*-$[Ru(bipy)_2(4\text{-}VP)X]^{n+}$ with styrene, MMA, and 4-VP (AIBN, 343–348 K, solvent—CH_3CN) have been described[66]. The structures of the polymers have been demonstrated by elemental analysis and infrared spectroscopy.

The vinylimidazole complexes of nickel(II), cobalt(II), iron(III), and copper(II) acetates copolymerise with vinylpyrrolidinone when divinylbenzene is added as the cross-linking agent (γ-irradiation, aqueous solution)[126]. After irradiation, the resulting polymer was ground and the metal ion as a "template" was removed by boiling the polymer powder in hydrochloric acid. It was found that each "template" polymer then adsorbed metal ions more effectively than pure polyvinylimidazole. The cobalt-containing "template" polymer adsorbed Co^{2+} ions most effectively, while selective adsorption was not observed for other "template" polymers

The radical copolymerisation of a series of cobalt-, nickel-, and palladium-containing complexes of styrylphosphines with styrene in various organic solvents has been reported[129].

We may note an interesting feature of the copolymerisation of MCM in complexes with olefins. In the copolymerisation of ethylene with vinylpyridines[130], acrylonitrile[131], or MMA,[132] the metal-containing monomer bound in complexes with VCl_4, $TiCl_4$, and $VOCl_3$ functions as a component of a metal complex catalytic system, on the one hand, and the formation of complexes by these monomers prevents the inhibiting effect of the heteroatoms on the anionic-coordination polymerisation of olefins and activates the double bond in the monomers, on the other. The mechanism of this process can be represented in the following form[132]:



The formation of complexes of $Al(C_2H_5)_2Cl$ with polar monomers (acrylonitrile, acrylic acid, and potassium methacrylate) leads to similar results, which facilitates their copolymerisation with ethylene in the presence of the $VO(OC_2H_5)_3$–$Al(C_2H_5)_2Cl$ catalytic system[133]. The content of the polar monomer in such copolymers reaches 2.5 wt.%.

4. Copolymerisation of MCM With a π-Bonded Transition Metal

The copolymerisation of π-bonded MCM with classical vinyl monomers is apparently the most thoroughly investigated branch of the polymer chemistry of MCM. The results of the study of the copolymerisation of styrenetricarbonylchromium, η^5-vinylcyclopentadienyltricarbonylmanganese, η^6-(2-phenylalkyl acrylates)tricarbonylchromium, and η^4-(hexa-2,4-dien-1-yl acrylate)tricarbonyl with styrene, vinyl acetate, acrylonitrile, MMA, butadiene, and other monomers have been summarised in review[1,84]. Methylvinylcyclopentadienyltricarbonylmanganese (the 1,2- and 1,3-isomers) was copolymerised[109] with styrene and 1,4-divinylbenzene; the products contained 27–50 mole % of MCM.

Two studies were devoted to problems of the copolymerisation of η^5-vinylcyclopentadienyltricarbonylmethyltungsten, η^5-vinylcyclopentadienyldicarbonylnitrosyl molybdenum, η^5-vinylcyclopentadienyldicarbonylnitrosylchromium, η^5-vinylcyclopentadienyldicarbonylnitrosyliridium, vinylruthenocene, and vinylosmocene[85,90]. Data on the copolymerisation parameters and the values of Q and e for the MCM considered are listed in Table 4. The copolymerisation of MCM with π-bonded metal is characterised by large negative values of e (from −1.6 to −2.1), which is associated with the powerful electron-donating character of the cyclopentadienyl ring and the conclusion[85] that the nature of the metal, the addition of the NO group and the two CO groups have little influence on the reactivity of the monomers is apparently quite justifiable.

We may note also that $r_1 = 0$ has been obtained for the radical copolymerisation of tricarbonylstyrenechromium (M_1) with styrene or MMA,[134] i.e. the growing chain terminating in the M_1 group cannot combine with M_1, which is consistent with the inability of styrenetricarbonylchromium to undergo homopolymerisation.

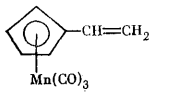
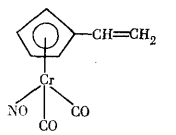
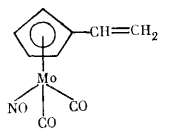
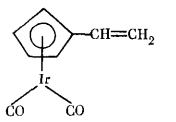
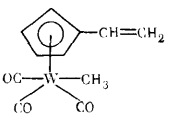
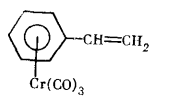
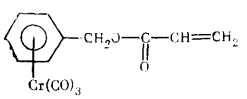
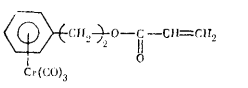
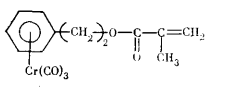
A characteristic feature of the copolymerisation of η^6-(2-phenylethyl acrylate)tricarbonylchromium with styrene, MMA, and acrylic acid is the formation of polymers with a broad bimodal molecular weight distribution: MW > 10^6 for the high-molecular-weight fraction and 1×10^4–6×10^4 for the low-molecular-weight fraction. The high-molecular-weight fraction consists of a highly branched polymer, which is also observed with copolymers of η^4-(hexa-2,4-dien-1-yl acrylate)-tricarbonyliron copolymers. The copolymer containing 28 mole % of MCM has been obtained by the copolymerisation of 3-vinylbisfulvalenedi-iron with styrene (monomer ratio 1 : 4).[88] Its treatment with TCNQ in benzene, $CHCl_3$, or benzonitrile led to the oxidation of 88% of the initial amount of iron(II) and the formation of the mixed-valence salts $[Fe^{II}–Fe^{III}][TCNQ]_2^-$ analogous to homopolymer salts. However, their conductivity (2.5×10^{-5} Ω^{-1} cm^{-1}) was lower than for the homopolymer salts [(6 – 9) × 10^{-3} Ω^{-1} cm^{-1}].

5. Copolymerisation of Various MCM With One Another

Studies of the copolymerisation of various MCM in order to obtain bimetallic metal-containing polymers have been extremely limited although such products might apparently be of definite interest (for example, in metal complex catalysis).

¶ It is of interest to note that a similar "adjustment" phenomenon was also observed in the formation of complexes of the corresponding cations with certain copolymers and subsequent cross-linking[127,128]. After the removal of ions there is in this instance an appreciable increase of sorption capacity and of the rate of sorption on the "adjusted" sorbents. However, in contrast to the study of Kato et al.[126], an increased selectivity in relation to the metal ion with respect to which the given sorbents had been "adjusted" was noted[127].

Table 4. The copolymerisation constants and the parameters Q and e for the copolymerisation of π-bonded MCM*.

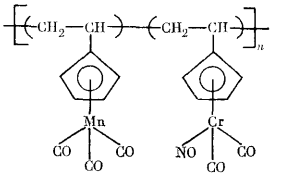
Monomer M_1	Parameter	Styrene	MA	MMA	AN	VA	Refs.
	r_1	0.10	—	0.19	2.35	0.19	[137]
	r_2	2.5	—	0.47	0.06	0.22	
	Q	1.03	—	—	—	—	
	e	−1.99	—	−0.95	−0.59	−2.9	
	r_1	0.30	—	—	—	5.3	[138]
	r_2	0.82	—	—	—	0.079	
	Q	3.13	—	—	—	—	
	e	−1.98	—	—	—	—	
	r_1	0.31	—	—	—	—	[85]
	r_2	0.83	—	—	—	—	
	Q	—	—	—	—	—	
	e	−1.97	—	—	—	—	
	r_1	0.29	—	—	—	—	[85]
	r_2	0.77	—	—	—	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	
	r_1	0.16	—	—	—	—	[89, 91]
	r_2	1.55	—	—	—	—	
	Q	1.66	—	—	—	—	
	e	−1.98	—	—	—	—	
	r_1	0	—	0	—	—	[134]
	r_2	1.39	—	0.75	—	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	
	r_1	0.10	0.56	—	—	—	[84]
	r_2	0.34	0.62	—	—	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	
	r_1	0.1	0.3	—	0.6	—	[135]
	r_2	0.5	1.0	—	0.2	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	
	r_1	0.04	—	0.90	0.07	—	[136]
	r_2	1.35	—	1.19	0.79	—	
	Q	—	—	—	—	—	
	e	—	—	—	—	—	

*For the notation, see Table 1.

Among the most significant advances in this field we may mention the copolymerisation of vinylcyclopentadienyltricarbonylmanganese with vinylferrocene (benzene, 343 K, AIBN), for which $r_1 = 0.44$, $r_2 = 0.49$, $e_1 = -2.6$, and $e_2 = -2.1$, while the polymer obtained had $\bar{M}_n = 7700$ and $\bar{M}_w = 13800$.[137]

The radical copolymerisation of η^6-(benzyl acrylate)tricarbonylchromium with ferrocenylethyl acrylate takes place readily in ethyl acetate[1].

The polymer having the structure



was obtained only for a specific ratio of the monomers, i.e. η^5-vinylcyclopentadienyltricarbonylmanganese and η^5-vinylcyclopentadienyldicarbonylnitrosylchromium[138].

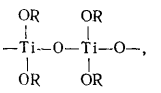
The copolymerisation of two monomers incorporating iron and zinc methacrylates together with unsubstituted methacrylic acid had been reported[139]. It has been suggested that a long-range interaction transmitted via the polymer chain takes place between the iron and zinc atoms.

The copolymerisation of different MCM is not the only method of synthesis of bimetallic polymers. For this purpose, one can also use polycondensation methods (see below) and methods involving the polymerisation of bimetallic monomers for which there are virtually no experimental data, as mentioned above. However, an attempt has been made[140] to combine clusters with traditional monomers and to polymerise and copolymerise them. This method is believed to be promising although its application is complicated by the reactions of the initiator with the cluster and also by the large differences between the relative reactivities of the monomers in clusters and the traditional monomers.

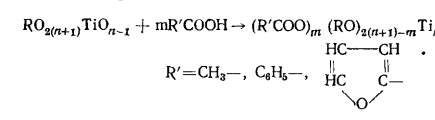
Thus the copolymerisation of MCM with traditional monomers makes it possible to determine the influence of the nature of the metal in the MCM on the relative reactivities of the copolymerising monomers. Although this influence is difficult to treat systematically owing to specific factors even in MCM-homologues, nevertheless allowance for it makes it possible in many instances to act effectively on the copolymerisation process and on the properties of the products formed (see Section VIII).

V. POLYMERISATION AND COPOLYMERISATION OF OLIGOMERIC METAL-CONTAINING MONOMERS

Metal-containing oligomers as well as polymers incorporating multiple bonds are capable of polymerisation and copolymerisation. Oligomeric MCM are frequently formed already in the stage involving the synthesis of the monomers as the main or side products. Only the homopolymerisation of titanium-containing polymers of the type



in which some of the surrounding groups are unsaturated, and their copolymerisation with vinyl monomers have been investigated. Such compounds have been obtained by polymer-analogue reactions based on the ease of substitution of the alkoxy-groups in polyalkoxytitanoxanes by acyl residues with multiple bonds[7,49,141]:



Thus the interaction between polybutoxytitanoxane and

methacrylic as well as furylacrylic and cinnamic acids leads to the formation of waxy or rosin-like substances (depending on the amount of acid introduced). Polybutoxytitanoxane methacrylate behaved analogously to its low-molecular-weight analogue—tributoxytitanium methacrylate—because in the presence of bonzyl peroxide polymerisation did not take place even after prolonged heating, while on initiation with AIBN and heating at 423 K for 5 h there was an appreciable decrease of the number of double bonds[49]. Polybutoxytitanoxane furylacrylate and polybutoxytitanoxane cinnamate copolymerise with styrene (373 K, 1–2% of benzoyl peroxide); transparent red-brown copolymers are formed; in contrast to the initial polybutoxytitanoxane, they proved to be insoluble in solvents such as acetone, benzene, and toluene and did not react even with boiling water. Similar reactions have not been described for oligomeric products containing other metals. Here we may also mention the oligomeric π-complexes of tungsten[201] obtained by exchange reactions.

VI. GRAFT POLYMERISATION

There are few data concerning the graft polymerisation of MCM and almost all the publications on this question have appeared only in the last ten years. Only the results of studies on the radical graft polymerisation of MCM have been described and chemical initiation methods have been usually employed. MCM based on non-transition metal salts of acrylic acid have been largely used for grafting, evidently due to the ease of their synthesis and ready polymerisability.

Thus the $(NH_4)_2S_2O_6$–$Na_2S_2O_3$ oxidation-reduction system[142] proved to be effective for the grafting of sodium acrylate to a polysaccharide and $(NH_4)_2S_2O_8$ was effective in the grafting of sodium acrylate and methacrylate to cellulose[143]. An interesting method for the grafting of acrylate and sodium ethylenesulphonate has been proposed[144]. Wool fibre was kept in an aqueous solution of the MCM after which it was treated with a gas discharge plasma, the yield of the graft copolymer reaching 2–5%. This method is extremely promising and can apparently be extended also to other MCM. The method of chemical initiation (by the Fe^{2+}–H_2O_2 oxidation-reduction system) has been used[145] also for the grafting of calcium acrylate to cellulose in aqueous solution. When a 20% solution was employed, the process took place at a high rate and terminated after 5 min. An increase of temperature from 292 to 353 K did not affect the yield of the graft copolymer, while a decrease of the MCM concentration to 16% sharply reduced it. Evidently, when 20–30% aqueous solutions of calcium acrylate are used, associated monomer species with an ordered molecular arrangement are involved in the grafting.

The grafting of zinc acrylate to polyolefins[146] and of the calcium and barium salts of acrylic and methacrylic acids to polypropylene and poly(vinyl chloride) fibres[147,148] has been reported.

However, the use of chemical grafting methods should lead to the formation of considerable amounts of the homopolymer together with the graft copolymer. The application of high-energy radiation (the radiation from the ^{60}Co isotope, an electron accelerator, and a glow discharge plasma) as the initiator of graft postpolymerisation has considerable advantages in this respect. The attempts at direct post-irradiation (accelerated electrons) grafting of sodium methylene- and styrene-sulphonates to a polyethylene film were unsuccessful[200]. On the other hand, these monomers were grafted after the preliminary hydrolysis of polyethylene.

The trapped radical method, involving contact between the grafting solution and a polymer support subjected to preliminary irradiation *in vacuo* has been used for the grafting of certain titanium- and vanadium-containing monomers to powdered polyethylene, polypropylene, polystyrene, and the ethylene–propene copolymer[149,150]. MCM of both acrylic and allylic series have been used. When $(C_5H_5)_2Ti(Cl).OCH_2CH{=}CH_2$, $(C_4H_9O)_2Ti[NH(CH_2CH{=}CH_2)]_2$, $Cl_3Ti(OCH_2.CH{=}CH_2)$, $(C_3H_7O)_3Ti(OCH_2CH{=}CH_2)$, and $CH_2{=}CHCH_2.OVOCl_2$ were grafted, the metal content in the graft copolymer did not exceed 0.10–0.12%, which is not surprising bearing in mind the low tendency of allylic compound towards polymerisation.

On the other hand, in the radiation-induced graft postpolymerisation of tributoxytitanium acrylate (preliminary irradiation dose *in vacuo* 200 kJ kg^{-1}) the maximum metal content also did not exceed the values quoted above[151]. This is apparently due to the steric hindrance to the chain propagation reaction associated with the large size of the $Ti(OC_4H_9)_3$ group. In the study of the temperature variation of the yield of the grafting process, a maximum was found in the region of 303 K, which can be accounted for by the superposition of two competing effects: the increase of the rate of chain propagation and the increase of the rate of destruction of the polymeric radicals with increase of temperature.

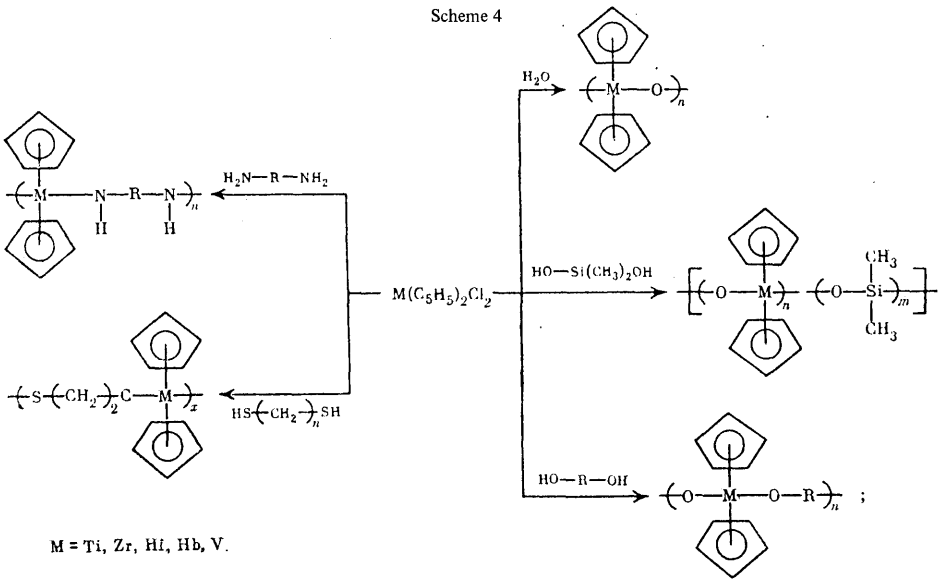
The grafting of monomers bound in complexes is an extremely promising branch of the graft polymerisation of MCM. The addition of the $ZnCl_2$, ZnI_2, or $AlCl_3$ salts proved to have an insignificant influence on the graft polymerisation of arcrylamide, MMA vinyl acetate, and styrene on 1,4-polybutadiene (benzene, 333 K, AIBN).[152] On the other hand, the grafting of MMA or styrene to 1,2-polybutadiene was greatly accelerated in the presence of these salts, which can be arranged in the following sequence in terms of their influence on the grafting parameters: $ZnCl_2 > AlCl_3 > ZnI_2$. The case considered is the only example illustrating the role of the steric structure of the polymeric support on the character of the grafting of MCM.

The possibility of grafting the complex of an organic or inorganic nickel salt with vinylpyridine (molar ratio from 0.1 : 1 to 1 : 1) to rubber in the presence of a radical initiator has been demonstrated[153].

All that has been said above concerning the polymerisation of allylic monomers bound in complexes holds also for their graft polymerisation. Allyl alcohol, allylamine, allyl acetate, allylmercaptan, etc. have been grafted to polyethylene, polypropylene, polystyrene, and poly(methyl methacrylate) in the presence of LiCl, CaCl, and $ZnCl_2$.[154,155] The method of joint irradiation has been used for this purpose. The rate of the graft polymerisation of allyl alcohol (AAl) increased by a factor of 5 for the molar ratio $[AAl] : [ZnCl_2] = 2 : 1$.[155] The graft copolymers of certain other allylic monomers have been obtained for the first time[154]. In addition, after the attainment of the same degree of grafting of vinyl monomers, the necessary irradiation dose increased considerably (by a factor greater than four).

The graft polymerisation of allylic monomers in the presence of certain transition metal salts has also been achieved. Allyl alcohol, allylamine, and diallylamine have been grafted to powdered polyethylene and polypropylene by the method of post-irradiation graft polymerisation (preliminary irradiation both *in vacuo* and in air) in the presence of $CoCl_2$, $Co(NO_3)_2.6H_2O$, NiI_2, and $CrCl_3.6H_2O$.[156] In the grafting of the complex $CoCl_2$(AAl) (the dose in the preliminary irradiation of polyethylene in air was 200 kJ kg^{-1}; molar ratio $AAl : CoCl_2 = 3 : 1$, 343 K, inert atmosphere) the rate of the process is constant over a considerable time interval, as shown by the linear relation between the cobalt content in the copolymer and the reaction time. The activation energy for this process has been calculated as 40 kJ mol^{-1}. This procedure can probably be used also for the graft copolymerisation of MCM

Scheme 4



probably be used also for the graft copolymerisation of MCM with vinyl or allyl monomers and possibly also heterometallic MCM. There are no data concerning the graft polymerisation of π-bonded MCM.

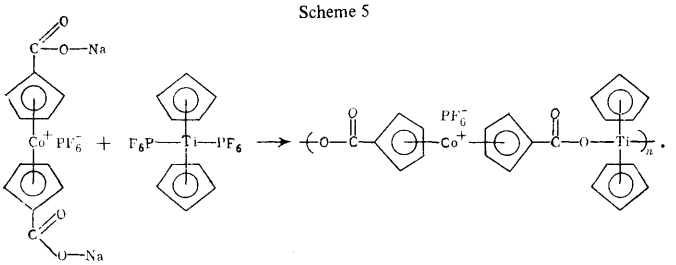
VII. POLYCONDENSATION REACTIONS OF METAL-CONTAINING COMPOUNDS

The condensation of metallocene compounds has been studied in fair detail; the comparatively early studies have been surveyed by Korshak[7] and Neuse and Rosenberg[157], while reviews of later work can be found in a number of other publications[158–164,203–205]. Reactions of this kind are presented in a general form in Scheme 4.

The degree of polycondensation in such products varies within wide limits—from 2 to 2000 depending on the nature of the reactants. A convenient method for the preparation of metallocene polymers by reaction with aldehydes has been described[165].

Polycondensation reactions of metallocenes, for example, between cobaltocene derivatives and titanocene[158] (Scheme 5), leading to the formation of a polymer chain incorporating different transition metal atoms, are known:

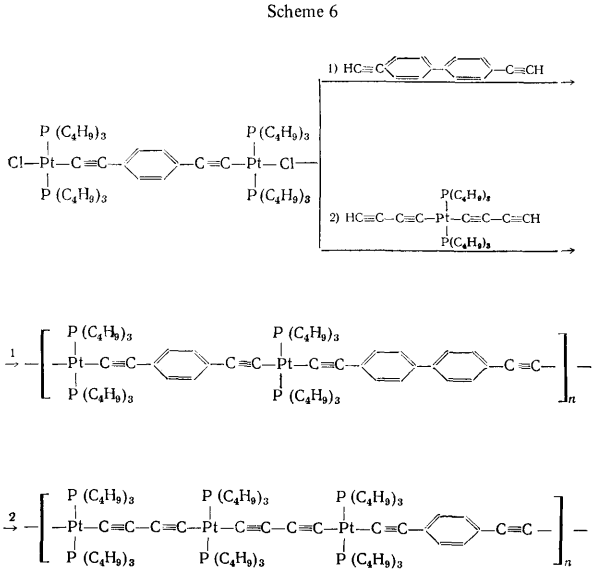
Scheme 5



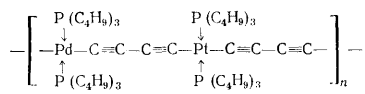
Many of the reactions considered will probably prove to be promising for the synthesis of polymers based not only on metallocene derivatives but also on alkoxy-, amido-, amino-, and carboxy-derivatives of transition metals. For example, linear conjugated coordination polymers have been obtained by the condensation of tetrakis(salicylhaldehydo)zirconium(IV) with 1,2,4,5-tetra-aminobenzene or dicarboxybis(5,7-dichloro-8-quinolato)(triphenylphosphine)tungsten with quinoline-5,8-diol.[166] The molecular weight of the polymers reaches 50000 and their characteristic feature is the inclusion of octacoordinate metals. The formation of similar products can be expected also for molybdenum, niobium, rhenium, etc.; vigorous researches are being prosecuted on these lines.

An interesting series of studies[167–174] has been devoted to the polycondensation of acetylenic MCM. In the presence of copper(I) iodide or chloride, such MCM are capable of forming polymers with chloro-derivatives of nickel, palladium, and platinum and some can undergo copolycondensation with diethynylbenzene. A wide variety of poly-yne polymers containing nickel, palladium, or platinum atoms in the main chain have been synthesised in this way (Scheme 6).

Scheme 6



The poly-yne polymers are soluble in various organic solvents despite the fact that they possess a rigid rod-like structure in solution. Polymers containing different metals in the main chain, for example palladium and platinum, have been obtained in the same way[170]:



These polymers had molecular weights ranging from 8000 to 120000 and under certain conditions they depolymerised with formation of polynuclear complexes with a Pt–C bond. It is striking that in all cases the products formed can be regarded as alternating copolymers. The characteristic features of the polycondensation of acetylenic derivatives of the ferrocene type have been surveyed in a recent review[175].

VIII. APPLICATIONS OF METAL-CONTAINING POLYMERS

Metal-containing polymers are finding a wide variety of applications which are sometimes unexpected; such data have been published mainly in the patent literature. It is possible to note two main trends: applications involving the improvement of some properties of polymers and compositions based on them and applications based on the appearance of new properties due to the presence of the metal in the main or side chain of the polymer.

Thus the introduction of lithium, sodium, or potassium methacrylate units into PMMA greatly increases the thermal-stability of the polymer and to a greater extent for shorter PMMA blocks[176]. Intramolecular cyclisation reactions involving neighbouring side groups take place in this instance with formation of anhydride rings and the corresponding metal methoxide. The introduction of sodium methylallenesulphonate into polyacrylonitrile has an appreciable influence on the glass point (T_g) of the copolymer[177]: a relation with a maximum corresponding to an MCM content in the copolymer of 8 wt.% was observed. The increase of T_g is apparently associated with the increase of the rigidity of the chain as a result of the incorporation in the latter of more bulky polar groups. With high MCM contents, the intermolecular interaction of the nitrile groups weakens as a consequence of the loosening of the structure.

The addition of sodium or zinc polyacrylate to certain compositions[178] greatly increases their heat resistance and resistance to a corona discharge; the copolymers of sodium or potassium acrylate with unsaturated polyesters have a high impact strength, dimensional stability, and fire resistance[179]. The styrene–methacrylic acid–sodium methacrylate ternary copolymer is characterised by an increased yield point, which has been attributed[180] to an increased degree of neutralisation of the carboxy-groups. Titanium-containing polymers exhibit properties known as "anomalous fibre formation"[90]; their mass and initial dimensions change little under the conditions of heat treatment.

All the polymers based on MCM incorporating transition metals are as a rule stable up to 473–523 K. Even their low content in copolymers with traditional monomers, for example, those of zirconyl acrylate or methacrylate with alkyl acrylates[53], leads to the formation of a cross-linked polymer with enhanced thermoplastic properties and improved resistance to organic solvents. These properties are used, especially in the case of titanium-containing polymers, to obtain various coatings, frequently with enamel-like surfaces. We may also note the application of metal-containing polymers, obtained by the polymerisation or copolymerisation of MCM, as the main components in the preparation of foam plastics[181], hydrophilic finishing preparations for crease-resistant cotton fabrics[182], and as materials with effective slip[183]. Alkaline earth metal and copper acrylates and methacrylates are used as the principal components in the preparation of soil structure-forming agents designed for the stabilisation of soils[184–186], as water isolating agents in the recovery of petroleum[187], and as flocculants and coagulants[188,189].

One of the most promising applications of metal-containing polymers is their use as metal complex catalysts in numerous processes. Thus polymers obtained by the polymerisation of styrylphosphines bound in complexes with cobalt, nickel, and palladium salts catalyse hydroformylation reactions[129], while ferrocene-containing polymers catalyse dehydrogenation and dehydration processes[175].

As was to be expected, metal-containing graft polymers proved to be even more effective catalysts: for example, the grafted complexes of nickel salts with vinylpyridine on natural rubber catalyse the dimerisation of ethylene[153]; titanium- and vanadium-containing monomers grafted on powdered polyolefins catalyse the polymerisation and copolymerisation of ethylene[150]. The complex of $PdCl_2$ with 4-vinylpyridine grafted on the surface of ethylene proved to be an effective catalyst of the stereospecific polymerisation of acetylenic monomers[190,191] and also of the reductive *N*-alkylation of nitrobenzene and its reudction products by carbonyl compounds[192]. Data concerning the possibility of employing polymerisation, copolymerisation, and graft polymerisation processes involving MCM for the preparation of deposited catalysts to be used in various processes have been summarised in two communications[193,194]. The fixation of molecular nitrogen by manganese-containing metallopolymers has been reported[199]. Metal-containing polymers based on lead and tungsten metallocene monomers have been used as coatings for targets in laser-induced thermonuclear synthesis[202].

Many metal-containing polymers have bactericidal properties. Platinum-containing condensation polymers have been used in the treatment of tumours[195], the platinum complex being slowly split off in the course of biochemical hydrolysis, which leads to prolonged action of this drug. Polymers of η^5-vinylcyclopentadienyltricarbonylmanganese and its copolymers are used as inhibitors of fungal growth[137]. Germanium-containing polymers are employed in the treatment of fibrosis of the lungs[196].

The potential applications of metal-containing polymers in this field have not yet been fully investigated. The consideration of metal-containing polymers for the purpose of imparting specific operational properties to the compositions formed merits attention. This concerns the application of Group I–IV metal acrylate and methacrylate polymers as well as their copolymers with vinyl monomers as thermostabilisers for chlorine-containing resins, for example poly(vinyl chloride)[206–208].

The method of stabilisation of such polymers at the stage of their synthesis, for example, by the copolymerisation of tin-containing monomers with vinyl chloride, is of special interest[19]. In this case the stabilising centres in the copolymer are distributed in a sequence determined by the copolymerisation parameters and are not removed from the polymer during its use (constitutionally stabilised polymers). Stable and uniform constitutional colouring of polyolefins, based on the use as cocatalyst of the product of the interaction of titanium(IV), vanadium(III), and vanadium(V) with diazoacetylenic alcohols containing a multiple bond and a chromophoric group, was achieved by similar method[209].

On the other hand, thermal and photochemical degradation of a metal-containing polymer can result in the formation of metals or their oxides, which leads in the first place to the

generation of systems with new properties. Thus ultraviolet irradiation of films of the η^6-(2-phenylethyl acrylate)tricarbonylchromium–styrene copolymer was accompanied by the elimination of a CO group and the formation of Cr_2O_3 incorporated in cross-linked films[135]. This also applies to polymers obtained by the polymerisation of monomers containing iron[210]. The decomposition of certain polymers to the oxide takes place only at temperatures above 1000 K.

Among other applications of metal-containing polymers, one may name the formation of light-sensitive media for photocopying devices, adhesives, combustion moderators, flame extinguishers, electrically conducting materials[88] and semiconductors, and ion exchangers. The products of the polymerisation and polycondensation of MCM have been used as photosensitisers and materials for protection against heat and radiation. Photopolymerisation systems for the rapid dry production of an image have been developed and investigated. Barium acrylate has been used as their main component[211,212]. The radical copolymerisation of MMA with palladium, calcium, barium, and strontium methacrylates has been carried out to prepare photoresistors with a high sensitivity and a satisfactory resolving power, which are resistant to the action of high temperatures and corrosive media[213].

The applications of metal-containing polymers are apparently not restricted to these fields. Their considerable expansion may be expected, since the synthetic possibilities in this rapidly developing branch of polymer chemistry have not been fully elucidated as yet and have been by no means completely realised.

At the same time this field of study involves a whole series of problems whose solutions will make it possible to discover general characteristics. We believe that the most important of these are as follows: the search for methods of stabilisation of MCM (especially organometallic MCM), the synthesis of bimetallic and polymetallic MCM; the development of methods for the effective activation of the multiple bonds in MCM, new methods for the initiation of polymerisation processes, and a detailed analysis of the influence of the nature of the metal on the elementary stages of the polymerisation process; problems of the stereoregulation and supermolecular organisation of metal-containing polymers; characteristic features of the alternating copolymerisation of MCM with one another and with traditional monomers; the study of the structure of the chains of metallopolymers, the changes undergone by metals following their incorporation in the polymer matrix, and also the cooperative interaction between metal atoms; problems of catalysis and the elucidation of specific features of the chain structure of metal complexes and its manifestation in catalytic processes; the study of the reactivity of the multiple bonds in MCM in other reactions involving these bonds. Only the hydrogenation of monomers bound in complexes, whose rate, as in the case of polymerisation, is higher than in the absence of a complex-forming agent, has been investigated on these lines[214,215].

Although the analysis of the results of the study of the polymerisation and copolymerisation processes involving MCM indicates a considerable progress in the understanding of many aspects of this problem and also the intensity of the studies in this field, the elucidation of fairly general characteristics of these processes requires concerted studies by chemists specialising in the field of organometallic synthesis and in polymer chemistry.

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