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# Macromolecular metal carboxylates

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**Abstract. Data on the synthesis and physicochemical studies of salts of mono- or dibasic unsaturated carboxylic acids and unsaturated metal oxo-carboxylates are generalised and described systematically. The structures and properties of the COO group in various compounds and characteristic features of the structures of carboxylate complexes are analysed. The main routes and kinetics of polymerisation transformations of unsaturated metal carboxylates are considered. The attention is focused on the effect of the metal ion on the monomer reactivity and the polymer morphology and structure. The possibility of stereochemical control of radical polymerisation of unsaturated metal carboxylates is demonstrated. The electronic, magnetic, optical, absorption and thermal properties of metal (co)polymers and nanocomposites and their main applications are considered. The bibliography includes 407 references.**

## I. Introduction

Metal carboxylates are encountered in many natural objects and find wide use in various fields of human activity. Being constituents of metalloproteins and other biomolecules, these compounds accomplish important biochemical functions in living organisms and determine specific features of behaviour of many enzymes and antibodies and specific features of interaction of intra- and extracellular structures.[1,2] The polynuclear carboxylate complexes are often used as catalytic and biomimetic systems in the studies of biological processes.

Among numerous metal carboxylate derivatives, a special place is occupied by salts of unsaturated carboxylic acids: acrylic, methacrylic, crotonic, oleic, fumaric, maleic, acetylenedicarboxylic, vinylbenzoic acids and so on, which are typical metal-containing monomers because they have a multiple bond able to be cleaved and a metal ion chemically bound to the organic part of the molecule.[3]

In recent years polymerisation of such monomers has been the subject of intense studies due to the practical importance of the resulting products and their compositions. The properties of polymers in which every repeating unit contains an equivalent of the metal differ appreciably from the properties of traditional polymeric materials. The presence of reactive functional groups and the diversity of the coordination environment of the metal create unique possibilities for the design of novel advanced materials. Fairly promising in this respect are metal oxo clusters containing unsaturated carboxylate groups, which can serve as nanostructure elements for the production of organic – inorganic hybrid nanocomposites.[4] These are highly organised systems with strictly defined sizes and shapes, which are retained in the final products, and therefore it is possible to attain their homogeneous distribution in the material and obtain monodisperse nanostructures. The polymeric films based on them have enhanced mechanical,[5,6] adhesive,[7] optical[8] and electrical[9] properties. Metal carboxylates are widely used to design magnetically active materials, in particular, molecular magnets.[10–13]

The main information on the preparation, structure, properties and applications of saturated metal carboxylates is presented quite comprehensively in a monograph[14] and reviews.[15–18] However, no reviews devoted to the salts of unsaturated carboxylic acids and their polymerisation transformations can be found in the literature. Some aspects of the synthesis and structure of these compounds are considered in monographs[3,19] and a Ph.D. thesis[20] and some representatives have been considered in recent reviews.[4,21,22]

This study covers a broad range of problems concerning methods of synthesis, structure and properties of unsaturated metal carboxylates, their polymerisation transformations and properties and characteristics of the resulting metallopolymers. This is the first almost exhaustive survey of studies in this field of chemistry.

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# II. Syntheses and structures of unsaturated metal carboxylates

## 1. Methods for the preparation of unsaturated carboxylic acid salts

The interest of researchers in unsaturated metal carboxylates is due, first of all, to their use as monomers for the preparation of metallopolymers. Therefore, in the stage of the synthesis of salts of unsaturated carboxylic acids it is possible to lay the foundation for chemical design of polymers with specified properties.

### a. Reactions of unsaturated carboxylic acids with bases

Unsaturated carboxylic acid salts are often prepared by neutralisation. The essence of the method is dissolution of a metal oxide, hydroxide or carbonate in an aqueous or aqueous ethanolic solution of the corresponding acid. The procedure used to isolate the target product depends on its solubility.[23–29]

In the case of alkali or alkaline-earth metal salts, stoichiometric amounts of the starting compounds or a slight excess of the acid are normally used.[30–34] In view of the high polymerising ability of alkali metal (meth)acrylates, the reaction is carried out in dilute solutions at reduced temperature, in some cases, in the presence of special compounds that inhibit polymerisation.[3,35] If the salts formed are readily hydrolysed, an excess of the acid is used or water is removed from the reaction mixture.

Transition metal acrylates and methacrylates are prepared in suspensions in ethanol or a hydrocarbon (benzene or toluene).[36–40] The use of non-aqueous media decreases the probability of formation of basic salts and favours the formation of the reaction products in high yields. In the case of tuiply charged metal cations, for example, $Fe^{3+}$, $Cr^{3+}$ and so on, depending on the reaction conditions and the reactant nature, either normal salts[41–44] or trinuclear oxo-carboxylates are formed (see Section II.5).

Metal dicarboxylates are obtained in a similar way. Thus in the reaction with zinc oxide in water, maleic acid behaves as a monobasic acid to give the mixed complex ZnH(*cis*-$O_2CCH{=}CHCO_2$)(OH)·$H_2O$, whereas in methanol it behaves as a dibasic acid.[34] The complexation of metal ions with dicarboxylic acids was studied by potentiometric titration[45–49] and spectrophotometric analysis.[47] It was found that 1 : 1 complexes are formed at pH 4.9–5.2 in the copper(II)–maleic acid system[47] or at pH 2.0–3.5 in the thallium(III)–fumaric (or maleic) acid system.[45] Neutral and protonated complexes exist in the metal ion–itaconic acid system at pH 3–4,[48] which was confirmed by preparative isolation of neutral itaconates $M_2[O_2CCH_2C(=CH_2)CO_2]_3\cdot n\,H_2O$ ($n$ = 3–6) and protonated complexes $MH[O_2CCH_2C(=CH_2)CO_2]_2\cdot n\,H_2O$ ($n$ = 1, 2) (M = lanthanide,[50] Cd,[51] Ba [52]).

A modification of this method consists of preparation of the metal hydroxide *in situ*.[53] If one of the products is poorly soluble, the reaction proceeds to completion.[54,55] Thus the reaction of beryllium sulfate, maleic acid and barium hydroxide in a 1 : 2 : 1 molar ratio in water results in immediate precipitation of barium sulfate:[55]

$$BeSO_4 + Ba(OH)_2 + \textit{cis}\text{-}HO_2CCH{=}CHCO_2H \xrightarrow{pH\ 3} BaSO_4 + Be(\textit{cis}\text{-}O_2CCH{=}CHCO_2)\cdot 2\,H_2O.$$

This is one of a few cases of preparation of beryllium carboxylate in an acidic medium. Monocarboxylic ligands are involved in the beryllium coordination sphere only in alkaline or neutral media to give oxo-carboxylates like $(RCO_2)_6[Be_4O]$.[56]

### b. Ligand exchange reactions

Reactions of unsaturated carboxylic acids with metal salts (most often, acetates) giving carboxylates are documented.[14] An advantage of this method is the ready availability of the starting reactants. If the acid evolved is volatile (for example, acetic acid), then unsaturated carboxylic acids are taken in stoichiometric amounts. The drawbacks include contamination of the products by traces of acetic acid and, in the case of salts of strong acids, side reactions, in particular, polymerisation, that often accompany the process.

Hydrothermal syntheses, which are of interest for the design of new materials with unusual structures have intensely been developed in recent years. Thus the reaction of copper(II) acetate monohydrate with fumaric acid under temperature and pressure gradient conditions gives air-stable copper(I) fumarate with high density ($\rho$ = 3.24 g cm$^{-3}$).[57]

The reactions of metal chlorides or sulfates with the corresponding sodium carboxylate in water gave liquid-crystalline monomeric complexes of Mg(II) and Zn(II), for example:[58]

$$MgCl_2\cdot 6\,H_2O + 2\,NaO_2CR \longrightarrow Mg(O_2CR)_2\cdot x\,H_2O + 2\,NaCl + (6-x)\,H_2O,$$

R = $(CH_2)_{11}O_2CCH{=}CH_2$, $C_6H_3(O(CH_2)_{11}O_2CCH{=}CH_2)_2$-3,4;
$x$ = 0, 2.

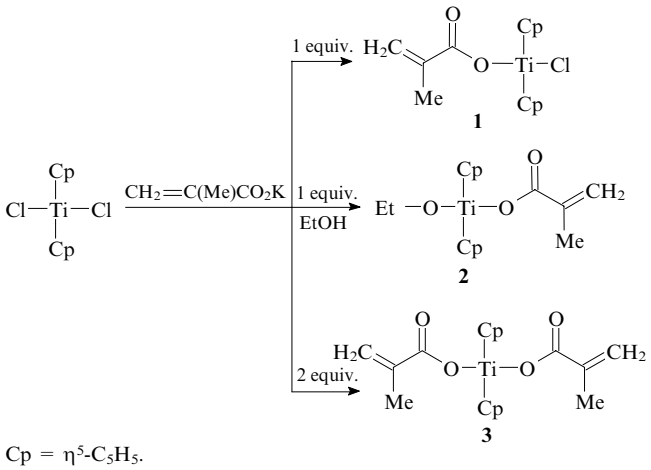
Manganese(II) acrylate and methacrylate complexes were prepared by a similar route in methanol.[59]

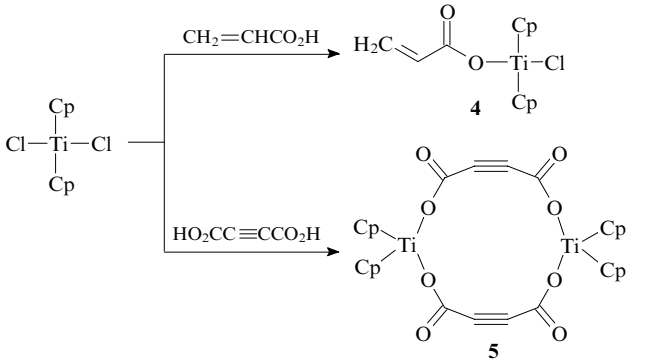
The exchange reaction of chromium(II) chloride with sodium acrylate in an inert atmosphere afforded a binuclear complex of chromium(II) acrylate.[60] However, this compound proved to be fairly sensitive to oxygen and self-ignited in air.

Metal complexes are often used as the starting metal-containing compounds for the synthesis of salts of unsaturated acids. For example, the reaction of terbium tris(acetylacetonate) with maleic acid[61] is exothermic over the whole concentration range. The change in the enthalpy can be attributed to a number of factors, including the formation of a stronger bond of the maleate with the $Tb^{3+}$ ion upon substitution of the maleate anion for acetylacetonate. Examples of such stabilising effect of a maleic acid fragment are rather frequent. The kinetics of formation of the stable complex $[Pd(H_2O)_2(\textit{cis}\text{-}O_2C.CH{=}CHCO_2H)]^+$ was studied.[62]

Mono- and di(acyloxy) derivatives of bis(cyclopentadienyl)titanium were first obtained by Nesmeyanov *et al.*[63] by treatment of bis(cyclopentadienyl)titanium dichloride with potassium methacrylate. The structures of the reaction products **1**–**3** were found to depend on the reaction conditions.

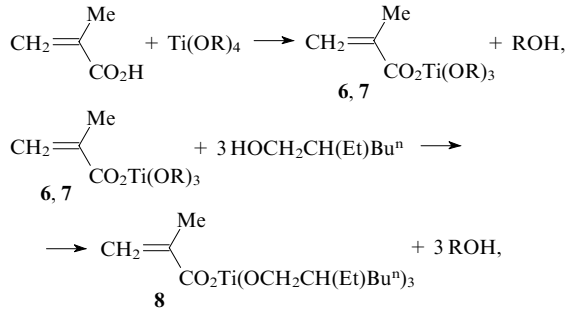
Acrylic and acetylenedicarboxylic acids react with bis(cyclopentadienyl)titanium dichloride in a similar way. This method can also be used to prepare other titanium carboxylate derivatives.[64–67] Compounds **1**–**5** are readily soluble in conventional organic solvents (benzene, acetone, DMF, pyridine) and partly soluble in methyl methacrylate (MMA).




The main drawback of this method is the formation of a large amount of finely dispersed chlorides difficult to remove. This problem can be eliminated by performing the synthesis of alkyl orthotitanates under phase transfer conditions, one of the non-miscible phases serving as the solvent for the resulting salt and the other, for alkyl orthotitanate.[68] Examples of using liquid ammonia as the solvent are known, as it dissolves ammonium chloride but does not dissolve alkyl orthotitanate. This approach ensures good yields but requires the use of elevated pressure in each stage of the process.

Metal carboxylates are often prepared by the reactions of metal alkoxides with organic acids or acid anhydrides. Compounds **6**, **7** were obtained by nucleophilic substitution from titanium(IV) alkoxide and methacrylic acid taken in a stoichiometric ratio.[69]

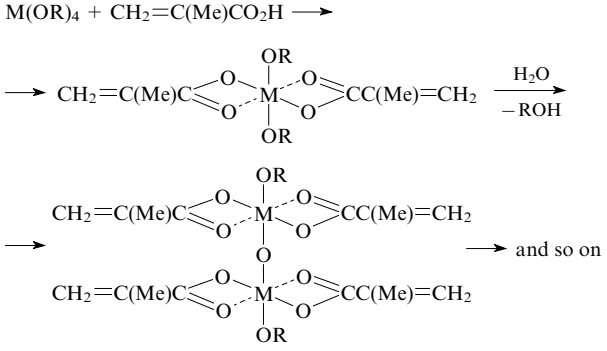



R = Bu$^t$ (**6**), *tert*-$C_5H_{11}$ (**7**).

The liberated alcohol is removed from the reaction mixture by continuous evaporation *in vacuo*. In those cases where the boiling point of the alcohol is higher than that of the initial acid, trialkoxytitanium methacrylates are used (see the preparation of compound **8**). Note that these syntheses were carried out without a solvent. Very high yields (up to 97%) of the target products attest to a low contribution of side processes, for example, polymerisation transformations, possible under these conditions.

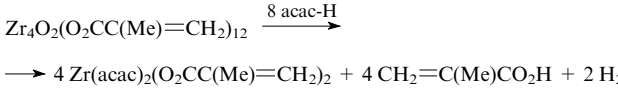
A method for the synthesis of anhydrous europium(III) methacrylate from europium triisopropoxide has been proposed.[70]

Sol–gel synthesis techniques are promising for the preparation of metal methacrylates. These techniques are based on hydrolysis of alkoxides $M(OR)_4$ (M is a tetravalent metal) in an organic medium in the presence of methacrylic acid.




R = Alk; M = Ti, Zr, Hf.

The condensation of intermediates produces a sol and then a gel.[71] This method can be used to prepare carboxylate-substituted metal oxo clusters. For example, the reaction of zirconium(IV) or hafnium(IV) alkoxide with excess methacrylic acid in propyl alcohol affords polynuclear oxo-carboxylate $M_4O_2(O_2CC(Me)=CH_2)_{12}$ (M = Zr, Hf).[72, 73] Note that in an attempt to replace the chelating methacrylate groups by acetylacetonate groups, the zirconium oxo cluster was converted into a mononuclear complex.[74]




In the general case, the subsequent modification of the resulting oxo cluster presents certain difficulties. It was shown that the clusters $Zr_6O_4(OH)_4(O_2CC(R)=CH_2)_{12}$ and $[Zr_6O_4(OH)_4(O_2CC(R)=CH_2)_{12}]_2$ (R = Me,[72] H[75]) are not interconverted,[76] although they do not differ much in structure.

Using exchange reactions, it is possible to replace all or some methacrylate ligands in $Zr_6O_4(OH)_4(O_2C.C(Me)=CH_2)_{12}$ by other ligands, for example, propionic or isobutyric acid.[77] The complex $Zr_6O_4(OH)_4(O_2CC(Me)=CH_2)_8(O_2CPr^i)_4(Bu^nOH)$ was also synthesised directly by the reaction of $Zr(OBu^n)_4$ with a mixture of methacrylic and isobutyric acid.

The key factors used efficiently to control the composition and size of the formed oxo clusters include the nature of the metal alkoxide and the organic acid : alkoxide molar ratio. For example, the reaction of tin(IV) isopropoxide with methacrylic acid at an equimolar reactant ratio results in the formation of $[Sn(OPr^i)_2(O_2CC(Me)=CH_2)_2]_2$ with six-coordinate tin atoms, while for 1.4 : 1 to 2 : 1 ratios the reaction gives the dimer $[Sn(\mu_2\text{-}OPr^i)(OPr^i)(O_2CC(Me)=CH_2)_2]_2$ (Ref. 78). However, even in the case where the $CH_2=C(Me)CO_2H$ : : $Sn(OPr^i)_4$ ratio was greater than 2 : 1, no polynuclear oxo complexes were obtained, the reaction giving unidentified polymers.

It was found[79] that the highest acid : titanium(IV) alkoxide molar ratio leading to the oxo cluster $Ti_6O_4(OEt)_8(O_2C.$

.C(Me)=$CH_2$)$_8$ is 1.33. At higher values polymeric or oligomeric structures are formed.[80]

The attempts to prepare yttrium oxo-carboxylate clusters failed. Only anhydrous yttrium methacrylate Y($O_2$C. .C(Me)=$CH_2$)$_3$ was isolated after esterification and characterised by X-ray crystallography.[81] However, mixed oxo complexes with different compositions and structures based on yttrium(III) and titanium(IV) with methacrylate ligands were synthesised in quantitative yields.[82]

Similar approaches are applicable to the synthesis of other heteronuclear complexes.[83–85] Thus for 1 : 1 and 1 : 2 ratios of titanium and zirconium alkoxides, the complexes $Ti_4Zr_4O_6$. .(OBu$^n$)$_4$($O_2$CC(Me)=$CH_2$)$_{16}$ and $Ti_2Zr_4O_4$(OBu$^n$)$_2$($O_2$C. .C(Me)=$CH_2$)$_{14}$, respectively, were obtained.[83]

Syntheses of heterometallic carboxylates containing transition metal and lanthanide ions were also reported.[86–89]

**c. Reactions involving organometallic compounds**

Examples of using organometallic compounds as the starting reactants for the preparation of unsaturated metal carboxylates are described.[90–93] The reaction of pentaphenylantimony with maleic acid (1 : 1) at room temperature results in the cleavage of the metal–carbon bond to yield Sb(V) monoacyl derivative,[90]

$$Ph_5Sb + cis\text{-}HO_2CCH{=}CHCO_2H \longrightarrow Ph_4Sb(cis\text{-}O_2CCH{=}CHCO_2H) + PhH.$$

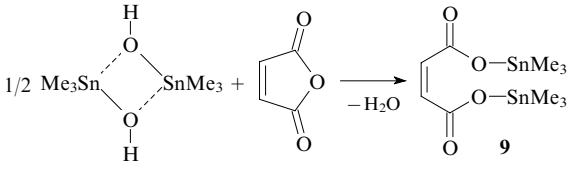
while the molar ratio 2 : 1 results in bis(tetraphenylantimonium) maleate. Note that the products are sensitive to atmospheric moisture and are easily hydrolysed.

Antimony(V) [or bismuth(V)] carboxylates are formed in one step by the oxidative reaction of triphenylantimony (or triphenylbismuth) with acrylic acid in the presence of *tert*-butyl hydroperoxide or hydrogen peroxide.[94]

$$Ph_3M + ROOH + 2CH_2{=}CHCO_2H \longrightarrow Ph_3M(O_2CCH{=}CH_2)_2 + ROH + H_2O,$$

M = Sb, Bi; R = H, Bu$^t$.

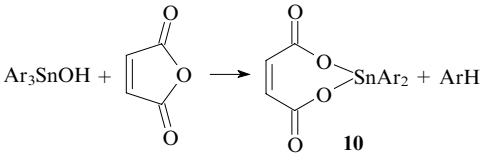
An unexpected product was obtained in the reaction of equimolar amounts of trimethylstannanol with maleic anhydride.[91] Irrespective of the reaction conditions, bis(trimethylstannyl) maleate **9** was formed instead of the expected monosubstituted derivative.




**9**

This reaction route is apparently related to the dimeric structure of the original $Me_3SnOH$.

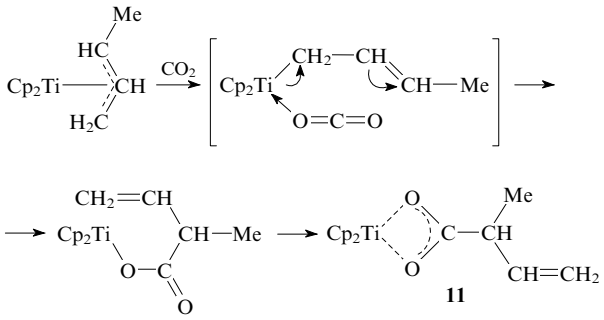
When aryl tin hydroxides are involved in the reaction, one aryl group is eliminated giving rise to cyclic organotin maleate **10**.




**10**

This method was also used to prepare organolead maleates.

Owing to the specific reactivity of allyltitanocene compounds with respect to carbon dioxide, it is possible to obtain carboxylates **11** as a result of $CO_2$ insertion into the Ti–$\eta^3$-$C_3H_4R$ bond.[95,96]







**11**

It was shown by theoretical[97,98] and experimental[99–101] studies that the formation of mono- and binuclear acrylate complexes is the key step of a catalytic reaction of carbon dioxide with ethylene.

**d. Other reactions**

The bimetallic maleate $Cu_xZn_{1-x}$(*cis*-$O_2$CCH=CHC$O_2$)· ·2$H_2O$ ($x$ = 0.06) was isolated from solutions of copper and zinc maleates by slow evaporation at 60 °C.[102] Linear heterometallic trinuclear crotonates $Co_2M(O_2CCH{=}CHMe)_6$. .(Quin)$_2$ (M = Mg, Mn; Quin is quinoline) were prepared in a similar way (yields > 80%).[103]

Some fumaric acid salts are obtained by catalytic isomerisation of maleic anhydride followed by the reaction of the resulting acid with a metal compound. For example, iron(II) fumarate was prepared using maleic anhydride in the presence of thiourea[104] or hydrochloric acid.[105]

It can be seen from the above examples that the methods of synthesis of unsaturated carboxylic acid salts are fairly diverse. In most cases, they are similar to the methods and procedures used to synthesise saturated metal carboxylates, except for the fusion technique. The last-mentioned technique is widely used in industry to obtain anhydrous saturated carboxylates in good yields; however, it is inapplicable to unsaturated acids due to possible polymerisation even during the synthesis of the monomer. It should be emphasised that readily hydrolysable carboxylates, for example, acyl derivatives of metal alkoxides are synthesised in non-aqueous media. Examples of unsaturated carboxylates and methods and conditions for their preparation are summarised in Table 1.

## 2. Spectral characteristics and molecular structure of unsaturated carboxylic acid salts

With respect to metal ions, carboxylic acid anions can act as mono-, bi, tri- and tetradentate ligands with various coordination. For example, for monobasic carboxylates of transition metals, 19 modes of metal binding to the carboxylate group were found to exist (Fig. 1).[106] Five modes of coordination of the carboxylate fragment to the metal are most common; the COO group can behave as a monodentate (structure **A** in Fig. 1), bidentate bridging (**B**), bidentate chelating (**C**), tridentate (**D**) or tetradentate ligand (**E**).[15,16,106] In the case of salts of unsaturated carboxylic acids, the number of coordination modes of the metal to the carboxy group is even larger as the multiple bond can be involved in the coordination to the metal giving a π-bond (structure **F**).

**Table 1**. Methods for preparation of metal salts containing unsaturated carboxylic acid fragments.

| Metal carboxylate [a] | Reactants | | Reaction conditions | Ref. |
|---|---|---|---|---|
| | acid | metal compound | | |
| Reactions of unsaturated carboxylic acids with bases | | | | |
| Metal (meth)acrylates | | | | |
| $NaO_2CCH{=}CH_2$ | acrylic acid | NaOH | pH 7.0 ± 0.1 | 30 |
| $LiO_2CC(Me){=}CH_2$ | methacrylic acid | $Li_2CO_3$ | MeOH, 15 °C | 31 |
| $NaO_2CC(Me){=}CH_2$ | the same | $Na_2CO_3$ | the same | 31 |
| $Cu_2(O_2CC(Me){=}CH_2)_4 \cdot 2\,H_2O$ | " | $(CuOH)_2CO_3$ | MeOH, 24 h | 40 |
| $Cu_2(O_2CC(Me){=}CH_2)_4 \cdot 2\,Py$ | " | $(CuOH)_2CO_3$ | MeOH, PyH, 24 h | 40 |
| $Cu_2(O_2CC(Me){=}CH_2)_4 \cdot 2\,(4\text{-}VPy)$ | " | $(CuOH)_2CO_3$ | MeOH, 4-VPyH, 24 h | 40 |
| $M(O_2CCH{=}CH_2)_2 \cdot n\,H_2O$ [M = Zn(II), Co(II), Ni(II), Cu(II)] | acrylic acid | metal hydroxides and (hydrogen)-carbonates | MeOH, DMF, PhH or PhMe | 36, 37 |
| $[M_3O(O_2CCH{=}CH_2)_6 \cdot 3\,H_2O]OH$ [M = Fe(III), Cr(III), V(III)] | the same | metal hydroxides | MeOH, EtOH | 38 |
| $Fe(O_2CC(Me){=}CH_2)_3$ | methacrylic acid | $FeCl_3$ | $NaHCO_3$, $H_2O$, 40 °C | 54 |
| $Cu_2(O_2CC(Me){=}CH_2)_4(H_2O)_2$ | the same | $Cu_2(OH)_2CO_3$ | MeOH | 39 |
| Metal dicarboxylates | | | | |
| $Co(cis\text{-}O_2CCH{=}CHCO_2H)_2 \cdot 5\,H_2O$ | maleic acid | $CoCO_3$ | $H_2O$, pH 7 | 23 |
| $Ni(cis\text{-}O_2CCH{=}CHCO_2) \cdot 2\,H_2O$ | the same | $NiCO_3$ | the same | 23 |
| $Cu(cis\text{-}O_2CCH{=}CHCO_2) \cdot H_2O$ | " | $(CuOH)_2CO_3$ | | 24 |
| $ZnH(cis\text{-}O_2CCH{=}CHCO_2)(OH) \cdot H_2O$ | " | ZnO | $H_2O$, 60 – 70 °C | 34 |
| $Be(cis\text{-}O_2CCH{=}CHCO_2) \cdot 2\,H_2O$ | " | $BeSO_4 \cdot 4\,H_2O$ | $Ba(OH)_2 \cdot 8\,H_2O$, $H_2O$, pH 3 | 55 |
| $(NH_4)_2[Be(cis\text{-}O_2CCH{=}CHCO_2)]$ | " | $BeSO_4 \cdot 4\,H_2O$ | 25% $NH_4OH$, $Ba(OH)_2 \cdot 8\,H_2O$, pH 5.5 | 55 |
| $Ag(cis\text{-}O_2CCH{=}CHCO_2H)$ | " | $Ag_2CO_3$ | $H_2O$, suspension | 27 |
| $Cu(cis\text{-}O_2CCH{=}CHCO_2H) \cdot H_2O$ | " | $(CuOH)_2CO_3$ | the same | 26 |
| $LnH(O_2CC(=CH_2)CH_2CO_2)_2 \cdot n\,H_2O$, ($n$ = 1, 1.5, 2; Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Lu, Er) | itaconic acid | rare earth carbonates | water, conc. acid | 50 |
| Other salts | | | | |
| $LiO_2CCH{=}CHCH{=}CHMe$ | sorbic acid | LiOH | $H_2O$, pH 8 | 32 |
| $Ca(O_2CCH_2CH{=}CH_2)_2 \cdot H_2O$ | but-3-enoic acid | $CaCO_3$ | $H_2O$ | 33 |
| Ligand exchange reactions | | | | |
| Metal dicarboxylates | | | | |
| $Cu_2(trans\text{-}O_2CCH{=}CHCO_2)$ | fumaric acid | $Cu(OAc)_2 \cdot H_2O$ | $H_2O$, 150 °C | 57 |
| $Cu(cis\text{-}O_2CCH{=}CHCO_2) \cdot H_2O$ | maleic acid | $CuSO_4 \cdot 5\,H_2O$, $Na_2CO_3 \cdot 10\,H_2O$ | $H_2O$ | 102 |
| $Zn(cis\text{-}O_2CCH{=}CHCO_2) \cdot H_2O$ | the same | $ZnSO_4 \cdot 7\,H_2O$ | $H_2O$, $Na_2CO_3 \cdot 10\,H_2O$ | 23, 102 |
| $ZnH(cis\text{-}O_2CCH{=}CHCO_2)(OH) \cdot H_2O$ | | $ZnCl_2$ | $NH_4OH$, $H_2O$ | 34 |
| $Cu(cis\text{-}O_2CCH{=}CHCO_2H) \cdot H_2O$ | maleic anhydride | CuCl | $H_2O$ | 26 |
| Miscellaneous salts | | | | |
| $Zn[O_2CC_6H_3(O(CH_2)_{11}O_2CCH{=}CH_2)_2\text{-}3,4]_2$ | see [b] | $ZnSO_4 \cdot 6\,H_2O$ | NaOH, $H_2O$ | 58 |
| $Mg[O_2CC_6H_3(O(CH_2)_{11}O_2CCH{=}CH_2)_2\text{-}3,4]_2$ | see [b] | $MgCl_2 \cdot 6\,H_2O$ | NaOH, $H_2O$, EtOH | 58 |
| $Mg[O_2C(CH_2)_{11}O_2CCH{=}CH_2]_2 \cdot H_2O$ | $CH_2{=}CHCO_2(CH_2)_{11}CO_2H$ | $MgCl_2 \cdot 6\,H_2O$ | NaOH, $H_2O$ | 58 |
| $Cp_2Ti(O_2CC(Me){=}CH_2)_2$ | $KO_2CC(Me){=}CH_2$ | $Cp_2TiCl_2$ | $CHCl_3$, 60 – 70 °C | 63 |
| $Cp_2Ti(cis\text{-}O_2CCH{=}CHCO_2)$ | $Na_2(cis\text{-}O_2CCH{=}CHCO_2)$ | $Cp_2TiCl_2$ | $H_2O$ | 64 |
| $Cp_2Ti(trans\text{-}O_2CCH{=}CHCO_2)TiCp_2$ | $Na_2(trans\text{-}O_2CCH{=}CHCO_2)$ | $Cp_2TiCl_2$ | $H_2O$ | 65 |
| $[Cp_2Ti(\mu\text{-}O_2CC{\equiv}CCO_2)]_2$ | $HO_2CC{\equiv}CCO_2H$ | $Cp_2TiCl_2$ | $H_2O$ – $CHCl_3$, 20 °C | 66 |
| $Ti(OR)_3O_2CC(Me){=}CH_2$ (R = $Pr^i$, $Bu^t$, *tert*-$C_5H_{11}$, $CH_2CH(Et)Bu^n$) | methacrylic acid | $Ti(OR)_4$ | no solvent, 50 – 55 °C | 69 |
| $[CuLa(O_2CC(Me){=}CH_2)_5(phen)(EtOH)]_2$ | $La(O_2CC(Me){=}CH_2)_3 \cdot 2\,H_2O$ | $Cu(NO_3)_2 \cdot 3\,H_2O$ | $H_2O$, EtOH, pH 4.1 | 86 |
| $Co_2M(O_2CCH{=}CHMe)_6(Quin)_2$ (M = Mn, Mg) | $M(O_2CCH{=}CHMe)_2$ | $Co(O_2C.CH{=}CHMe)_2$ | EtOH | 103 |

**Table 1** (continued).

| Metal carboxylate [a] | Reactants | | Reaction conditions | Ref. |
|---|---|---|---|---|
| | acid | metal compound | | |
| Miscellaneous reactions | | | | |
| $Ph_4Sb(cis\text{-}O_2CCH{=}CHCO_2H)$ | maleic acid | $Ph_5Sb$ | PhH – dioxane, 20 °C | 90 |
| $Ph_4Sb(cis\text{-}O_2CCH{=}CHCO_2)SbPh_4$ | the same | $Ph_5Sb$ | dioxane, 60 °C (see [c]) | 90 |
| $Me_3Sn(cis\text{-}O_2CCH{=}CHCO_2)SnMe_3$ | maleic anhydride | $Me_3SnOH$ | PhH, 80 °C | 91 |
| $Ph_2Pb(cis\text{-}O_2CCH{=}CHCO_2)$ | the same | $Ph_3PbOH$ | the same | 91 |

Notation: Py is pyridine, 4-VPy is 4-vinylpyridine, phen is phenanthroline; [b] 3,4-bis(11-acryloyloxyundecyloxy)benzoic acid; [c] reactant molar ratio 1 : 2.

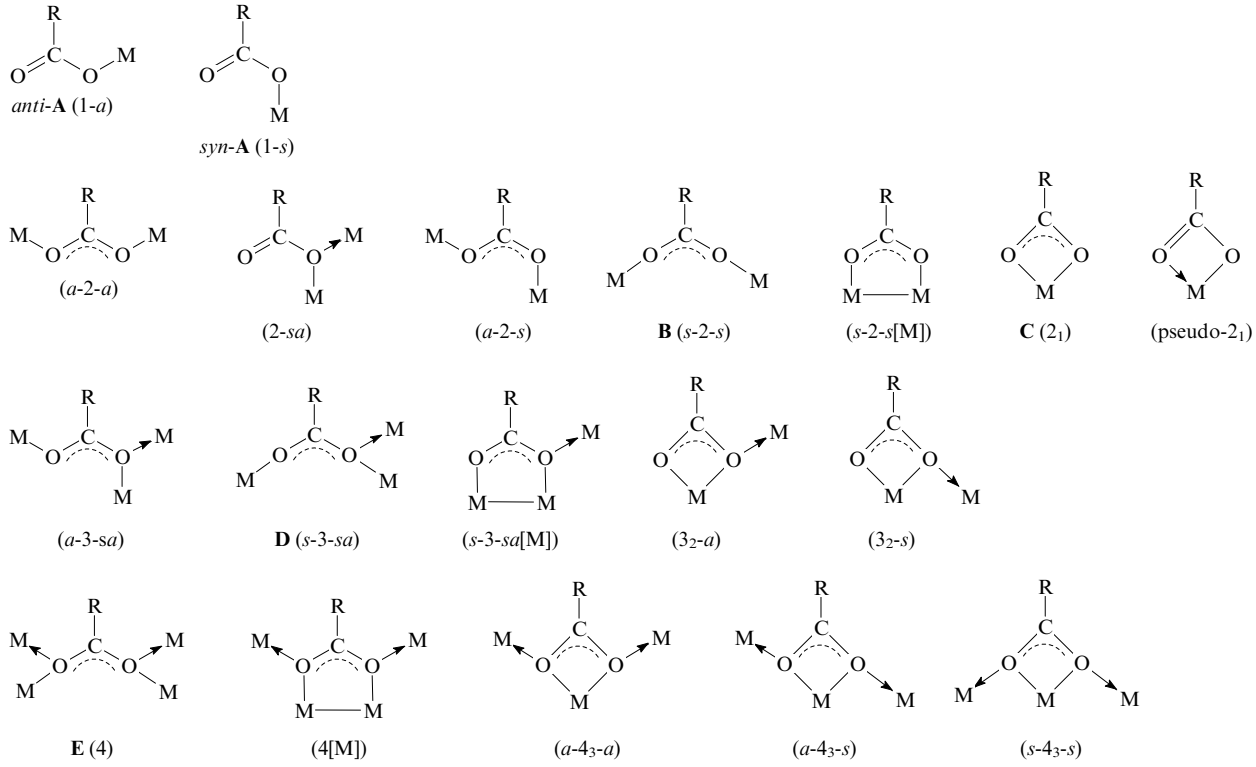
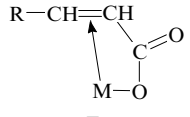



**Figure 1.** Coordination modes of the carboxyl ion.
The numeral in parentheses is the denticity of the RCOO group, the subscript is the number of metal atoms when differs from the denticity, [M] is the presence of a metallacycle, and letters *a* and *s* imply *anti* and *syn* arrangements of the metal atoms.



**F**

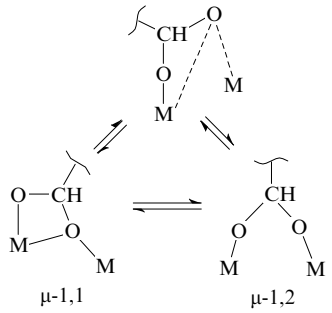
Oligomeric and polymeric metal complexes with different numbers (from one to four) of carboxyl bridges between each pair of metal atoms are also known.

The mode of coordination is determined by many factors: the nature of the metal and the presence of competing acidic or electrically neutral ligands, outer-sphere cations and a system of hydrogen bonds. For example, IR spectroscopy [107] (see †) and extended X-ray absorption fine structure (EXAFS) [108, 109] studies of the zinc salt of an ethylene – methacrylic acid copolymer showed that depending on the external conditions, zinc ions have a hexagonal [$\nu_{as}$(COO) at 1624 and 1538 $cm^{-1}$] or tetragonal [$\nu_{as}$(COO) at 1585 $cm^{-1}$] coordination.

The structural transformations of the COO groups were also observed during photopolymerisation of 10,12-pentacosadiynic acid [$n\text{-}C_{12}H_{25}C{\equiv}C{-}C{\equiv}C(CH_2)_8CO_2H$] at the air – water interface in the presence of doubly charged metal ions, $Ba^{2+}$ (at pH 7.7), $Cd^{2+}$ (pH 6.8) and $Pb^{2+}$ (pH 6.0).[110] In a monolayer on aqueous subphases containing $Ba^{2+}$ and $Pb^{2+}$ ions, the carboxylate group of this diacetylenic acid transforms from bridging to bidentate coordination upon polymerisation, whereas on a $Cd^{2+}$-containing aqueous subphase the bidentate structure is retained and the area occupied by a single acid molecule decreases from 0.8 to 0.18 $nm^2$, *i.e.*, polymerisation results in a closer packing of carboxyl groups in the monolayers. Experimental data and theoretical calculations indicate

† In the carboxylate anion, the double bond is delocalised and the CO stretching vibration sensitive to the geometry and environment of the COO group is split into high-frequency ($\nu_{as}$) and low-frequency ($\nu_s$) components.

that a change in the coordination mode (the so-called 'carboxylate shift') is a low-energy process playing an important role in, for example, catalytic cycles of metalloenzymes.[111]



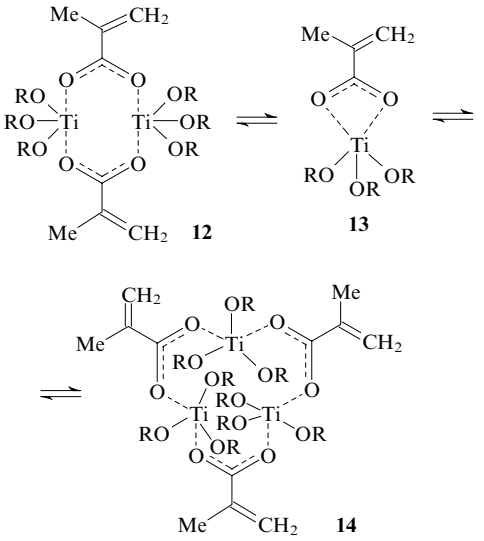

The carboxylate shift from bidentate chelating (μ-1,1) to bidentate bridging (μ-1,2) coordination for zinc carboxylate complexes was directly observed[112] by $^{1}H$ and $^{13}C$ NMR spectroscopy.

## 3. Metal (meth)acrylates

### a. Structures

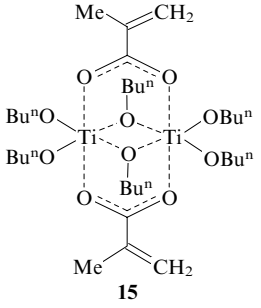
Structures **A**–**E** (see Fig. 1) imply the presence of equivalent and non-equivalent oxygen atoms in the carboxyl group, which is clearly seen in the IR spectra of metal carboxylates. For monodentate complexes, the difference $\Delta\nu = \nu_{as}(COO) - \nu_s(COO)$ in the IR spectra is much greater than for ionic compounds (164–171 $cm^{-1}$), while for bidentate carboxylate complexes, the $\Delta\nu$ values are much smaller.[16] For example, the binuclear complex of copper(II) methacrylate $Cu_2(O_2C.C(Me)=CH_2)_4(H_2O)_2$ in methanol is converted into a mononuclear complex upon replacement of the coordinated water by a more potent donor ligand such as benzimidazole (BIm), and the bidentate coordination of the methacrylate ion becomes monodentate ($\Delta\nu = 203$ $cm^{-1}$)[39] (Table 2). As was to be expected, the CO bond for the coordinated oxygen atom is longer than for the non-coordinated one (see Table 2).

The structure of the carboxylate fragment is appreciably affected by steric factors. Thus trialkoxytitanium(IV) methacrylate complexes, $Ti(OR)_3(O_2CC(Me)=CH_2)$, are equilibrium mixtures of structures **12**–**14** with bridging and chelating bidentate methacrylate groups.[69] For $R = Pr^i$, $CH_2CH(Et)Bu^n$, the equilibrium mixture contains structures **12** and **13** and for $R = Bu^t$, *tert*-$C_5H_{11}$, structures **12**–**14**.




R = $Pr^i$, $Bu^t$, *tert*-$C_5H_{11}$, $CH_2CH(Et)Bu^n$.

Meanwhile, tri(n-butoxy)titanium methacrylate containing less bulky n-butoxy groups forms dimer **15** in which titanium atoms are linked by carboxyl or butoxy bridges.




The four-membered rings formed upon chelate coordination of the carboxylate group are usually highly strained. No

**Table 2**. Structural parameters of the RCOO group.

| Compound | $\nu_{as}$ /$cm^{-1}$ | $\nu_s$ /$cm^{-1}$ | $\Delta\nu$ /$cm^{-1}$ | Coordination mode | Distance M–O /Å | Ref. |
|---|---|---|---|---|---|---|
| $Cu_2(O_2CC(Me)=CH_2)_4(H_2O)_2$ | 1572 | 1415 | 157 | **B** | | 39 |
| $Cu(O_2CC(Me)=CH_2)_2(BIm)_2$ | 1564 | 1361 | 203 | **A** | 1.9752(7) [a] | 39 |
| $Cu_2(O_2CC(Me)=CH_2)_4(BIm)_2$ | 1583 | 1420 | 163 | **B** | 1.961, 1.994 | 39 |
| $Ti(OBu^n)_3(O_2CC(Me)=CH_2)$ | 1556 | 1424 | 132 | **B** | | 69 |
| $Ti(OPr^i)_3(O_2CC(Me)=CH_2)$ | 1561, 1516 | 1424 | 137, 92 | **B**, **C** | | 69 |
| $Ti(OBu^t)_3(O_2CC(Me)=CH_2)$ | 1588, 1550, 1525 | 1425 | 163, 125, 100 | **B**, **C** | | 69 |
| $Ti(OC_5H_{11}$-*tert*$)_3(O_2CC(Me)=CH_2)$ | 1586, 1554, 1517 | 1423 | 163, 131, 94 | **B**, **C** | | 69 |
| $Ti(OCH_2CH(Et)Bu^n)_3(O_2CC(Me)=CH_2)$ | 1556, 1519 | 1423 | 133, 96 | **B**, **C** | | 69 |
| $[CuLa(O_2CC(Me)=CH_2)_5(phen)(EtOH)]_2$ | 1550 | 1419 | 131 | | 2.484,[b] 2.582 [c] | 86 |
| $Ca(O_2CCH_2CH=CH_2)_2 \cdot H_2O$ | 1582, 1547 | | | **B**, **C** | 2.318(15)–2.356(13),[b] 2.597(13)–2.562(14) [c] | 33 |
| $LiO_2CC(Me)=CH_2$ | 1572 | 1423 | 149 | | | 31 |
| $NaO_2CC(Me)=CH_2$ | 1558 | 1419 | 139 | | | 31 |

[a] The C=O [1.2620(13) Å] and C–O [1.2452(13) Å] distances were also found; [b] the distance to the bridging metal ion; [c] the distance to the metal ion in the chain.

**Table 3**. Magnetic properties of metal (meth)acrylates.

| Compound | $\mu_{eff}/\mu_B$ | | Antiferromagnetic exchange | Ref. |
|---|---|---|---|---|
| | 295 K | 78 K | | |
| $Cu_2(O_2CCH{=}CH_2)_4 \cdot 2\,EtOH$ | 1.40 | 0.22 | strong exchange | 37 |
| $Cu_2(O_2CC(Me){=}CH_2)_4 \cdot 2\,H_2O$ | 1.35 | – | – | 40 |
| $Cu_2(O_2CC(Me){=}CH_2)_4 \cdot 2\,Py$ | 1.39 | – | – | 40 |
| $Cu_2(O_2CC(Me){=}CH_2)_4 \cdot 2\,(4\text{-}VPy)$ | 1.45 | – | – | 40 |
| $Cr_2(O_2CC(Me){=}CH_2)_4 \cdot 4\,H_2O$ | 1.45 | 1.22 | exchange | 60 |
| $[CuLa(O_2CC(Me){=}CH_2)_5(phen)(EtOH)]_2$ | 1.95 | 1.91 | no exchange | 86 |
| $Co(O_2CCH{=}CH_2)_2 \cdot H_2O$ | 5.10 | 4.53 | the same | 37 |
| $Ni(O_2CCH{=}CH_2)_2 \cdot H_2O$ | 3.60 | 3.47 | " | 37 |
| $Fe(O_2CCH{=}CH_2)_2 \cdot 2\,H_2O$ | 4.92 | 4.35 | " | 86 |

such strain is present in rare earth compounds, and the possibility of bidentate chelating coordination increases. Apparently, strain relief is facilitated by the higher polarity of the metal – ligand bond and high coordination numbers of the lanthanide atom. For example, in the heteronuclear $Cu_2La_2$ (see Refs 86, 89) and CoCe complexes [113] with methacrylate ligands, the lanthanide atom bears both the bridging and chelating RCOO groups. Transition from the bridging to chelating coordination of the RCOO group results in elongation of the MO bonds (see Table 2).[33]

It is noteworthy that even in essentially ionic compounds, for example, in lithium and sodium methacrylates,[31] the $\Delta\nu$ values may deviate from those for purely ionic salts and the degree of covalence of the metal – ligand bond may increase.‡

**b. Magnetic properties**

Antiferromagnetic interactions play an important role in the studies of the nature of the metal – metal bond and the structure of metal carboxylates. The effective magnetic moments for a number of copper (meth)acrylates are 1.4 $\mu_B$ ($\mu_B$ is the Bohr magneton), which is much lower than the purely spin values and is consistent with the dimeric structure of the corresponding carboxylates (Table 3). The temperature dependence of the magnetic susceptibility ($\mu_{eff}$) in these systems attests to strong antiferromagnetic exchange interactions of the unpaired electrons of the metal ions, which may be either direct or occur through the OCO bridge.

Most often, carboxylates of divalent transition metals, Mn, Fe, Co, Ni, have the composition $M_2(O_2CR)_2L$ or $M_4(O_2CR)_2L$ (L = $H_2O$, ROH, Py, *etc.*) and are monomeric.[15] This fact is confirmed by the lack of exchange interactions in (meth)acrylate complexes of these metals. According to magnetic measurement data, these compounds are high-spin octahedral complexes the $\mu_{eff}$ values of which change only slightly with temperature (see Table 3). The magnetic susceptibility values of methacrylate heteronuclear CuLa [86] and CuTb complexes [87] correspond to the presence of two uncoupled spins of copper ions. Over the whole temperature range studied, the magnetic susceptibility obeys the Curie – Weiss law with relatively low Weiss constants ($\Theta = -0.82$ K), *i.e.*, the exchange interactions between the copper atoms are weak.

‡ The predominantly covalent nature of the Ti – O bond was established for the cyclopentadienyl Ti(III) maleate and fumarate derivatives [64] the molar conductivities of which in methanol are 18.3 and 6.0 $cm^2\ \Omega^{-1}\ mol^{-1}$, respectively (for $Cp_2TiCl_2$, the conductivity is 86.4 $cm^2\ \Omega^{-1}\ mol^{-1}$).

**c. Crystallographic studies**

On the basis of spectral data alone, it is impossible to establish exactly the bond nature and the ligand coordination mode in metal carboxylates. However, crystallochemical studies of unsaturated carboxylates are few.

The X-ray diffraction data available from the literature are mainly concerned with copper and lanthanide complexes. The (meth)acrylate complexes $[Cu_2(O_2CCH{=}CH_2)_4(EtOH)_2]$. .(EtOH), $Cu_2(O_2CCH{=}CH_2)_4(MeOH)_2$,[114] $Cu(O_2CC(Me){=}CH_2)_2(BIm)_2$, $Cu_2(O_2CC(Me){=}CH_2)_4(BIm)_2$,[39] $Cu(O_2C$. .$C(Me){=}CH_2)_2(bipy)_2$ (bipy is 2,2′-bipyridine),[115] $Cu_2(O_2C$. .$C(Me){=}CH_2)_4[(NH_2)_2CO]_2$,[116] $Eu(O_2CC(Me){=}CH_2)_3$,[117] $[La(O_2CC(Me){=}CH_2)_3(phen)(CH_2{=}C(Me)CO_2H)]_2$ [118] and heteronuclear compounds $[CuLa(O_2CC(Me){=}CH_2)_5(phen)$. .$(EtOH)]_2$,[86] $[CuNd(O_2CC(Me){=}CH_2)_5(phen)(EtOH)]_2$,[89] $NdZn_2(O_2CC(Me){=}CH_2)_6(phen)(EtOH)$ [88] were studied.

A typical feature of the compounds considered, as well as their saturated analogues, is the formation of binuclear lantern type complexes $LM(RCOO)_4ML$. For example, in copper acrylate (Fig. 2), the copper atoms are bound into binuclear complexes by four $\mu_2$-O,O′-acrylate groups, the apical ligands being represented by various donor molecules (ethanol, methanol, benzimidazole, bipyridine, phenanthroline).

According to X-ray diffraction data, the coordination of copper atoms in these compounds is square pyramidal with a typical elongation of the apical bond.[39, 114] The C – O bond lengths vary insignificantly, indicating π-electron delocalisation in the carbonyl groups and the bidentate bridging coordination mode. According to the results of different researchers, the Cu – Cu distances are 2.609 and 2.617,[37] 2.662 [39] or 2.609 Å.[116] Changes in the steric conditions of the packing of complexes and in the nature of the axial ligands induce the metal atom to deflect from the equatorial plane of the oxygen atoms, *i.e.*, result in an increase in the Cu – Cu distance. Although the relatively short distances (2.61 – 2.66 Å) allow

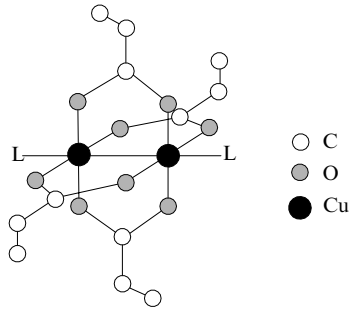
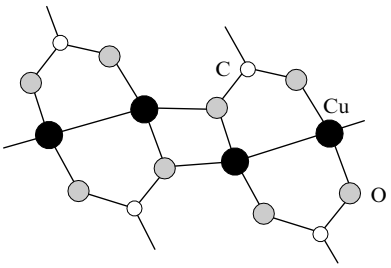



**Figure 2.** Fragment of the structure of copper(I) acrylate.[37, 114]

the existence of the direct metal–metal bond, it is not always obvious whether the exchange interactions between the metal atoms occur directly or through a bridge. Therefore, the statement [39] of direct strong metal–metal interaction in the benzimidazole complex $Cu_2(O_2CC(Me)=CH_2)_4(BIm)_2$ does not appear adequately substantiated without invoking physicochemical data on the magnetic and resonance properties. The C=C double bonds in the complexes in question have usual lengths (1.32–1.36 Å); hence, these bonds are not involved in the additional coordination to the metal atom.

The above-described dimers can be combined into oligomeric and polymeric structures.




Most often, the axial ligands in these complexes are represented by the oxygen atoms of the neighbouring carboxylate fragments; this gives rise to chains. The monovalent copper acrylate ($CuO_2CCH=CH_2$) has a similar structure.[60] The carboxylate groups occupy the *trans*-position relative to each other and the neighbouring fragments are bound into ribbons by additional Cu–O bonds, *i.e.*, acrylate ions behave as tridentate ligands.

The competition between the carboxyl groups and the outer-sphere ligands for the formation of strong bonds with the metal is known to be an important factor determining the structure of carboxylate complexes. In some cases, this may result in a change in the structure of the carboxylate ligand. In particular, in the presence of a donor ligand, imidazole (Im), the mononuclear copper methacrylate $Cu(O_2C.C(Me)=CH_2)_2(Im)_2$ is formed in addition to the dimer $Cu_2(O_2CC(Me)=CH_2)_4(Im)_2$.[119] The former complex has a square planar structure owing to copper coordination to two monodentate methacrylate groups and to imidazole molecules in the equatorial plane. Each molecule is connected to four neighbouring molecules by a system of hydrogen bonds, which favours the formation of a 2D supramolecular structure. In some cases, the replacement of ligands by other ligands is accompanied by reduction of the metal ion, as was observed in the prepatation of the mixed-valence complex $Cu^{I}_2Cu^{II}_2(O_2C.C(Me)=CH_2)_6(PPh_3)_4(MeOH)_2$ from the corresponding binuclear Cu(II) methacrylate crystal hydrate.[120]

## 4. Metal dicarboxylates

The presence of two carboxyl groups in dicarboxylic acid molecules extends the scope of their functional properties as ligands and increases the structural diversity of the resulting metal carboxylates. Depending on the nature of the metal and reaction conditions, monosubstituted acid salts, linear or 3D coordination polymers are formed most often.

### a. Monomeric salts

Acid maleates $M(cis\text{-}O_2CCH=CHCO_2H)_2 \cdot n H_2O$ ($n$ = 4, 6) with Co,[121] Fe,[122] Ni,[123] Zn,[124] Mn [125] and Mg [126, 127] cations have been studied in most detail. In these centrosymmetric complexes, the metal atom is linked to two monodentate maleic acid residues, the octahedral metal coordination being completed by two water molecules. The planar structure of the maleate ligand in these complexes is stabilised by the formation of an intramolecular hydrogen bond. Note that the binuclear complex $[Cu_2(trans\text{-}O_2CCH=CHCO_2)(phen)_4](trans\text{-}O_2C.CH=CHCO_2) \cdot 11 H_2O$ (**16**) [25] contains two non-equivalent fumaric acid residues, one being a bridge connecting two copper atoms and the other functioning as a counter-ion. The $COO^-$ groups are coordinated to the metal as monodentate ligands ($\Delta\nu = 197$ cm$^{-1}$).

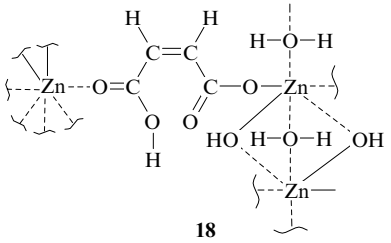
The acyl derivatives of metallocenes appear in diverse structural types including mononuclear, binuclear and tetranuclear complexes. The reaction of $Cp_2TiCl_2$ with acetylenedicarboxylic acid at room temperature in a two-phase system yields the binuclear carboxylate $[Cp_2Ti(\mu\text{-}O_2CC\equiv CCO_2)]_2$ (**5**), while in the presence of phase transfer catalyst ($Bu^n_4NBr$) and at lower temperatures, the isostructural tetranuclear compound $[Cp_2Ti(\mu\text{-}O_2CC\equiv CCO_2)]_4 \cdot 5 CH_2Cl_2$ (**17**) is formed.[66] The formation of macrocyclic complex **17**, obviously, in the presence of solvent molecules fitting the central cavity of the macrocycle is more favourable.

The monomeric structures of dicyclopentadienyltitanium(III) maleate and fumarate were confirmed by spectroscopic and magnetic measurements.[64] According to IR spectroscopy, the $\Delta\nu$ values are relatively low (75 cm$^{-1}$ for maleate and 100 cm$^{-1}$ for fumarate), which corresponds to symmetrically bound carboxyl groups with chelating coordination. As in the case of monomeric complexes of metal (meth)acrylates, relatively low Weiss constants (−4 K) indicate that exchange interactions in these systems are weak. However, parameters of the antiferromagnetic exchange interactions (the exchange interaction constant $J = -1.6$ cm$^{-1}$ and $g$-factor is 1.98) in $Cp_2Ti(trans\text{-}O_2CCH=CHCO_2)TiCp_2$ are similar to those found for the saturated analogue containing a succinate bridge.[65] This means that a multiple bond does not affect intramolecular exchange interactions which are mainly accomplished through overlap of the σ-orbitals.

### b. Coordination polymers

As noted above, the polydendate nature of dicarboxylic acids, on the one hand, and the tendency of the central metal ion toward coordination saturation, on the other hand, are important factors that favour the formation of polymeric structures. These systems are stabilised through the formation of additional intra- and intermolecular hydrogen bonds.

Thus zinc hydrogen maleate $Zn(cis\text{-}O_2CCH=CH.CO_2H)OH \cdot H_2O$ (**18**) has a polymeric structure consisting of metal atoms connected through dicarboxylate bridges.[34]




**18**

In metallopolymer **18**, each zinc ion forms two covalent bonds with one hydrogen maleate group and one hydroxyl group and four coordination bonds with the hydrogen maleate group and hydroxyl group of neighbouring molecules and two water molecules. Thus, the hydrogen maleate ligand connects two zinc atoms giving rise to a helical macromolecular chain typical of the *cis*-configuration of the starting acid. Owing to

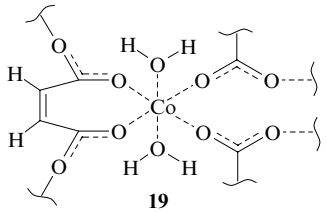
**Table 4**. Ferromagnetic properties of metal dicarboxylates.[12, 25]

| Compound | $J$ /cm$^{-1}$ | $g$ | $\Theta$ /K | $\mu_{eff}/\mu_B$ ($T$/K) |
|---|---|---|---|---|
| Cu(*cis*-$O_2CCH{=}CHCO_2$)·$H_2O$ | + 4.3 | 2.0 | +8 | 4.4 (5.9)<br>1.9 (66) |
| Cu(*trans*-$O_2CCH{=}CHCO_2$)·2 $H_2O$ | +1.05 | 2.09 | + 3.2 | – |
| [$Cu_2$(*trans*-$O_2CCH{=}CHCO_2$)(phen)$_4$](*trans*-$O_2CCH{=}CHCO_2$)·11 $H_2O$ (**16**) | −34 (2$J$, <130 K)<br>+17 (2$J$, >130 K) | 2.20<br>2.03 | –<br>– | 1.73 (75.4)<br>1.80 (145.4) |

the intermolecular interactions of the hydroxyl groups connecting the zinc atoms of neighbouring threads, a secondary structure of the polymer is formed like a several-wire twisted cable. Thermal dehydration of compound **18** affords a powdered anisotropic product [ZnH(*cis*-$O_2CCH{=}CHCO_2$).$(OH)]_n$.

The planar structure and the *cis*-arrangement of the carboxyl groups in the maleic acid molecule accounts for its proneness to form metal chelates. The valence bonds with the metal can be formed by both carboxyl groups of maleic acid (denticity >4); therefore, in most cases, seven-membered chelate rings are formed.[12, 121, 128, 129]

This type of chelation is observed in cobalt(II) maleate trihydrate (**19**);[121, 130] the $Co^{2+}$ coordination polyhedron is a distorted octahedron. The acid residue connected to the metal ion through two oxygen atoms of the carboxyl groups forms a seven-membered chelate ring.[121]



**19**

The coordination of oxygen atoms to the cobalt atoms gives rise to a three-dimensional framework structure. Maleic acid acts in this case as a tetradentate ligand, and the coordination octahedron comprises additionally two $H_2O$ molecules in *cis*-positions relative to each other. The third water molecule is water of crystallisation. A polymeric structure is also typical of a bimetallic CuZn complex with a maleate fragment.[102]

As was to be expected, in the case of *trans*-isomer, fumaric acid, the formation of chelate structures is hampered since the functional groups are remote from each other. Thus in the cobalt(II) fumarate pentahydrate [Co(*trans*-$O_2CCH{=}CH.CO_2$)·4 $H_2O]_n$·$n$ $H_2O$ (**20**), two oxygen atoms of different carboxyl groups link the neighbouring cobalt atoms in the monodentate mode thus functioning as bridges.[121, 131] Four $H_2O$ molecules complete the metal coordination polyhedron to an octahedron, the fifth water molecule being water of crystallisation. Two crystallographically independent Co atoms are located in special positions at a twofold axis, giving rise to an infinite chain of a coordination polymer with *cis*-arranged fumaric acid residues. The water molecules of crystallisation form strong hydrogen bonds (2.69–2.73 Å) with the polymeric chains thus joining the chains into a three-dimensional framework.

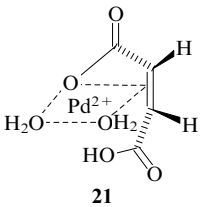
A typical feature of coordination polymers of itaconates Cd[$O_2CC(=CH_2)CH_2CO_2$]($H_2O$)$_2$ (Ref. 51) and Ba[$O_2C.C(=CH_2)CH_2CO_2$]$_2$($H_2O$)[52] is the presence of short (<4.2 Å) contacts between the double bonds of neighbouring molecules, which creates conditions for polymerisation of these compounds on heating or irradiation.

One more important feature of metal carboxylates related to their polymeric structure, first of all, layered 2D or 3D structure, is ferromagnetism of some complexes of this type. In copper(II) maleate monohydrate,[12] the $Cu^{2+}$ ion has a square pyramidal coordination and each maleate group connects three copper atoms thus forming polymeric layers linked by hydrogen bonds. These features of the crystal structures result in long-range interactions in the system. An increase in the magnetic moment at low temperatures and positive Weiss constant suggest ferromagnetic nature of these interactions (Table 4). It was shown[132] that the molecule of copper(II) hydrogen maleate tetrahydrate has a lower $J$ parameter (+0.6 cm$^{-1}$), *i.e.*, superexchange interactions between the metal atoms through water molecules are not so effective as those through maleate bridges. Weak antiferromagnetic and ferromagnetic interactions were also found in the copper fumarate complex with phenanthroline (**16**)[25] and in the compound {[$Dy_2(O_2CCH{=}CHMe)_6(H_2O)$]·0.5 (MeCH=CH.$CO_2H$)·$H_2O$}$_n$.[133]

**c. π-Complexes**

The presence of effective π-dative interactions in the molecules of unsaturated metal carboxylates has a pronounced effect on the geometry of carboxyl groups. For example, in copper hydrogen maleate hydrate, Cu(*cis*-$O_2CCH{=}CHCO_2H$)··$H_2O$,[26] the metal atom forms a π-bond with the doubly bonded carbon atoms [as a result, the C=C bond length increases to 1.405(10) Å]. In a similar silver(I) complex with maleic acid, the double bond in the hydrogen maleate ion does not participate in the coordination to metal; therefore, the C=C double bond length [1.336(8) Å] and the geometry of the carboxyl groups are similar to these parameters for free maleic acid. In the polymeric complex [$Ag_2$(*cis*-$O_2CCH{=}CHCO_2$)]$_n$, one silver ion is coordinated by the double bond of the maleate anion [the Ag–C distances are 2.448(5) and 2.529(4) Å][134] and thus acquires a tetrahedral configuration, whereas the other Ag atom, which does not form π-bonds, has a pseudo-trigonal-pyramidal configuration. It is noteworthy that this type of π-complexes are relatively stable[135, 136] unlike organometallic compounds in which the olefinic ligand is connected to the metal only through a $\eta^2$-bond.[137–139] Apparently, owing to the presence of the metal–oxygen bond, the carboxylate anion is firmly incorporated into the crystal lattice, thus preventing the insertion of the $O_2$ or $H_2O$ molecule into the metal–olefin bond as in the case of copper(I) fumarate.[57]

For maleic acid, the *cis*-positions of the carboxyl groups with respect to the M–O bond is practically possible but sterically unfavourable. This may create an asymmetric ligand coordination. For example, the reaction of palladium(II) with maleic acid results in asymmetric olefin carboxylate chelate **21**.[62]

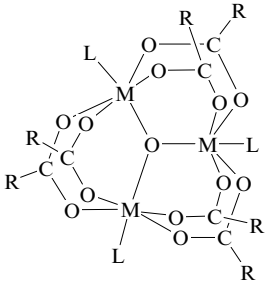


**21**

The $^1$H NMR spectrum of compound **21** exhibits signals for two non-equivalent protons at $\delta$ 4.2 and 3.3 corresponding to coordinated maleic acid; in the 2D proton-decoupled $^{13}$C NMR spectrum, the signals of the alkene carbon atoms occur at higher fields ($\Delta\delta \approx 58$ and 107 ppm) than in the case of free acid ($\delta$ 131). The observed shift ($\Delta\delta \approx 80$ ppm) is typical of metal alkene complexes.[140] Note that complex **21** is much more stable than other Pd(II) carboxylate complexes.[141]

## 5. Unsaturated metal μ-oxo-carboxylates

Trinuclear oxo-centred carboxylates derived from saturated acids and transition metals $[M_3O(O_2CR)L_3]^{n+}$ (R = H, Me, Ph, *etc.*; L = $H_2O$, Py, *etc.*) are widely used as oxidation catalysts of many organic substrates [142, 143] and as models of metalloprotein active sites.[144, 145] Intensive studies of their structures and spectroscopic, magnetic and redox properties are currently in progress.[146–150] In compounds containing metal oxo-carboxylate fragments, the oxygen atom is located in the plane through the three surrounding metal atoms, which form a nearly regular triangle and the carboxylate groups form bridges between the metal atoms.



Polynuclear transition metal complexes with unsaturated carboxylate ligands are little studied, the first data being obtained rather recently.[60, 151–153] These compounds are also of interest, first of all, for the preparation of metal-containing polymers with unusual structures and properties.

The $COO^-$ stretching frequencies observed for these oxo complexes suggest a bridging mode of coordination of the carboxylate ligands. However, the IR spectra of iron(III) [38] and chromium(III) [153] acrylates exhibit very strong bands at 1515–1520 and 1435–1440 $cm^{-1}$, which can be assigned to antisymmetric and symmetric stretching vibrations of the carboxyl group coordinated in the bidentate chelating mode.

When no X-ray diffraction data are available, the cluster structures of the compounds of interest are often confirmed by mass spectrometric analysis with extraction of ions from a solvent. Thus it was reported [38] that in the mass spectrum of iron(III) acrylate, ions with $m/z$ 539, 468 and 397 correspond to the elimination of one, two or three acrylate fragments from the molecular ion $[Fe_3O(O_2C.CH{=}CH_2)_6]^+$, and the ion with $m/z$ 341, to the elimination of the $Fe(O_2CCH{=}CH_2)_3$ molecule. A cluster structure is confirmed also by EXAFS data. In iron(III) maleate,[154] the Fe–Fe bond length is 3.29 Å and the distances to the bridging oxygen atom and to the oxygen atoms of the ligand environment are in good agreement with the distances determined by X-ray crystallography for the complex $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-betaine})_6(H_2O)_3]ClO_4 \cdot 7\,H_2O$.[155]

X-Ray crystallography data on unsaturated metal μ-oxo-carboxylates are quite limited and refer mainly to polynuclear zirconium and titanium alkoxy derivatives. For example, the complex $Zr_6(OH)_4O_4(O_2CC(Me){=}CH_2)_{12}$ (**22**) [72] is composed of the octahedral core $Zr_6O_4(OH)_4$ in which the triangular faces of the $Zr_6$ octahedron are covered with $\mu_3$-O and $\mu_3$-OH 'caps' and the chelating or bridging methacrylate ligands occupy the remaining Zr coordination vacancies. Thus, the coordination sphere of each Zr atom consists of two $\mu_3$-O atoms, two $\mu_3$-OH groups and four O atoms of the methacrylic acid. Note that structural parameters of this complex determined from the Zr-K edge EXAFS spectra are in good agreement with X-ray diffraction data.[156] Unlike cluster **22** described as spherical, in the heteronuclear oxo carboxylates $Ti_2Zr_4O_4(OBu^n)_2[O_2CC(Me){=}CH_2]_{16}$ (Ref. 83), metal atoms form oblong zigzag-like chains made of dodecahedral ([$ZrO_8$]) and octahedral ([$TiO_6$]) units.

X-Ray crystallography data were obtained for a number of titanium oxo clusters: $Ti_6O_4(OEt)_8(O_2CC(R){=}CH_2)_8$,[157, 158] $Ti_4O_2(OPr^n)_8(O_2CC(R){=}CH_2)_8$ (Ref. 158), $Ti_4O_2(OPr^i)_6 \cdot (O_2CC(R){=}CH_2)_6$ (Refs 157 and 158) and $Ti_9O_8(OPr^n)_4 \cdot (O_2CC(R){=}CH_2)_{16}$ (Ref. 159) (R = H, Me). The cluster $Ti_9O_8(OPr^n)_4(O_2CC(Me){=}CH_2)_{16}$ contains the largest number of carboxylate ligands per Ti atom (1.78).[80] Therefore, the molecule has a rather open structure representing a ring of six vertex-sharing octahedra and two edge-sharing octahedra. In this compound, only two oxo bridges have $\mu_3$-coordination and the other six bridges have $\mu_2$-coordination. An uneven alternation of methacrylate bridges and alkoxy groups gives rise to an unsymmetrical macrocycle.

It can be seen from the above data that unsaturated metal carboxylates, like their saturated analogues, exist as diversified structures ranging from mono- or binuclear ones to clusters and polymeric complexes. The type of bonding between the carboxyl group and the metal atom ranges from purely ionic to covalent. The bidentate bridging and bidentate chelating modes of coordination of the carboxylate ligand are most abundant; the monodentate coordination is less common and these are often encountered within one molecule. A specific feature of the unsaturated carboxylate ligand is the ability of involvement in the formation of π-complexes with metal atoms. These complexes are typical first of all of copper(I), silver(I) and palladium(II) carboxylates. Almost all of the above types of coordination were confirmed by X-ray crystallography. Examples of different structures formed from unsaturated metal carboxylates can be found elsewhere.[117, 129, 160–164]

# III. Polymerisation and copolymerisation of salts of unsaturated carboxylic acids

In most cases, polymeric metal salts are prepared by radical polymerisation, which comprises the same elementary steps as for conventional monomers. The steady-state rate of radical polymerisation ($W_p$) is described by the known equation

$$W_p = \frac{d[M]}{dt} = k_p \left(\frac{k_i}{k_t}\right)^{0.5} [M][I]^{0.5}, \qquad (1)$$

where $k_i$, $k_p$ and $k_t$ are the rate constants for chain initiation, propagation and termination; [M] and [I] are the concentrations of the monomer and the initiator.

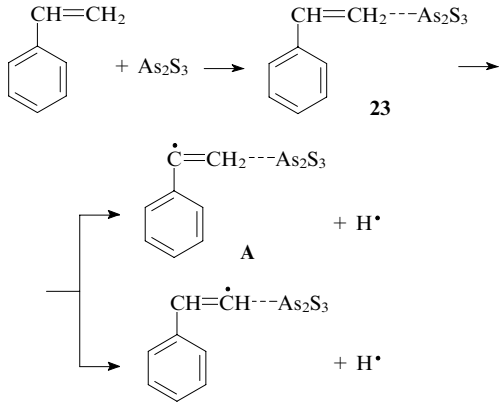
Deviations from Eqn (1) are due to specific features of the monomers used.

It is noteworthy that determination of the molecular masses of metallopolymers is faced with certain difficulties. Of direct methods, gel permeation chromatography (GPC) and ebullioscopy are suitable, but still only in some particular cases, while indirect methods for molecular mass determination can be used only if the metal has been removed from the final product (for example, by treatment with, or dialysis against, HCl, by ion exchange, displacement by zinc amalgam in an HCl solution in water or methanol, by treatment with sodium ethylenediaminetetraacetate, and so on). The molecular masses of the polymers thus formed are most often relatively low. Thus polymerisation of maleic acid salts (initiated by *tert*-butyl hydroperoxide) at 80 °C for 4–10 h results in the formation of a polymer with a number-average molecular mass ($M_n$) ranging from 300 to 5000.[165]

Chain transfer involving the initiator plays a significant role in the polymerisation processes of metal-containing monomers. Indeed, in the polymerisation of tributyltin acrylate, it was found [166] that the initiator, azobis(isobutyronitrile) (AIBN), is a more potent chain transfer agent than lauryl peroxide (the relative constants for chain transfer to initiator are 0.087 and 0.015, respectively).

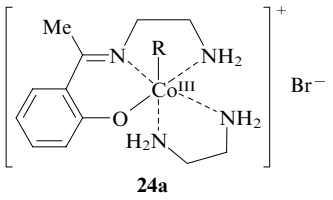
## 1. Types of initiation

The radical polymerisation of the salts of unsaturated carboxylic acids can be induced by any initiator or initiating radiation. However, azobis(isobutyronitrile), benzoyl peroxide (BP), potassium or ammonium persulfates, $H_2O_2$, *tert*-butyl hydroperoxide, various redox systems are used most often. The radical polymerisation of metal acrylates has been initiated by the styrene–arsenic sulfide complex (**23**),[167] which decomposes in a polar medium according to the donor-acceptor mechanism to give the H$^{\bullet}$ radical. The formation of more stable tertiary radical **A** is probably the preferable reaction route.




The kinetic parameters of the polymerisation process in the presence of complex **23** (see below) correspond to the classical radical polymerisation equation, as is also indicated by the power dependence of the viscosity ($\eta$) of the resulting polymer on the initiator concentration: $\eta = f([I]^{0.5})$.

Alkylcobalt chelates [RCo(7-Me-sal-en)(en)]Br (**24a**) [7-Me-sal-en is *N*-(7-methylsalicylidene)ethylenediamine, en is ethylenediamine] containing tridentate Schiff bases proved to be efficient initiators of low-temperature radical polymerisation of some metal acrylates in the presence of acidic reagents.[168]




**24a**

R = Me, Et, Pr$^{i}$.

It is known [169] that complexes **24a** generate alkyl free radicals upon treatment with an acid under mild conditions. Polymerisation of magnesium, zinc, barium and lead diacrylates ($MAn_2$) induced by these organocobalt initiators proceeds at 5–10 °C even in the absence of acidic additives. Apparently, the function of acidic reagents in these reactions is played by monomers themselves for which the degree of dissociation ($K_d$) in methanol is rather high: at 20 °C it is equal to $3.22 \times 10^{-5}$, $3.15 \times 10^{-5}$ and $2.60 \times 10^{-5}$ for Zn, Pb and Ba salts, respectively.[170] The $MAn^+$ cations can be coordinated by ethylenediamine giving rise to the active form of the initiator, complex **24b**.

$$MAn_2 \rightleftharpoons MAn^+ + An^-,$$

$$[RCo(7\text{-Me-sal-en})(en)]^+ + MAn^+ \overset{MeOH}{\rightleftharpoons}$$

**24a**

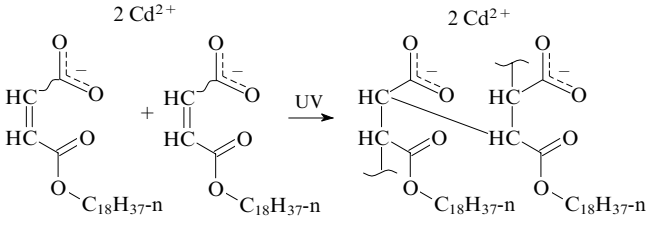
$$\rightleftharpoons [RCo(7\text{-Me-sal-en})(MeOH)_2]^+.$$

**24b**

The rate of diacrylate polymerisation depends on the nature of the metal and decreases in the series Zn > Mg > Ba, which is in line with the change in the acidity of the $M^{2+}$ cation. As expected, the obtained metal polyacrylates had higher molecular masses and high syndiotacticity (see below).

Polymerisation of metal carboxylates in the solid state [32, 33, 54, 171] and under matrix devitrification conditions [172] is often initiated by $\gamma$-radiation. Owing to relatively low activation energies for the formation of free radicals, the radiation initiation is effective over a broad temperature range, primarily at low temperatures. For example, the overall activation energy for emulsion polymerisation of sodium acrylate in the presence of $K_2S_2O_8$ is equal to 94.8 kJ mol$^{-1}$, whereas for $^{60}$Co-$\gamma$-induced polymerisation this value is equal to 16.7 kJ mol$^{-1}$ (Ref. 30).

Examples of photoinduced polymerisation are documented. Note that the metallopolymers obtained using UV irradiation have a more regular molecular packing compared to the thermally initiated reaction products. Thus in the Langmuir–Blodgett films based on cadmium octadecylfumarate or -maleate,[173] the polymer formed had the same orientation of the aliphatic part of the chain irrespective of the double bond configuration in the starting monomer.




Photoinduced polymerisation ($\lambda = 365$ nm) of liquid-crystalline metallomonomers with terminal acrylate groups gave highly oriented anisotropic polymers in good yield (up to 80%) with quantitative content of the metal.[58]

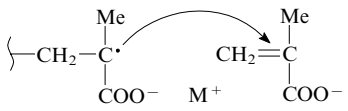
Controlled radical polymerisation in the presence of catalytic amounts of transition metal halides by the ATRP (Atom Transfer Radical Polymerization) mechanism has been actively developed in recent years.[174–176] These controlling additives are capable of reversible interaction with reactive radicals in the reaction system to give labile adducts, which creates conditions for 'living-chain' radical polymerisation. Ashford *et al.*[177] reported the first example of ATRP polymerisation of a metal-containing monomer, namely, sodium methacrylate. The process occurs in an aqueous solution at 90 °C in the presence of a macroinitiator based on poly(ethylene oxide), copper(I) bromide catalyst and 2,2′-bipyridine in a 2:2:5 molar ratio. At pH < 6, the reaction does not take place, which may be due to protonation of bipyridine and the lack of solubility of the catalyst under these conditions. The resulting poly(ethylene oxide-block-sodium methacrylate) copolymer had a relatively low molecular masses and narrow polydispersity (1.2–1.3). Recently a similar method has been used to carry out polymerisation of sodium methacrylate on the surface of various substrates modified by an initiator of ATRP polymerisation.[178,179] This procedure gives polyelectrolyte layers of controlled composition, thickness and density.

Published data on the initiation of anionic or cationic polymerisation of the considered monomers are virtually missing. To our knowledge, only one example of anionic polymerisation of sodium methacrylate under the action of phenylmagnesium bromide at −5 to 2 °C has been reported.[180]

## 2. Kinetic and stereochemical effects of polymerisation processes

### a. Radical polymerisation of alkali and alkaline earth metal salts of unsaturated carboxylic acids

The main data on the polymerisation of alkali and alkaline earth metal salts are comprehensively presented in a monograph.[3] The specific features of this process are described using the hypothesis of the kinetic role of ionic pairs in the radical polymerisation of the ionising monomers formulated and developed in a monograph.[181] According to this hypothesis, at pH > 7 the chain propagation rate is determined only by the rate of the reaction of macroradicals with the terminal ion pair. The observed kinetic effects are interpreted from the standpoint of change in the reactivity of macroradicals: the growing ionised macroradicals are either separated ion pairs or ionic associates. Within the framework of these views, in the polymerisation of metal-containing monomers the metal cation acts as a counter-ion the nature of which (the charge, the electrostatic and crystallographic radii, solvation ability) affects the stability of ion pairs and the chain propagation rate.




One of the first quantitative studies of polymerisation of magnesium, strontium, barium and calcium acrylates was performed in 1955.[182] The effects of concentrations of the monomer and the $K_2S_2O_8-Na_2S_2O_3$ initiating system and temperature on the yield of the polymerisation product of $Ca(O_2CCH{=}CH_2)_2$ were studied (Fig. 3 *a–c*).

The activation energy (134.2 kJ mol$^{-1}$) and the rate constants for initiation of radical polymerisation of lithium methacrylate at various temperatures

| $T$/K | 333 | 338 | 343 |
|---|---|---|---|
| $2k_df \times 10^5$/s$^{-1}$ | 3.30 ± 0.02 | 6.19 ± 0.21 | 14.31 ± 0.60 |

where $k_d$ is the constant for initiator decomposition, $f$ is the initiation efficiency coefficient, were estimated [183] using inhibition by a stable radical, *N*,*N*-diphenyl-*N*′-picrylhydrazyl.

Polymerisation of akaline earth metal acrylates initiated by ammonium persulfate was studied.[184] The dependences of the rates of these reactions on the initial monomer concentration are presented in Fig. 4 *a–c*. The maximum polymerisation rates ($W_{max}$) were found and the molecular masses of the resulting polymers were determined:

| Metal | Mg | Ca | Sr |
|---|---|---|---|
| $10^6$ $W_{max}$/mol litre$^{-1}$ s$^{-1}$ | 160 | 433 | 400 |
| $10^{-3}$ $M_n$ | 92.5 | 848 | 990 |

The differences in the polymerisation rates and the $M_n$ values of polymers were attributed to different charge density on the macroradical anion determining the interactions in the growing macroradical–monomeric anion system.

It was found [185] that the polymerisation rate of sodium methacrylate in concentrated aqueous solutions in the presence of $K_2S_2O_8$ obeys zero-order kinetics, *i.e.*, the rate does not depend on the initial monomer concentration, while the order with respect to the initiator is 0.51 ± 0.20. The presence of metal in the monomer molecule does not prevent the emulsion (latex) polymerisation (in the usual emulsion polymerisation, salts cause coagulation of the latex). Emulsion polymerisation

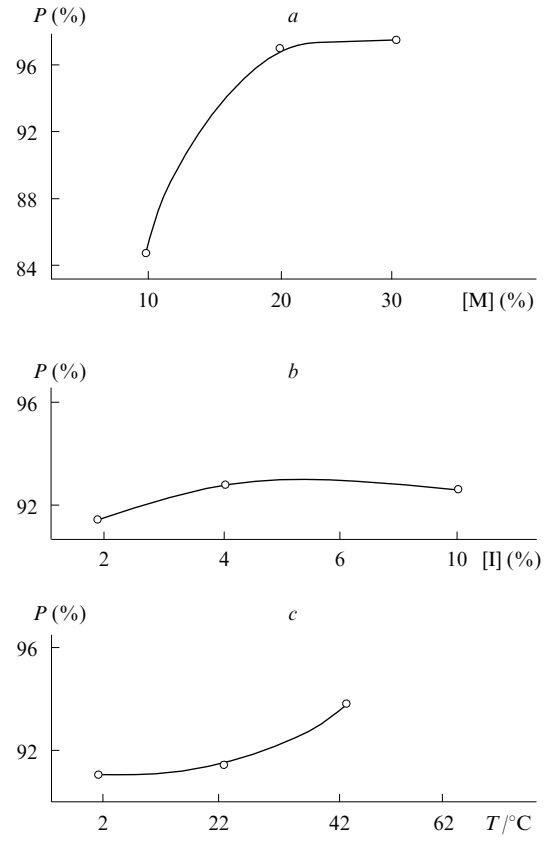



**Figure 3.** Yield of calcium polyacrylate *vs.* monomer (*a*) and initiator (*b*) concentrations and *vs.* polymerisation temperature (*c*).[182]

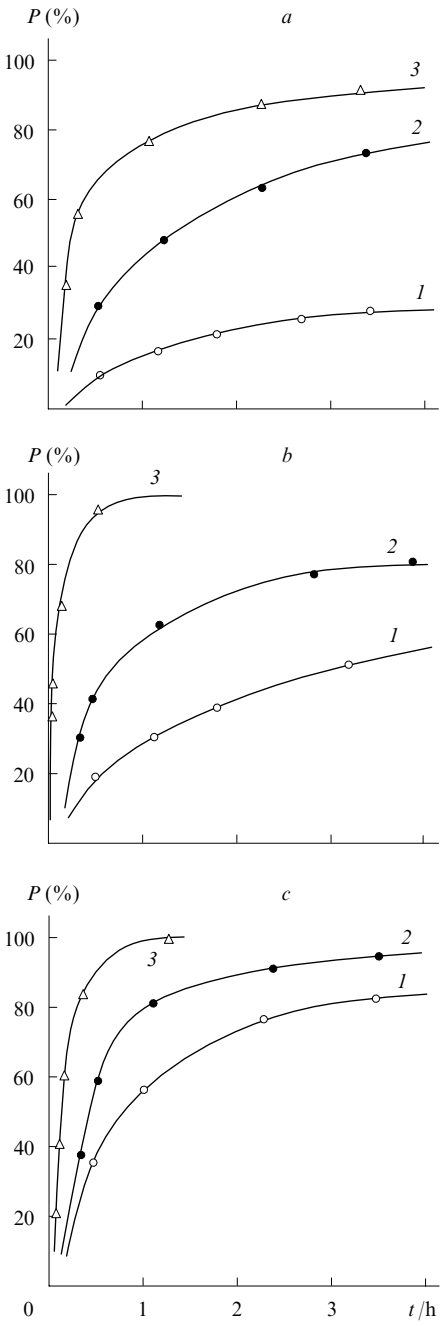



**Figure 4.** Yields of calcium (*a*), strontium (*b*) and magnesium (*c*) polyacrylates *vs*. time for initial monomer concentrations of 0.2 (*1*), 0.5 (*2*) and 0.8 mol litre$^{-1}$ (*3*).[184]
Polymerisation temperature, 80 °C; initiator concentration, 0.25 mol %.

of water-soluble sodium acrylate in reverse micelles in an non-aqueous phase follows a nuclear 'monomer–drop' mechanism, *i.e*., the reaction starts in the monomer drops, because the initiator is dissolved in the 'internal' aqueous phase.[30] The particle size of the monomer emulsion and the resulting polymer latex is virtually the same and is equal to $\sim 1$ μm. The maximum polymerisation rate and the molecular mass of sodium polyacrylate formed can be determined from the equations

$$W_{max} = [K_2S_2O_8]^{0.78}[M]^{1.5}[\text{Span 80}]^{0.1},$$

$$M_n = [K_2S_2O_8]^{-0.37}[M]^{2.9}[\text{Span 80}]^{-0.2},$$

where [Span 80] is the concentration of the Span 80 emulsifier.

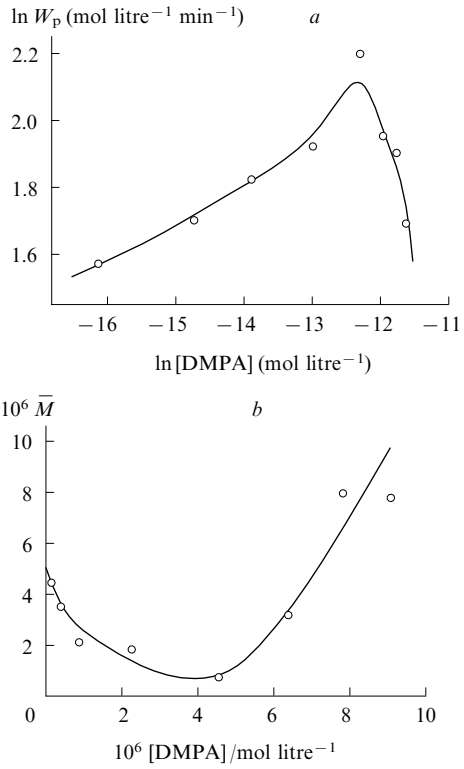



**Figure 5.** Rate of emulsion polymerisation of sodium acrylate (*a*) and viscosity-average molecular mass of the polymer (*b*) *vs*. DMPA concentration.[186]

It is noteworthy that the polymerisation rate and the molecular mass of the polymer formed in this system depend little on the emulsifier concentration (unlike the case of usual emulsion polymerisation).

A similar dependence of the reaction rate on the monomer concentration was observed in the photoinduced emulsion polymerisation of sodium acrylate.[186] However, in this case, an increase in the concentration of the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), entails first a gradual increase in $W_p$ and then a sharp decrease, while the molecular mass follows an opposite dependence on the DMPA concentration (Fig. 5 *a,b*). This behaviour of $W_p$ is attributable, on the one hand, to the adsorption effects of the photoinitiator and, on the other hand, to recombination of primary radicals at high concentrations.

**b. Radical polymerisation of transition metal (meth)acrylates**

Usually polymerisation of transition metal (meth)acrylates is carried out in non-aqueous media, *i.e*., under conditions that rule out dissociation. According to electrical conductivity measurements in ethanol and DMF,[170] transition metal acrylates are weak electrolytes [$K_d = (1.97 - 2.25) \times 10^{-5}$] and under experimental conditions where the monomer concentration is $10^{-3} - 10^{-1}$ mol litre$^{-1}$, their dissociation can be neglected. Thus polymerisation of chromium(III) acrylates in DMF in the presence of complex **23** follows a radical mechanism and has the orders of 1.0 and 0.5 with respect to the monomer and the initiator, respectively (Table 5).[167] Zinc, cobalt, nickel and copper acrylates show different reactivities in methanol and DMF in the presence of AIBN. The polymerisation rate of zinc acrylate is the highest, the long induction period being followed by fast exothermic reaction.[36, 187, 188] For other salts, no induction period was observed. Copper acrylate polymerises

**Table 5**. Kinetic parameters of polymerisation of metal (meth)acrylates.

| Monomer | Polymerisation conditions | $k_p(2k_df/k_t)^{0.5}$ /litre$^{0.5}$ mol$^{-0.5}$ s$^{-1}$ | Order of reaction | | $E_a$ /kJ mol$^{-1}$ | Ref. |
|---|---|---|---|---|---|---|
| | | | with respect to monomer | with respect to initiator | | |
| Chromium(III) acrylate | DMF, **23**, 90 °C | $31.0\times10^{-3}$ (see [a]) | 1 | 0.5 | 67.0 | 167 |
| Cobalt(II) acrylate | DMF, AIBN, 65–75 °C | 0.84–1.74 | $1.27\pm0.06$ | $0.54\pm0.04$ | $74.0\pm2.3$ | 187 |
| | EtOH, AIBN, 78 °C | – | 0.9 | 0.6 | – | 190 |
| Nickel(II) acrylate | the same | 0.56–1.40 | $1.21\pm0.09$ | $0.53\pm0.05$ | $89.3\pm3.2$ | 187 |
| Zinc(II) acrylate | " | 4.95–10.28 | $1.49\pm0.10$ | $0.86\pm0.06$ | $71.6\pm3.5$ | 188 |
| Sodium acrylate | $H_2O-H_2O$–kerosene, $K_2S_2O_8$, Span 80, 50 °C | – | 1.5 | 0.78 | 94.8 | 30 |
| Sodium methacrylate | $H_2O$, $K_2S_2O_8$ | – | 0 | 0.5 | 91.5 | 185 |
| Tributyltin acrylate | n-$C_{10}H_{22}$–PhH, lauryl peroxide | – | 1.05 | 0.49 | – | 166 |
| | n-$C_{10}H_{22}$–PhH, AIBN | – | 1.10 | 0.45 | – | 166 |

[a] The value of $(k_p^2/k_t)$ /litre mol$^{-1}$ s$^{-1}$.

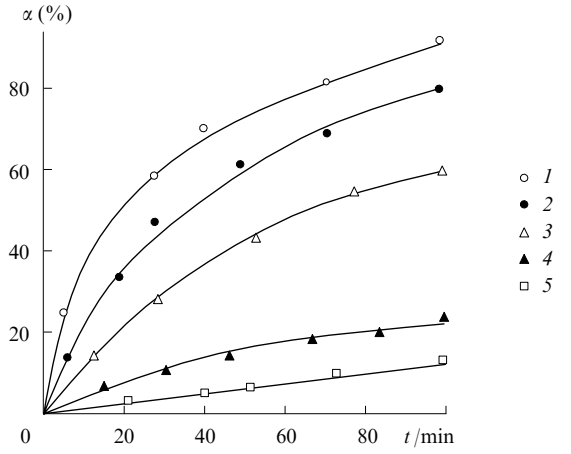



**Figure 6.** The degree of conversion of acrylic acid (*1*) and cobalt (*2*), nickel (*3*), iron(III) (*4*) or copper (*5*) acrylates during polymerisation.[190] Monomer concentration 0.9 mol litre$^{-1}$, [AIBN] = $2.5\times10^{-2}$ mol litre$^{-1}$, EtOH, 78 °C.

in a low yield (Fig. 6). Studies of the initiation rate of polymerisation have shown that the rate constants for polymerisation of metal acrylates vary in the series of cations $Zn^{2+} > Ni^{2+} > Co^{2+}$ and, hence, the activation energy of initiation varies in the same way (Table 6).[189] For cobalt(II) acrylate, the activation energy of initiation ($E_{a,\,2k_df}$) is low, which is in line with the variation of the overall activation energy of polymerisation in the series of these monomers. This decrease in the activation energy for cobalt(II) acrylate is attributed to the possible formation of the complex

**Table 6**. Rate constants and activation energies for initiation of polymerisation of transition metal acrylates.[189]

| Metal | $2k_df\times10^5$ /s$^{-1}$ | | $E_{a,\,2k_df}$/kJ mol$^{-1}$ |
|---|---|---|---|
| | 343 K | 353 K | |
| Zn(II) | 2.93 | 10.6 | $128.2\pm1.1$ |
| Co(II) | 2.93 | 7.90 | $116\pm1.5$ |
| Ni(II) | 2.62 | 9.52 | $129.8\pm0.3$ |

[$Co^{2+}\cdots$AIBN], but no experimental evidence supporting this view was presented.

Under comparable conditions (EtOH, AIBN), the rate of radical polymerisation of transition metal acrylates is lower than the rate of homopolymerisation of acrylic acid, decreasing in the series of cations $Co^{2+} > Ni^{2+} > Fe^{3+} > Cu^{2+}$ (Refs 190 and 191). An increase in the initial monomer and initiator concentrations results in an increase in the reaction rate, which is in good agreement with general rules of radical polymerisation. Polymerisation of metal acrylates comprises the same elementary steps as polymerisation of conventional monomers but is affected by the nature of the transition metal. In view of the fact that the initial and current concentrations of monomers are related to the degree of conversion ($\alpha$) in the following way:

$$[M] = [M_0](1-\alpha),$$

in the quasi-steady-state approximation with respect to macroradicals, the polymerisation rate can be represented by the equation

$$\frac{d\alpha}{d\tau} = k_p\left(\frac{k_i}{k_t}\right)^{0.5}[I]^{0.5}(1-\alpha). \qquad (2)$$

Solution of Eqn (2) provided that $[I] = [I_0]\exp(-k_it)$ ($[I_0]$ is the initial concentration of the initiator) gives the dependence

$$\ln\left\{\ln(1-\alpha) + 2k_p\left(\frac{[I_0]}{k_ik_t}\right)^{0.5}\right\} = \ln 2k_p\left(\frac{[I_0]}{k_ik_t}\right)^{0.5} - 0.5k_it, \qquad (3)$$

which satisfactorily describes the polymer accumulation kinetics in the liquid-phase radical polymerisation of cobalt(II) acrylate.[190]

In this case, the equation for the limiting conversion ($\alpha_\infty$) *vs*. the initial initiator concentration is in good agreement with experimental data (Fig. 7):

$$\ln(1-\alpha_\infty) = 2k_p\left(\frac{[I_0]}{k_ik_t}\right)^{0.5}. \qquad (4)$$

However, as noted above, polymerisation of the carboxylates in question can be accompanied by a number of trans-

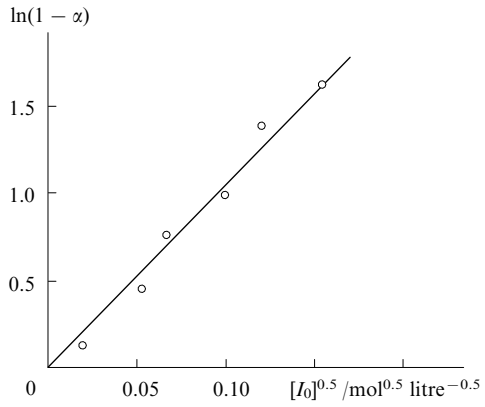
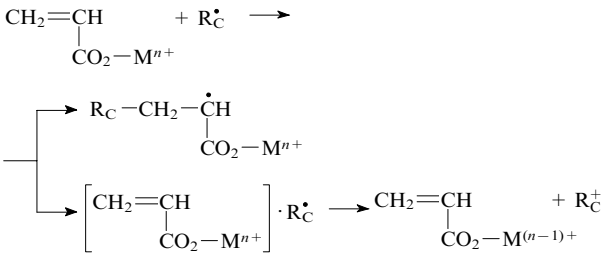
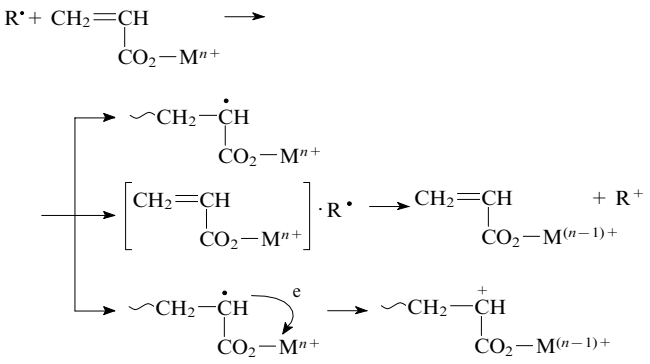



**Figure 7.** The degree of limiting conversion of the monomer *vs.* initial initiator concentration during radical polymerisation of cobalt(II) acrylate.[190]

formations. For example, the coordination of the monomer to the primary radicals ($R_C^{\bullet}$) at the initiation step results in the deactivation of radicals and decreases the initiation efficiency.



Obviously, the competitive binding of polymeric radicals ($R^{\bullet}$) also accompanies chain propagation and the coordinated radicals thus formed can also undergo intramolecular deactivation.



The observed deviations of the reaction orders with respect to the monomer and the initiator in these systems (see Table 5) may be due to these side reactions that complicate the polymerisation mechanism. For example, the increased orders of reaction attest to a dependence of the initiation rate on the monomer concentration and to an increase in the contribution of the monomolecular termination to the overall kinetic chain termination.

**c. Stereochemistry of radical polymerisation of metal carboxylates**

It is known that the problem of stereospecific radical polymerisation relates to the slight differences between the rate constants for the growth of isotactic ($k_i$) and syndiotactic ($k_s$) sequences. The difference between the corresponding activation energies equals $\sim 1$ kcal mol$^{-1}$. According to the expression

$$\frac{k_i}{k_s} = \exp\left(\frac{-\Delta(\Delta F)^{\neq}}{kT}\right), \qquad (5)$$

where $\Delta(\Delta F)^{\neq} = \Delta F_i^{\neq} - \Delta F_s^{\neq}$ is the difference between the free activation energies for iso- and syndiotactic additions, $k$ is the Boltzmann constant, the microstructure of the polymeric chains in the radical polymerisation should be affected by factors that can change the ratio of the constants. First of all, this is low polymerisation temperature, because the predominant formation of the syndiotactic conformation with respect to the isotactic one is mainly due to the enthalpy factor. The directed growth of the polymer chain is also facilitated by steric factors and polarity of the medium.

Using quantum chemical calculations and according to the ion pair mechanism,[181] it was shown that the formation of the growing radical–counter-ion pairs is accompanied by preferred syndiotactic addition. Polymerisation of the salts of unsaturated carboxylic acids creates additional prerequisites for the formation of regular polymers. Apparently, owing to the presence of the polarised metal carboxylate group, the growing centre changes its stereochemical configuration to the opposite one in every chain elongation step. As a result, configurations of the carboxylate units in the polymer alternate. The crucial role is played by electrostatic interactions between the ionised growing radical and the polar metal-containing group; the coordination bonds of the metal can also have a directing effect.

It was shown[192] that the radical polymerisation of alkali metal methacrylates carried out in water gives mainly syndiotactic polymers (the content of the syndiotactic fraction ranges from 90% to 95%). The anionic polymerisation of sodium methacrylate affords isotactic polymer containing 78.2%–97.8% of the isotactic fraction.[180] Meanwhile, the radical polymerisation of this monomer at 70 °C in benzene yields a polymer in which the syndio- to heterotactic ratio is 72.1 : 26.2. Even a relatively low content of (meth)acrylate units in copolymers allows effective control over the polymer microstructure. Thus in methyl methacrylate–methacrylic acid (MAA)–sodium methacrylate terpolymers, an increase in the salt content from 0.1 mol % to 0.5 mol % results in an increase in the number of alternating dyads (Table 7) and gives more sterically ordered products, *i.e.*, isotactic configurations appear and the fraction of syndiotactic triads increases.[193]

**Table 7.** Microstructure of methyl methacrylate–methacrylic acid–sodium methacrylate terpolymers.[193]

| Concentration of $NaO_2CC(Me)=CH_2$ (mol %) | Content of MMA–MAA dyads (%) | Content of triads [a] (%) | | |
|---|---|---|---|---|
| | | *i* | *h* | *s* |
| 0 | 37 | 0 | 45 | 55 |
| 0.10 | 50 | 4 | 36 | 60 |
| 0.25 | 52 | 9 | 28 | 63 |
| 0.50 | 54 | 11 | 24 | 65 |

[a] Here and in Table 8 the triad configurations are designated as follows: *i* isotactic, *h* heterotactic, *s* syndiotactic.

**Table 8**. Stereoregular composition of organotin polymers.[194]

| Macrocomplex | Content of triads (%) | | |
|---|---|---|---|
| | *i* | *s* | *h* |
| *iso*-PMAA + $[(Bu^nO)_3Sn]_2O$ | 100 | 0 | 0 |
| *syndio*-PMAA + $[(Bu^nO)_3Sn]_2O$ | 0 | 78 | 22 |
| Atactic PMAA + $[(Bu^nO)_3Sn]_2O$ | 15 | 44 | 41 |
| Atactic PMAA [a] | 6.5 | 56.5 | 37.0 |
| TBTM polymerisation product [b] | 18 | 50 | 32 |

[a] Polymerisation in toluene initiated by benzoyl peroxide.
[b] Bulk polymerisation at 60 °C initiated by AIBN.

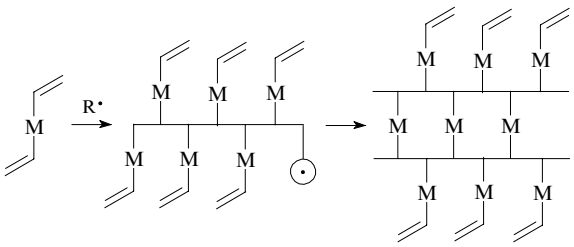
It is worth noting that the content of syndiotactic units in the growing polymeric chain may be determined by the nature of the counter-ion and its sorption ability, the polarity of the medium and so on. For example, bulk radical polymerisation of tributyltin methacrylate (TBTM) gives a polymer structure similar to that of the macrocomplex resulting from the reaction of $[(Bu^nO)_3Sn]_2O$ with atactic polymethacrylic acid (PMAA) (Table 8).[194] Apparently, this is related to polymerisation conditions: in bulk polymerisation, the effect of ion pairs is less pronounced than in polymerisation in polar solvents. This was confirmed by polymerisation of cobalt and nickel acrylates in ethanol at 60 °C and their radiation-induced low-temperature polymerisation on defrosting of glassy matrices.[172, 190] After hydrolysis of the resulting metallopolymers, up to 60% – 65% of syndiotactic polyacrylic acid (PAA) was isolated (the fraction soluble in a dioxane – water mixture).

Note that the microstructure of the metallopolymers formed upon polymerisation of metal (meth)acrylates is determined by both the structure of the active site, the reaction temperature and the nature of the solvent and by the stereochemistry of the spatial cross-linked metallopolymer structure. Indeed, low-temperature radical polymerisation of zinc, barium and lead acrylates affords a higher content of the regular fraction, as indicated by the fractionation data for PAA isolated from these metallopolymers (Table 9).[168]

According to a known scheme,[195] the process of polymerisation of bifunctional monomers can be conventionally divided into two stages. The first stage yields a comb-shaped linear polymer (apparently, stereoregular fractions are formed during this period) and the second stage includes the formation of a three-dimensional network structure, as chain propagation reactions involve mainly the C=C bonds of the side chains of the macroradical. At this stage, chain growth takes place under high steric strain and is accompanied by an increase in the internal stress, giving rise to an atactic polymer.

**Table 9**. Stereoregular composition of polyacrylic acid formed upon hydrolysis of metal polyacrylates and upon polymerisation.[168]

| Starting polymer | $T$/°C | Yield of the fraction (%) | |
|---|---|---|---|
| | | atactic | syndiotactic |
| Zinc polyacrylate | 9 | 20 | 80 |
| | 70 | 58 | 42 |
| Barium polyacrylate | 9 | 26 | 74 |
| PAA | 70 | 59 | 41 |




Thus analysis of the low-frequency IR spectra of metal polyacrylates [168] shows that in the region of $-O-M-O-$ vibrations, the spectrum of the polymer exhibits one broad band with a maximum at 340 $cm^{-1}$ instead of two narrow bands (at 300 and 400 $cm^{-1}$) typical of the metal-containing monomer. This effect is a consequence of distortion of the geometry of bridging groups caused by internal stress in the network structure. In some cases, the above two stages can be separated in time, as was demonstrated recently in a study of thermal transformations of cobalt(II) acrylate by dielectric spectroscopy *in situ*.[196] Figure 8 presents the Arrhenius plot of the relaxation time ($\tau_m$). It can be seen that in regions *1* and *2* the spectral pattern is typical of relaxation processes, namely, the relaxation times decrease with an increase in temperature. The occurrence of polymerisation in region *1* is confirmed by the deviation of the experimental $\tau_m(T)$ values from the theoretical curve. On further increase in temperature, the experimental and theoretically calculated data approach each other. At higher temperatures polymerisation involving the 'residual' double bonds apparently takes place, *i.e.*, a cross-linked polymer is formed. The topochemical factors are also crucial in the formation of isotactic oligomers in the solid-phase polymerisation of zinc bis(but-3-enoate).[197]

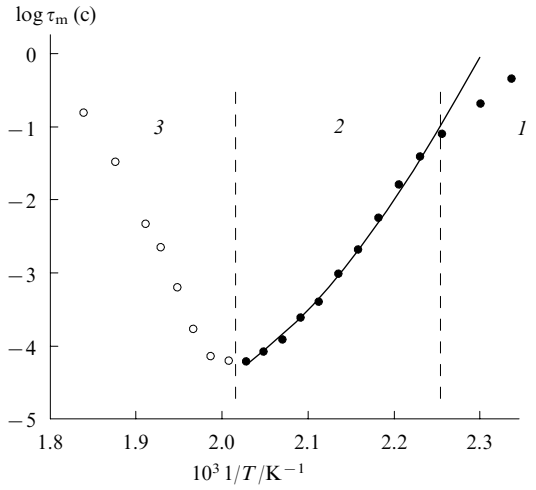



**Figure 8.** Relaxation time in the polymerisation of cobalt(II) acrylate *vs.* temperature (the points are the experiment and the curve shows the results of calculation).[196]
(*1*) polymerisation region, (*2*) α-relaxation region, (*3*) cross-linking.

Since the presence of the polarised metal carboxylate group dictates the polymerisation stereochemistry, it is possible to obtain crystalline metallopolymers. Thus the degree of crystallinity of iron(III) polymethacrylate synthesised by γ-induced polymerisation depends on the radiation dose. The highest degree of crystallinity (39%) is obtained in the range of 10 to 25 kGy, although no obvious trend for increasing or decreasing of this value with the dose can be followed.[54]

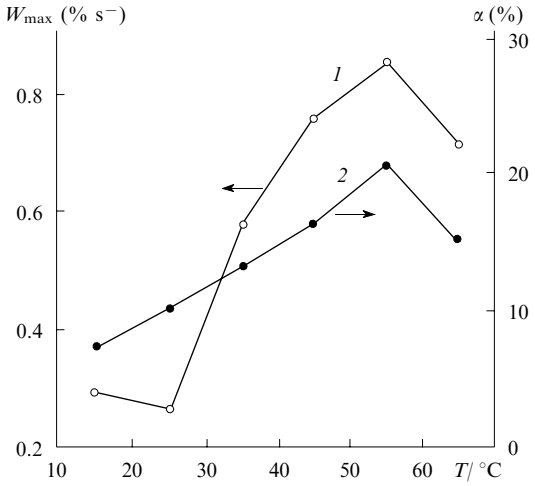



**Figure 9.** Maximum photopolymerisation rate (*1*) and conversion (*2*) of the liquid-crystalline monomer $Zn\{O_2CC_6H_3[O(CH_2)_{11}O_2CCH{=}CH_2]_2$-3,4$\}_2$ *vs.* temperature.[58]

The photopolymerisation of liquid-crystalline metal long-chain carboxylates containing terminal acryloyloxy groups gives anisotropic polymers.[58] The resulting metallopolymers have a hexagonal columnar structure, which was confirmed by X-ray diffraction. The mesormorphic structure of the monomer is not changed essentially during polymerisation, although the column-to-column distance in the polymer is 33.7 Å instead of 39.2 Å observed in the monomer, *i.e.*, the hexagonal packing is compressed. Note that the maximum reaction rate and the degree of conversion increase with temperature in the region of existence of the folded mesophase of the monomer (45 – 55 °C) and decrease in the isotropic phase region at 65 °C (Fig. 9). The observed kinetic effects are apparently related to ordering of the structure and self-assembling of the polymerising metal carboxylate in the mesophase, on the one hand, and loss of orientation of the monomer in the isotropic phase, on the other hand. Similar effects are also known for traditional monomers.[198 – 200]

## 3. Copolymerisation and terpolymerisation

Copolymerisation and terpolymerisation of carboxylates with other monomers are widely used for the preparation of metallopolymers based on metal carboxylates. This can be used to polymerise carboxylates that cannot undergo homopolymerisation but copolymerise rather easily with other monomers. Yet another aspect appears of interest: since the copolymer composition depends on many parameters, study of copolymerisation allows one to elucidate the factors affecting the reactivity of the double bond in a metal carboxylate molecule. As in the classical copolymerisation, the composition of the metallocopolymers formed depends on the composition of the initial monomer mixture, the reactivity ratio of the monomers and their radicals according to the Mayo – Lewis equation:[201]

$$\frac{[m_1]}{[m_2]} = \frac{[M_1]r_1[M_1] + [M_2]}{[M_2][M_1] + r_2[M_2]}, \qquad (6)$$

where $r_2 = k_{22}/k_{21}$ is the copolymerisation constant characterising the relative reactivity of metal carboxylate towards the addition to the 'domestic' and 'foreign' radicals, $[m_2]$ and $[M_2]$ are the contents of metal carboxylate in the copolymer and in the monomer mixture, respectively; similar characteristics $r_1 = k_{11}/k_{12}$, $[m_1]$ and $[M_1]$ refer to the metal-free monomer.

The capability of a monomer for copolymerisation is known to increase with an increase in the difference between the resonance stabilisation energy of the monomer being added and the radical formed. The resonance stabilisation of the monomer during copolymerisation is described by the parameter $Q$, and the polar effect of the substituent at the double bond is described by the factor $e$. These parameters are related to the copolymerisation constants (or the relative reactivity) of the monomers by the empirical relations

$$r_1 = \left(\frac{Q_1}{Q_2}\right)\exp\left[-e_1(e_1 - e_2)\right],$$
$$r_2 = \left(\frac{Q_2}{Q_1}\right)\exp\left[-e_2(e_2 - e_1)\right], \qquad (7)$$

where the subscripts correspond to different monomers.

### a. Key regular features of copolymerisation of alkali and alkaline earth metal salts

Most studies dealing with this subject note a substantial effect of the nature of the reaction medium, first of all, ionic strength and solvent polarity, on the kinetic and copolymerisation process parameters and on the composition and the molecular mass of the copolymers. It is also necessary to take into account the changes in the character of interaction in the macroradical – metal cation – monomer anion systems upon variation of the medium. In particular, for copolymerisation of acrylic acid salts with acrylamide in an aqueous medium, it was shown [202] that at pH 7.1 – 7.2 where the salts are dissociated the copolymerisation rate decreases in the series that reflects the decrease in the degree of cation binding to the polyacrylamide unit of the macroradical. The degree of cation binding to acrylate groups depends on the cation bulk and increases in the series $Li^+ < Na^+ < K^+$. The kinetic features [203] of MMA copolymerisation with alkali metal methacrylates in methanol were explained by electrostatic repulsion of the functional groups of the salt and the MMA radical. The relative reactivity constants of the monomers (Table 10) indicated that the radical with the metal methacrylate terminal unit adds preferably the metal-free monomer, MMA. This ability expressed through the $1/r_2$ ratio decreases with an increase in the alkali metal ion radius (Fig. 10). Assuming that simultaneously the $k_{22}$ value increases, while $k_{21}$ remains almost invariable, it is possible to establish a correlation between the relative reactivity and the homopolymerisation rate of these salts.

Similar trends are found for other salts of this type. Most often, the copolymers are enriched in the metal-free monomer $M_1$ ($r_1 > 1$, $r_2 < 1$; see Table 10). Only in the copolymerisation involving lithium salts, for example, for the lithium methacrylate – MMA [203] and lithium acrylate – styrene systems,[204] do monomer units tend to regularly alternate. In addition, the product of the copolymerisation constants $r_1r_2 = 0.94$ for the styrene – lithium methacrylate system is close to unity, which implies nearly ideal copolymerisation.

The differences in the reactivity of acrylate and methacrylate ligands are reflected in the parameters $Q$ and $e$. For example, for sodium methacrylate and acrylate, the $Q$ values are 0.64 and 0.07, respectively, which is consistent with the higher values of this parameter for 1,1-disubstituted ethylenes compared to monosubstituted ones. The replacement of the hydrogen atom by a methyl group changes the double bond polarity in the methacrylate not only in magnitude but also in the sign (for lithium acrylate $e = +0.02$ and for lithium

**Table 10**. Copolymerisation parameters of alkali and alkaline earth metal salts (initiated by AIBN).

| Comonomers | | Reaction conditions | Parameters | | | | Ref. |
|---|---|---|---|---|---|---|---|
| $M_1$ | $M_2$ | | $r_1$ | $r_2$ | $Q_2$ | $e_2$ | |
| MMA | $LiO_2CC(Me)=CH_2$ | MeOH, 60 °C | 0.59 | 0.073 | 0.64 | 0.3 | 203 |
| Styrene | $LiO_2CC(Me)=CH_2$ | DMSO, 60 °C | 1.30 | 0.72 | 0.62 | −0.54 | 204 |
| | $LiO_2CCH=CH_2$ | the same | 7.29 | 0.07 | 0.07 | 0.02 | 204 |
| MMA | $NaO_2CC(Me)=CH_2$ | MeOH, 60 °C | 3.97 | 0.126 | 1.36 | −0.18 | 203 |
| | $KO_2CC(Me)=CH_2$ | the same | 5.65 | 0.173 | 0.54 | 0.01 | 203 |
| Styrene | $Mg(O_2CCH=CH_2)_2$ | DMSO, 70 °C | 5.31 ± 0.07 | 0.18 ± 0.14 | 0.16 | −0.59 | 205 |
| | $Ca(O_2CCH=CH_2)_2$ | the same | 6.10 ± 0.22 | 0.12 ± 0.02 | 0.11 | −0.24 | 205 |
| | $Sr(O_2CCH=CH_2)_2$ | " | 4.12 ± 0.02 | 0.14 ± 0.05 | 0.13 | −0.06 | 205 |
| | $Ba(O_2CCH=CH_2)_2$ | " | 3.95 ± 0.15 | 0.11 ± 0.02 | 0.12 | 0.11 | 205 |

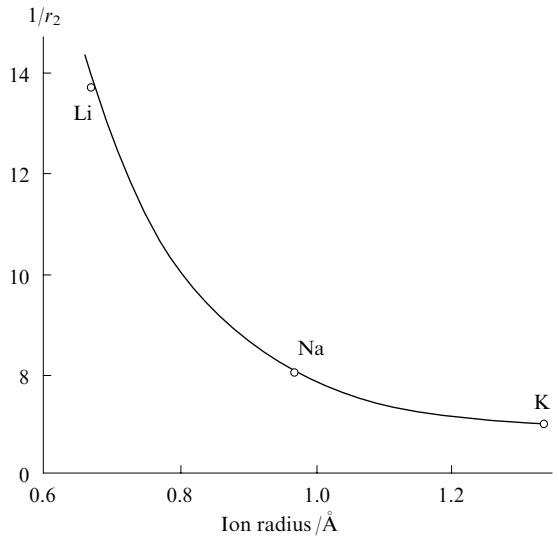



**Figure 10.** Ratio $1/r_2$ *vs.* cation radius in the copolymerisation of MMA with alkali metal methacrylates.[202]

methacrylate $e = -0.54$). The negative $e$ value suggests an increase in the electron density of the vinyl group due to the electron-donating effect of the methyl group. Polar effects play a pronounced role in the copolymerisation of Mg, Ca, Sr and Ba acrylates salts with styrene in DMSO.[205] For the monomers in question, the $e$ value increases in the series of metals Mg < Ca < Sr < Ba. The degree of alternation of units increases in the same series, *i.e.*, the $r_1r_2$ value regularly decreases.

**b. Reactivity of tin-containing carboxylates**

The key features of copolymerisation of trialkyltin (meth)-acrylates and maleates with vinyl monomers[206–210] are that the comonomers are randomly distributed over the chain, the trend for alternation increasing with an increase in the length of the alkyl chain in the tin-containing monomer. The type of variation of the copolymerisation parameters on going from acrylate to methacrylate ($r_1r_2$ increases from 0.09 to 1.24) for copolymerisation of acrylamide with tributyltin (meth)acrylate[206] (Table 11) is similar to that found for lithium salts.

In the copolymerisation of tributyltin maleate with traditional monomers, the copolymers are enriched in the latter, which is manifested as abnormally high values of the effective constants, especially for acrylamide ($r_1 = 122.44$, $r_2 = 0.06$). Hence, tributyltin maleate copolymers with styrene, MMA, butyl acrylate or acrylamide are composed of large blocks of the metal-free monomer separated by single maleate units. Moreover, in all cases, the $r_2$ value is close to zero (see Table 11), which is indicative of the inability of the maleate monomer to homopolymerisation.

Good agreement was found between the theoretically calculated and experimental contents of the triads in the

**Table 11**. Copolymerisation parameters of tin-containing unsaturated carboxylates.

| Comonomers | | Parameters | | | | Ref. |
|---|---|---|---|---|---|---|
| $M_2$ | $M_1$ | $r_1$ | $r_2$ | $Q_2$ | $e_2$ | |
| $Bu^n_3Sn(cis\text{-}O_2CCH=CHCO_2H)$ | MMA | 15.40 ± 0.98 | 0.01 ± 0.02 | 0.05 | 1.40 | 206 |
| | styrene | 6.70 ± 0.39 | 0.05 ± 0.10 | – | – | 206 |
| | butyl acrylate | 9.39 ± 0.21 | 0.11 ± 0.08 | – | – | 206 |
| | acrylamide | 122.44 ± 6.04 | 0.06 ± 0.20 | – | – | 206 |
| $Bu^n_3SnO_2CCH=CH_2$ | " | 0.11 ± 0.02 | 0.82 ± 0.06 | 0.38 | 0.74 | 206 |
| | itaconic acid | 0.011 ± 0.109 | 1.088 ± 0.044 | 0.313 | 0.774 | 210 |
| | dimethyl itaconate | 0.767 ± 0.181 | 0.932 ± 0.040 | – | – | 210 |
| $Bu^n_3SnO_2CC(Me)=CH_2$ | acrylamide | 1.460 ± 0.40 | 0.85 ± 0.10 | 0.62 | 0.57 | 206 |
| | itaconic acid | 0.073 ± 0.090 | 2.272 ± 0.080 | 0.575 | 1.300 | 210 |
| | dimethyl itaconate | 0.829 ± 0.101 | 1.223 ± 0.036 | – | – | 210 |
| $Bu^n_3SnO_2CCH_2C(=CH_2)CO_2SnBu^n_3$ | styrene | 0.643 ± 0.039 | 0.139 ± 0.058 | – | – | 211 |
| | MMA | 1.729 ± 0.129 | 0.316 ± 0.100 | – | – | 211 |

**Table 12**. Triad sequences in the methyl methacrylate ($M_1$) and bis(tributyltin) itaconate ($M_2$) copolymer.[211]

| $\varphi_1$ | $\varphi_{111} + \varphi_{112}$ | | $\varphi_{212}$ | |
|---|---|---|---|---|
| | experiment | calculation | experiment | calculation |
| 0.50 | 0.8333 | 0.8636 | 0.1667 | 0.1364 |
| 0.55 | 0.8750 | 0.8861 | 0.1250 | 0.1140 |
| 0.65 | 0.9280 | 0.9411 | 0.0720 | 0.0589 |
| 0.75 | 0.9688 | 0.9713 | 0.0312 | 0.0287 |
| 0.90 | 1.0000 | 0.9951 | 0.0000 | 0.0040 |

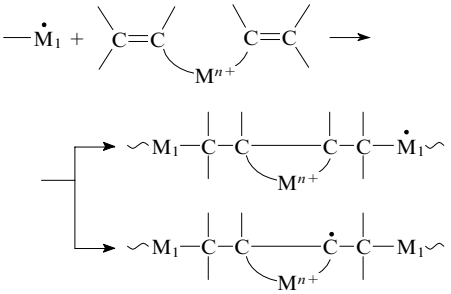
chain sequences of bis(tributyltin) itaconate and MMA copolymer[211] (Table 12, $\varphi$ is the content of a unit in the polymer chain, the subscript refers to the corresponding monomer). This fact confirms the preferred addition of methyl methacrylate units to the growing macroradical and, hence, the formation of longer polymer chains from them.

**c. Copolymerisation involving transition metal salts**

Since metal di(meth)acrylates and dicarboxylates are non-conjugated divinyl monomers, the equation of copolymerisation in these systems has the form:

$$\frac{[m_1]}{[m_2]} = \frac{[M_1]}{2[M_2]} \frac{r_1[M_1] + 2[M_2]}{[M_1] + 2r_2[M_2]} . \qquad (8)$$

It is assumed that intramolecular cyclisation or intermolecular ion cross-linking can be neglected, at least, at low degrees of conversion.



It was shown by special studies[212,213] that the products formed in initial copolymerisation stages are soluble in organic solvents; hence, no intermolecular cross-linking by acrylate groups takes place. The fraction of the non-consumed double bonds in acrylates increases in the series $Zn^{2+}$ (35%) < $Co^{2+}$ (39%) < $Ni^{2+}$ (49%).

Copolymers based on carboxylic acid salts may differ considerably in the microstructure of polymeric chains which depends on the comonomer nature and reaction medium. In the copolymerisation of transition metal acrylates with styrene in methanol, it was found that $r_1 > 1$ and $r_2 < 1$ (Table 13).[214] It is obvious that with these copolymerisation constants, the resulting copolymer will be enriched in styrene irrespective of the composition of the reaction mixture. Conversely, when the reaction is carried out in DMF, alternation of the monomer units is observed in the polymer formed from the same monomer pairs. In the nickel acrylate–styrene copolymer, 46% of the acrylate units are incorporated in regularly alternating structures.[213] This may be due to the change in the double bond polarity and, hence, parameters of the reactivity of acrylates in polar solvents, as is the case, for example, of styrene copolymerisation with acrylamide in DMSO.[215] However, in the case of copolymerisation of copper acrylate with styrene in methanol or acetonitrile the copolymerisation parameters are not changed much.[214] The effective values of relative activity of the monomers (see Table 13) attest to a statistical structure of copolymer of MMA with chromium,[42] copper [216,217] and nickel [218] acrylates obtained by bulk polymerisation. In the metal acrylate–acrylonitrile system, the opposite signs of double bond polarity (parameters $e$ and $Q$ for acrylonitrile are 1.2 and 0.6, respectively) account for S-shaped composition curves according to the classical copolymerisation theory and for the clear-cut trend for alternation of copolymer units in the product (Fig. 11).[219–221] The trend for comonomer alternation is also found in the copper maleate–styrene copolymer: the product $r_1 r_2 < 1$ (the regularly alternating structures account for > 50% of elementary units).[222] However, in the cobalt hydrogen maleate–styrene system, the trend for alternation is slight: as the styrene concentration in the monomer mixture increases, long ($n > 10$) polystyrene chains separated by maleate units are formed in the copolymer.

**Table 13**. Copolymerisation parameters of transition metal salts.

| Comonomers | | Conditions | Parameters | | | | Ref. |
|---|---|---|---|---|---|---|---|
| $M_2$ | $M_1$ | | $r_1$ | $r_2$ | $Q_2$ | $e_2$ | |
| $Zn(O_2CCH{=}CH_2)_2$ | acrylonitrile | MeOH, AIBN | $1.10 \pm 0.02$ | $0.90 \pm 0.07$ | 0.84 | −0.70 | 214 |
| | " | DMF, AIBN, 60 °C | $0.41 \pm 0.02$ | $0.24 \pm 0.03$ | 0.24 | −0.30 | 220 |
| $Co(O_2CCH{=}CH_2)_2$ | styrene | MeOH, AIBN | $1.74 \pm 0.03$ | $0.56 \pm 0.09$ | 0.51 | −0.64 | 214 |
| | acrylonitrile | DMF, AIBN, 60 °C | $0.14 \pm 0.02$ | $0.15 \pm 0.01$ | 0.42 | −0.75 | 219 |
| $Ni(O_2CCH{=}CH_2)_2$ | styrene | MeOH, AIBN | $1.83 \pm 0.02$ | $0.53 \pm 0.06$ | 0.48 | −0.63 | 214 |
| | acrylonitrile | DMF, AIBN, 60 °C | $0.09 \pm 0.02$ | $0.17 \pm 0.02$ | 0.59 | −0.85 | 219 |
| | MMA | bulk, PB, 60 °C | 0.99 | 0.85 | – | – | 218 |
| $Cu(O_2CCH{=}CH_2)_2$ | styrene | MeOH, AIBN, 80 °C | 6.34 | 0.11 | – | – | 214 |
| | " | MeCN, AIBN, 80 °C | $5.94 \pm 0.05$ | $0.12 \pm 0.08$ | 0.11 | −0.22 | 214 |
| | acrylonitrile | DMF, AIBN, 60 °C | $0.21 \pm 0.01$ | $0.08 \pm 0.02$ | 0.26 | −0.82 | 219 |
| | MMA | bulk, PB, 60 °C | 1.05 | 0.8 | – | – | 216 |
| $Cr(O_2CCH{=}CH_2)_3$ | MMA | the same | 1.08 | 0.95 | – | – | 42 |
| | acrylonitrile | DMF, **23**, 85 °C | 0.18 | 0.03 | – | – | 221 |
| $Co(cis\text{-}O_2CCH{=}CHCO_2H)_2$ | styrene | EtOH, AIBN, 70 °C | $1.45 \pm 0.001$ | $0.34 \pm 0.001$ | 0.35 | 0.04 | 222 |
| $Co(cis\text{-}O_2CCH{=}CHCO_2)$ | " | the same | $0.45 \pm 0.004$ | $0.07 \pm 0.004$ | 0.50 | 1.04 | 222 |

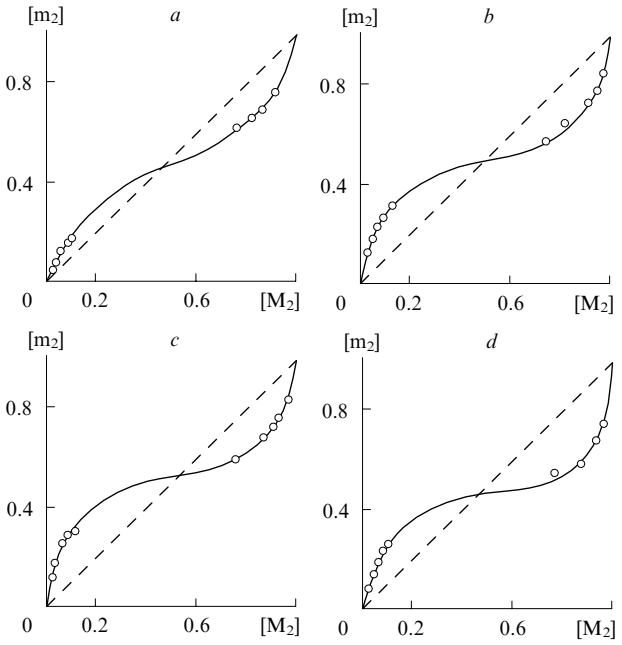



**Figure 11.** Copolymerisation diagrams of the systems acrylonitrile–zinc (*a*), cobalt (*b*), nickel (*c*) or copper (*d*) acrylates. The metal acrylate concentration in the copolymer [$m_2$] and in monomer mixture [$M_2$] are given in mole fractions.[219]
Dashed line shows the 'ideal copolymerisation' case.

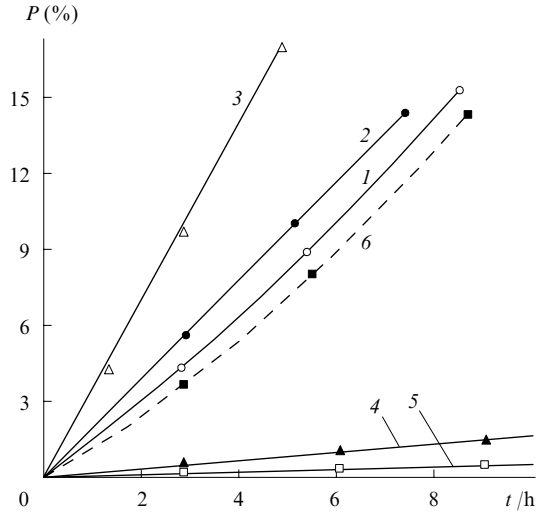



**Figure 12.** Yield of the product of styrene copolymerisation with metal acrylates *vs.* time.
Content of zinc acrylate in the comonomer mixture: 2 (*1*), 6 (*2*) and 10 mass % (*3*); content of copper acrylate: 2 (*4*) and 6 mass % (*5*). For comparison, the curve for styrene homopolymerisation is given (*6*).[214]

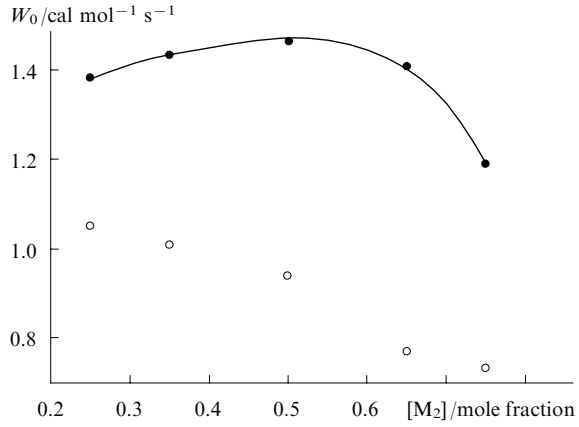



**Figure 13.** Initial rate of styrene copolymerisation with Co(*cis*-$O_2C.CH{=}CHCO_2H)_2$ (*1*) and Co(*cis*-$O_2CCH{=}CHCO_2$) (*2*) *vs.* carboxylate content.[222]
The reaction rate was measured by calorimetry.

**d. Kinetic features**

The rate of radical copolymerisation of styrene or acrylonitrile with zinc, cobalt and nickel acrylates increases with an increase in the salt content in the comonomer mixture.[212–214] This is especially pronounced in the case of zinc acrylate (Fig. 12), because this compound has the highest electron density delocalisation due to the lowest electronegativity of $Zn^{2+}$ ion in this series of metals. Copper acrylate sharply inhibits the process, probably, by a mechanism similar to the mechanism of its homopolymerisation. When dicarboxylic acid salts are used, *e.g.*, cobalt hydrogen maleate, the rate of styrene copolymerisation with this salt decreases monotonically with an increase in the fraction of the dicarboxylate monomer in the initial mixture, whereas in the case of neutral cobalt maleate–styrene system, this dependence passes through a maximum at the equimolar reactant ratio (Fig. 13).[222] This type of behaviour is often attributed to the donor-acceptor interactions between the comonomers, as, for example, in the copolymerisation of sodium 2-acrylamido-2-propanesulfonic acid with *N*-vinylpyrrolidone in water and DMSO.[223] Mathematical simulation gave equations that describe adequately the dependence of the rate of copolymerisation of zinc, cobalt, nickel and copper acrylates with acrylonitrile.[224, 225]

$$W_p = K_\Sigma ([M_1] + [M_2])^{n_1} [I]^{n_2}, \quad (9)$$

$$W_p = A_0 ([M_1] + [M_2])^{n_1} [I]^{n_2} \exp(E_a/RT), \quad (10)$$

where $n_1$ and $n_2$ are the orders of reaction with respect to the total concentration of monomers ($[M_1]+[M_2]$) and the initiator ([I]), respectively, $K_\Sigma$ is the overall reaction rate constant, $A_0$ is the preexponential factor, $E_a$ is the overall activation energy.

The kinetic parameters of copolymerisation for the monomer pairs considered suggest an intricate influence of the nature of the metal on the elementary steps of the polymerisation process (Table 14). As in the homopolymerisation, the general trend of variation of the reaction rate constant in the series $Zn^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}$ is retained. However, copolymerisation of chromium(III) acrylate with acrylonitrile follows the 'ideal' radical polymerisation kinetics (see Table 14).[221]

It is noteworthy that when a great excess of acrylonitrile is present, the rate constant $[(1.6 \pm 0.26) \times 10^{-5}\ s^{-1}]$ and the activation energy ($126.8 \pm 3.7$ kJ mol$^{-1}$) for initiation of its copolymerisation with zinc acrylate do not differ much from those found for homopolymerisation of acrylonitrile.[226]

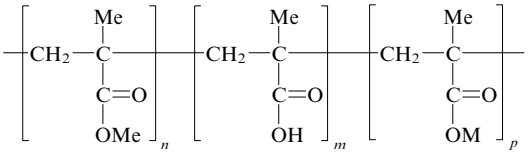
**e. Terpolymerisation**

Terpolymerisation is important for practical purposes as it provides the possibility of varying the properties of the final product. In most cases, two termonomers are present in the

**Table 14**. Copolymerisation kinetic parameters of transition metal acrylates with acrylonitrile.

| Parameter | Metal | | | | |
|---|---|---|---|---|---|
| | $Zn^{2+}$ (see [224]) | $Co^{2+}$ (see [225]) | $Ni^{2+}$ (see [225]) | $Cu^{2+}$ (see [224]) | $Cr^{3+}$ (see [221]) |
| $A_0$ /litre$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$ | $(4.67 \pm 0.06) \times 10^7$ | $(4.4 \pm 0.3) \times 10^{10}$ | $(3.3 \pm 0.3) \times 10^9$ | $(6.8 \pm 1.1) \times 10^9$ | – |
| $n_1$ | $1.67 \pm 0.10$ | $1.59 \pm 0.10$ | $1.65 \pm 0.05$ | $1.12 \pm 0.10$ | 1 |
| $n_2$ | $0.61 \pm 0.07$ | $0.57 \pm 0.14$ | $0.55 \pm 0.07$ | $0.78 \pm 0.07$ | 0.5 |
| $E_a$ /kJ mol$^{-1}$ | $72.5 \pm 4.9$ | $92.6 \pm 6.8$ | $86.0 \pm 3.6$ | $88.2 \pm 5.0$ | $96.2 \pm 0.2$ |
| $k_p^2/k_t$ /litre mol$^{-1}$ s$^{-1}$ | – | – | – | – | $1.0 \pm 10^{-5}$ |
| $K_\Sigma$ /litre$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$ | $6.16 \pm 10^{-4}$ | $5.55 \pm 10^{-4}$ | $4.15 \pm 10^{-4}$ | $3.98 \pm 10^{-4}$ | – |

terpolymer in greater amounts and are responsible for its key properties, while the third one is added only for modification of the required property of the polymeric material. The use of salts of unsaturated acids as the third monomers allows control of the reactivity of vinyl monomers and determination of the spatial configuration and morphology of the products. Indeed, even minor additives (0.5 mol % – 2.0 mol %) of alkali and alkaline earth metal methacrylates introduced in the MMA – methacrylic acid system (90 : 10) in the bulk copolymerisation have a noticeable effect on the parameters $r_1$ and $r_2$ and radical copolymerisation kinetics, thus determining the physicochemical properties of the copolymers.[193, 227, 228]



$n$ = (88.1 – 88.7) mol %, $m$ = (11.12 – 11.25) mol %, $p$ = (0.05 – 1.94) mol %.

The introduction of metal methacrylate increases the yield and molecular mass of terpolymerisation products, which may be due to complexation of the salt with the system components. This process affects the intermolecular interactions, giving rise to specific areas (billets) with a definite orientation of the monomer molecules. As a result, the reaction is accelerated and more regular and extended macrochains are formed (similarly to polymerisation of complexed monomers [229]). In addition, in the presence of the salt, the product $r_1 r_2$ decreases, which corresponds to an increase in the degree of alternation of monomer units, as is also indicated by the change in the Harwood parameter (Table 15).

The formation of terpolymers, for example, in the systems tributyltin methacrylate – butyl methacrylate – acrylonitrile (AN),[230] bis(tributyltin) itaconate (TBTI) – methyl acrylate (MA) or ethyl acrylate (EA) – acrylonitrile [231] follows copolymerisation kinetics for binary systems of monomer pairs. This fact was also noted for terpolymerisation of zinc,[232] chromium [233] and copper [234] acrylates with styrene and acrylonitrile. Ternary azeotropic compositions, for example, for the TBTI – MA – AN and TBTI – MA – EA are equal to 37 : 48 : 15 and 9 : 80 : 11 (mol %), respectively,[231] and are in good agreement with theoretically calculated values (Fig. 14), *i.e.*, the terpolymerisation in such systems obeys the 'ideal' copolymerisation laws. The kinetic parameters of terpolymerisation for the monomers in question are also in line with the classical views on the effects of initiator and monomer concentrations on the reaction rate. Thus the terpolymerisation rate of copper acrylate, styrene (St) and acrylonitrile initiated by *p*-acetylbenzylidenetriphenylarsenic ylide is described by the equation [234]

$$W_p = \frac{[I]^{0.5}[St][AN]}{[Cu(O_2CCH{=}CH_2)_2]}. \qquad (11)$$

As in many examples mentioned previously, an increase in the concentration of copper acrylate results in a decrease in the polymerisation rate (Table 16). However, in copolymerisation of copper methacrylate with hydroxyethyl methacrylate in the presence of trimethacrylate of 1,1,1-tris(hydroxymethyl) propane, the terpolymer yield is rather high (70% – 80%) and does

**Table 15**. Copolymerisation constant of of methyl methacrylate ($M_1$) and methacrylic acid ($M_2$) in the presence of metal methacrylate.[228]

| Metal | $r_1$ | $r_2$ | $r_1 r_2$ | Harwood parameter |
|---|---|---|---|---|
| None | $0.37 \pm 0.06$ | $0.85 \pm 0.03$ | 0.315 | 36.90 |
| Li | $0.12 \pm 0.02$ | $0.16 \pm 0.02$ | 0.019 | 66.45 |
| Na | $0.19 \pm 0.03$ | $0.11 \pm 0.03$ | 0.021 | 53.76 |
| K | $0.27 \pm 0.02$ | $0.08 \pm 0.04$ | 0.022 | 45.05 |
| Cu | $0.36 \pm 0.02$ | $0.34 \pm 0.02$ | 0.122 | 41.7 |
| Co | $0.59 \pm 0.01$ | 0 | 0 | 30.7 |

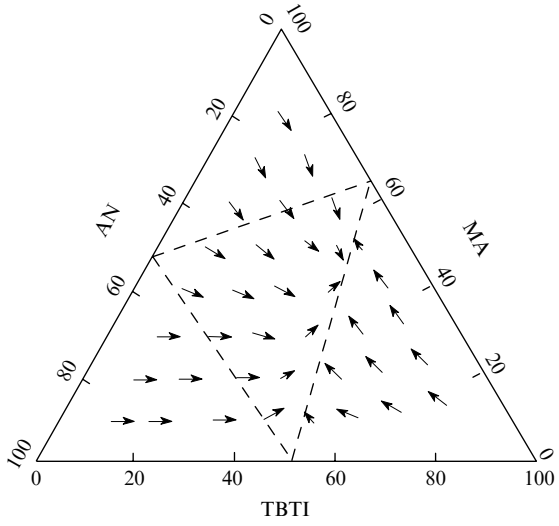



**Figure 14.** Composition of the bis(tributyltin) itaconate – methyl acrylate – acrylonitrile terpolymer *vs.* composition of the initial mixture.[231] The ends of arrows point to the molar composition of the copolymer obtained from monomer mixtures with contents corresponding to the coordinates of points in the arrow; the azeotrope boundary is shown by the dashed line.

**Table 16**. Effect of concentration of copper acrylate on the rate of its terpolymerisation with styrene and acrylonitrile.[234]

| Concentration of $Cu(O_2CCH{=}CH_2)_2$ /mol litre$^{-1}$ | Conversion (%) | $10^5 W_p$ /mol litre$^{-1}$ s$^{-1}$ |
|---|---|---|
| 0.062 | 12.3 | – |
| 0.093 | 10.3 | 2.1 |
| 0.124 | 7.9 | 1.7 |
| 0.155 | 6.6 | 1.3 |

not change substantially upon the variation of the salt concentration from 2.7 mol % to 3.82 mol %.[235]

The presence of metal ions in the molecules of unsaturated carboxylic acid salts induces coordination reactions and electron density redistribution on the growing polymerisation centre, which dictates the specific features of each elementary step and the process on the whole.

## IV. Molecular and structural organisation of metallo(co)polymers

The properties of (co)polymer-based materials are known to be substantially dependent on the sequence of different units in the polymer chains. The differences in the distribution of units are reflected in the type of intermolecular interactions, they are responsible for the diversity of supramolecular structures and affect the properties of materials.

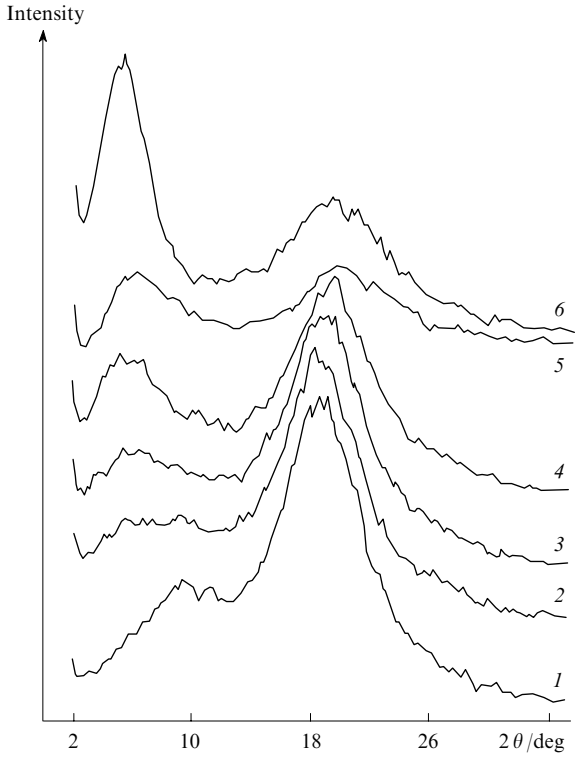



**Figure 15.** WAXS spectra of zinc acrylate – styrene copolymer with a salt content of 3.67 (*1*), 5.51 (*2*), 7.02 (*3*), 9.83 (*4*), 17.59 (*5*), 19.48 mol % (*6*).[242]

### 1. Ionic aggregates and multiplets

Many properties of metallopolymers are determined by ion aggregation. This is especially pronounced for alkali and alkaline earth metals, which allows them to be considered as ionomers. Polymerisation and copolymerisation of unsaturated acid salts provide unique possibility of one-stage synthesis of these polymers, whereas traditional methods for the preparation of ionomers include two stages: first, the component containing the ionogenic functional groups is introduced into the neutral core and then these groups are completely or partially neutralised.

The ionomer morphology is described using a variety of models, for example, the multiplet – cluster,[236,237] core – shell,[238–240] cylinder,[241] hard sphere[239] models and other. The formation of stable ion pair aggregates,[236] which may form either multiplets or clusters depending on the concentration, is believed to be the key factor determining the structure and properties of ionomers. Multiplets are small compact aggregates of ion pairs, while clusters are aggregates formed from a number of multiplets. It is assumed [237] that a region with lower mobility of polymeric chains appears around each multiplet. In the case of high concentrations of charged groups in the polymeric matrix (> 5% – 7%), these regions start to overlap, thus forming extended ion-enriched structures called domains (or clusters), which often behave as an individual phase. The contents of separate aggregates are determined by physicochemical methods and estimated from dynamic, mechanical, rheological or dielectric properties of metallopolymers. The methods used most often include small-angle X-ray scattering (SAXS),[239,242,243] near-range Raman and IR spectroscopy, EXAFS[244,245] and rare earth probe methods.[246,247] For example, in the Raman spectra of sodium polymethacrylate,[248] the absorption band at 254 cm$^{-1}$ was assigned to $CO_2^-$ vibrations in multiplets and the band at 166 cm$^{-1}$ was assigned to their vibrations in clusters. This is due to the fact that in complex aggregates the electrostatic interactions are more shielded and the frequencies of ion vibrations decrease with respect to the principal vibrational band for a particular cation or multiplet. Analogous regularities were also observed in the case of alkali metal acrylate copolymer with styrene:[249] the vibrational bands of the $COO^-$ group in the clusters occurred at about 155 cm$^{-1}$ for $K^+$ and $Na^+$ ions and at 95 cm$^{-1}$ for the $Cs^+$ ions. These aggregates were described in detail.[250]

It is noteworthy that the structures of ionic aggregates depend on many factors, for example, on the nature of the cation, the microstructure of the polymer chain, the methods for the ionomer preparation, *etc*. Thus it was shown by wide-angle X-ray scattering (WAXS) and SAXS[242] that in the zinc acrylate – styrene copolymer small ionic aggregates are mainly formed§ (Refs 251 and 252). In the WAXS spectrum, the ion peak at $2\Theta = 5.5°$ appears at a zinc acrylate concentration of 7.02 mol % and its intensity increases with an increase in the salt content (Fig. 15). Alkali metal acrylates copolymerised with styrene form ~70 – 100 Å cluster aggregates in addition to ion pairs and multiplets[243,253] even at concentrations of 3.85 mol % and 5.16 mol % (Ref. 249). As a rule, an increase in temperature of SAXS measurements, especially above the glass transition temperature ($T_g$) of the polymeric matrix, results in an increase in the size and number of clusters due to aggregation of free ion pairs and multiplets.[242,243] However, in the case of the zinc acrylate – styrene copolymer the sizes of

§ This is also typical of other Zn-containing ionomers. For example, in ethylene – methacrylic acid copolymers (the degree of neutralisation with zinc of 0.32 to 0.83), the size of ionic aggregates equals 0.45 nm over the whole range of metal ion concentrations; the same is true for the copper and iron ethylene ionomers.[251,252]

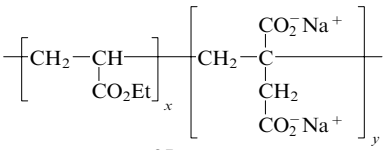
**Table 17**. Characteristics of ionomers based on zinc acrylate and styrene at different zinc acrylate concentrations (SAXS data).[242]

| Concentration (mol %) | $10^3 Q$ /(mol cm$^{-3}$)$^2$ | $d$ /Å | $R$ /Å |
|---|---|---|---|
| 7.02 | 0.109 | 17.3 | 3.7 |
| 9.83 | 0.147 | 17.7 | 3.8 |
| 17.59 | 2.11 | 15.8 | 3.7 |
| 19.48 | 5.34 | 19.8 | 4.0 |

**Note**. $Q$ is scattering invariant, $d$ is the average distance between the domains, $R$ is the ionic domain radius.

ionic aggregates and distances between them do not change noticeably under the same conditions, only the volume fraction of the aggregates does increase, as indicated by the change in the $Q$ value (Table 17).

The nature of the ionic associates is largely determined by the nature of the surrounding polymeric matrix. Thus the removal of the charged groups from the backbone favours the formation of ionic multiplets due to relief of steric restrictions. The multiplets affect slightly the phase behaviour of a macromolecule. This was demonstrated in relation to functionalised liquid-crystalline ionomers containing carboxyl groups of acrylic acid, 3-acryloyloxypropionic acid, *etc*.[254] Whereas in acrylic acid copolymers, the smectic phase is formed even at low metal ion concentrations ($\sim$2 mol %), an increase in the distance between the ionogenic groups and the polymer backbone is manifested as the inability of the ionomer to form the smectic $S_A$ phase. The change in $T_g$ of the polymeric matrix is yet another tool for effective control of the properties of ionomers.[255] Poly(ethyl acrylate-co-itaconate) (**25**) containing two ionic groups in one unit,



**25**

shows a higher tendency for cluster formation than the analogous ionomer based on polystyrene, which tends to form only several multiplets. This is confirmed by the logarithm of the relaxation modulus (6–9 Pa), mechanical and dielectric loss tangent (0 to 2.5) for these copolymers [256] and by much smaller $T_g$ value for the poly(ethyl acrylate) matrix compared to polystyrene one (by $\sim$125 °C).[257]

Thus, experimental results suggest that, owing to the presence of ions, ionomers tend to undergo microphase separation into polar and non-polar domains not only in the bulk or in the swollen state, but also in solution. The ion pairs and multiplets were detected in sodium polymethacrylate gels in methanol [258] and in a methanolic solution of PAA neutralised by singly charged cations.[259] According to a model proposed in the literature,[260, 261] in low dielectric constant solvents, the ion pairs of the polymer chain are collapsed and then associated to multiplets, being transformed into the 'supercollapsed state' or into ionic state. In polar solvents, ion pairs dissociate and the polymer is converted into polyelectrolyte. The type of interactions responsible for one or another state depends on the solvent nature and counter-ions and on the type of ionic groups in the polymer and on pH. For example, in the case of doubly charged complexing cations, *e.g*., $Cu^{2+}$ or $VO^{2+}$, the anionic fragments of the polymeric chain can be combined into charged associates even in polar media (in water).[262]

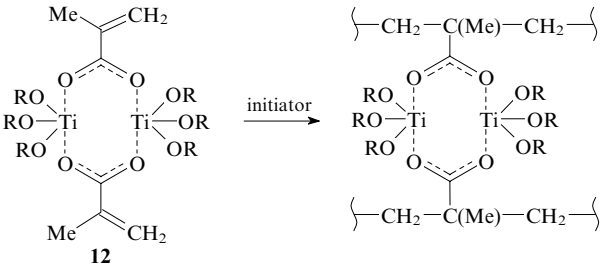
Various aggregates of the 'clusters of clusters' type were identified also for organic-inorganic hybrid polymers containing oxometallic cluster units (see Section II.5), although the nature of their formation is currently unknown.[263]

## 2. Morphology and topological structure of metallo(co)polymers

The structural organisation of metallo(co)polymers based on metal carboxylates is determined by the presence of a metal-containing coordination polyhedron, the polyfunctional character of the starting monomeric salt and the diversified nature of inter- and intramolecular links of the polymeric chains. Despite the regular, mainly syndiotactic structure of the polymers (see Section III.2.c) and the extended system of intermolecular interactions that create favourable conditions for compact packing of polymer chains and for crystallisation, most of the considered metallocopolymers are amorphous. Apparently, this is due to the large number of cross-links and the presence of ionic groups, resulting in an increase in the rigidity of macromolecular chains and thus hampering packing of the chains.

### a. Three-dimensional network polymers

Even minor changes in the chemical composition or nature of coordination bonds in the original monomer molecule results in changes in the structure and properties of the polymeric product. This can be demonstrated in relation to methacrylate derivatives of titanium(IV) alkoxides.[69, 264] As it was shown previously (see Section II.3), the $Ti(OR)_3[O_2CC(Me)=CH_2]$ molecule can be described by equilibrium structures **12** and **13** for R = $Pr^i$, $CH_2CH(Et)Bu^n$; or by structures **12**, **13** and **14** for R = $Bu^t$, *tert*-$C_5H_{11}$; or by structure **15** for R = $Bu^n$ (Ref. 69). The presence of the bidentate carboxylate bridge in the Ti(IV)-containing monomer molecule **12** accounts for the formation of a three-dimensional network polymer upon (co)polymerisation.



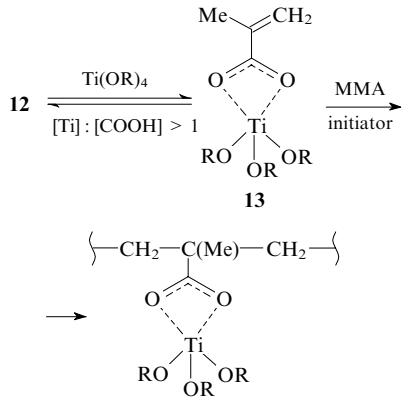

**12**

Esterification of titanium alkoxides with a tetrapolymer (MAA–MMA–EA–ethyl methacrylate) and a terpolymer (MAA–MMA–butyl methacrylate) containing acidic groups was studied.[264] It was shown that the formation of cross-linked structures can be efficiently controlled by varying the molar ratio of titanium tetraalkoxide to the amount of acidic groups, the nature of alkoxide groups and the concentration and composition of the polymer. For the ratio [Ti] : [COOH] $\leqslant$ 1, instantaneous formation of a three-dimensional gel was observed. However, on a gradual increase in the titanium alkoxide content ([Ti] : [COOH] > 1), the character of the mixture changed: in particular, the gel became less thick and, at a definte ratio called the 'threshold ratio', the gel transformed into a stable solution. The IR spectra of the polymeric film obtained from this solution exhibited vibrational bands

for the COO group: $\nu_{as} = 1550\ cm^{-1}$ and $\nu_s = 1450\ cm^{-1}$, which was indicative of a bidentate chelating coordination of the carboxylate group by titanium ($\Delta\nu = 100\ cm^{-1}$). In the formation of cross-linked polymers, the ligand environment of the metal atom in the interchain space is also significant. The longer the alkyl group in $Ti(OR)_4$ the lower the threshold ratio [Ti] : [COOH] and the easier the formation of chelate structures: [69]

| R | Et | $Pr^n$ | $Pr^i$ | $Bu^n$ | $CH_2CH(Et)Bu^n$ |
|---|---|---|---|---|---|
| Threshold ratio [Ti] : [COOH] | 13 | 12 | 17 | 7 | 3 |

These findings were successfully used for preventing the formation of a three-dimensional network in copolymerisation of titanium(IV) alkoxide methacrylates with MMA.




The efficiency of cross-linking of the gel formed increases on an increase in the concentration of sodium methacrylate in the presence of a cross-linking agent, *N*,*N*′-methylenebis(acrylamide).[265] The dielectric properties of polymers prove to be especially sensitive to changes in the mutual arrangement of chains. This is indicated by a sharp increase in the real part of the dielectric constant ($\varepsilon'$) of dry cross-linked metallopolymers upon an increase in the concentration of the initial salt in the hydrogel (Fig. 16). This change in $\varepsilon'$ is attributed to the presence of residual water the content of which is determined by the structure of the polymer network.

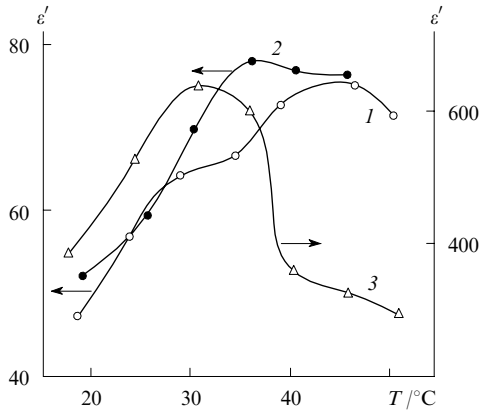
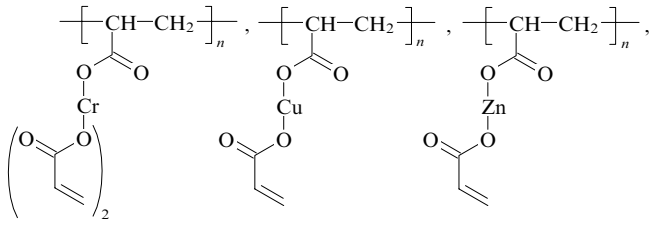


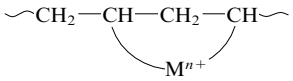

**Figure 16.** Temperature dependences of $\varepsilon'$ for cross-linked sodium polymethacrylate for an initial concentration of methacrylic acid of 20 (*1*), 30 (*2*) and 40% (*3*) (1 kHz).[265]

**b. Interpenetrating polymer networks**

The ability of metallocopolymers to form spatially cross-linked structures is very important for the production of polymer blends or alloys based on them and provides broad possibilities for modification of polymer properties. Interpenetrating polymer networks (IPPN) are combinations of two cross-linked polymers where the synthesis and cross-linking (of at least one of them) are carried out in the presence of the other. The main components of such systems can be represented, on the one hand, by metal polyacrylates (*e.g.*, zinc,[266, 267] chromium and copper [267] polyacrylates) or the monomeric salts, and, on the other hand, vinyl monomers or their (co)polymers. Most often, an additional cross-linking agent is used, for example, divinylbenzene (DVB) (up to 20 mol % – 25 mol %). Examples of preparation of interpenetrating polymer networks based on various metal polyacrylates were reported.[93, 268–270] The metal polyacrylates used as precursors are usually represented by linear polymers soluble in benzene, DMF, DMSO and dioxane [266, 267, 269, 270] and containing some unreacted acrylate fragments.




The number of unsaturated bonds depends on the nature of the monomeric salt, type of reaction and the degree of monomer conversion; for bifunctional carboxylates, it ranges from 4% to 49% according to different estimates.[212, 213, 271] Almost in all cases studied, the degree of unsaturation is $< 0.5$. The decrease in the number of residual double bonds can be attributed, for example, to the formation of intramolecular ring structures:




Intermolecular cyclisation steps giving rise to cross-linked chains also cannot be ruled out. Thus on heating of cobalt polyacrylate for 0.5 h at 100, 150 and 200 °C, the intensity of the IR band of residual double bonds (at 1640 $cm^{-1}$) substantially decreased, and on heating to 250 °C this band virtually disappeared.[190] However, the role of cyclisation in the cross-linking of the systems under consideration is most often insignificant. For example, in the preparation of IPPN based on zinc polyacrylate, styrene and MMA, an increase in the polymeric salt concentration leads to an increase in the degree of swelling of the polymer network (in DMF) and in the average molecular mass of chains between the cross-links ($M_c$) (Table 18).[266] However, when a monomeric salt is used as the starting compound in the preparation of IPPN, the opposite effects are observed: as the concentration increases, the degree of cross-linking increases but the degree of swelling and $M_c$ decrease.[92]

The polymer networks comprise a continuous phase of one component with characteristic inclusions of spherical,[269] cellular [92] or other structures of the second component (Fig. 17).

Many physicochemical properties of polymer blends are determined first of all by compatibility of the components. The

**Table 18**. Effect of the zinc(II) polyacrylate concentration on the properties of interpenetrating polymeric networks based on it.[266]

| Concentration /$10^{-2}$ mol litre$^{-1}$ | Yield (%) | Swelling (%) | $M_c$ /g mol$^{-1}$ |
|---|---|---|---|
| 14.49 | 6.3 | 41.4 | 322 |
| 9.66 | 16.7 | 39.3 | 294 |
| 4.78 | 20.8 | 37.0 | 241 |
| 2.42 | 24.0 | 36.1 | 198 |

**Note**. The concentrations of the initiator, styrene, MMA and DVB are $5.19 \times 10^{-3}$, 1.38, 1.44 and 0.83 mol litre$^{-1}$, respectively.



**Figure 17.** Photomicrograph of the polymer network based on the zinc polyacrylate – styrene copolymer with MMA (magnification 790).[266]

degree of compatibility of two polymers can be evaluated from glass transition temperature. The arsenic polyacrylate – polyacrylonitrile (PAN) system (1 : 1 ratio)[269] has two close $T_g$ values (146 and 152 °C), indicating a rather homogeneous distribution of two phases, each being enriched in one of the polymers. Studies of the composition of polymer blends by differential scanning calorimetry (DSC) confirmed the formation of a polymer alloy also in the bismuth polyacrylate – PAN system where a single, rather high glass transition temperature was found (281 °C). The effective compatibility of polymeric components is apparently favoured by intermolecular van der Waals interactions and complexation involving the CN groups of PAN and the polyacrylate metal ions. This is confirmed by the shift of stretching vibrations $\nu(C\equiv N)$ to longer wavelengths in the IR spectra of polymer alloys (from 2260 to 2241 and 2243 cm$^{-1}$ for bismuth polyacrylate – PAN and arsenic polyacrylate – PAN systems, respectively).

**c. Hybrid supramolecular structures**

As noted above (see Section II.5), the binuclear metal carboxylates $M_2(O_2CR)_4L_2$ tend to form lantern type structures (see Fig. 2). Polymerisation of binuclear carboxylates with linear dicarboxylate bridges yields highly symmetric 2D structures (Fig. 18 *a*), and the interplane contacts in such systems produce an infinite chain of linear micropores (Fig. 18 *b*). This structure is characteristic of both fumarates and *trans*,*trans*-muconates containing binuclear $Mo_2^{4+}$ (Refs 272–274) and $Rh_2^{4+}$ (Ref. 275) ions or $Ru^{2+} - Ru^{3+}$ units.[276] The synthesis of this type of dimetal carboxylates in the presence of linear polymers, for example, poly(ethylene glycol) gives rise to supramolecular inclusion complexes **26**.[272, 273]

$$Mo(OAc)_4 \xrightarrow[MeOH,\ Ar]{X(CO_2H)_2} Mo(O_2C{-}X{-}CO_2)_2 \cdot P_n$$

**26**

X = CH=CH, CH=CH–CH=CH;

$P_n$ = HO–[$CH_2$–CHR–O]$_n$–H (R = H, Me).

The products are non-covalenly bound assemblies of 'host – guest' type supramolecules: the polymer chain is located in micropores (see Fig. 18 *b*). In molybdenum(II) fumarate complexes with polyesters,[272] the number of polymer guest molecules depends on the polymer molecular mass: in the case of poly(ethylene glycol), this number is maximum at the polymer molecular mass of $>3000$, which corresponds to four ethylene glycol units per $Mo_2$ unit, and for poly(propylene glycol) this value is twice smaller due to the greater size of the monomer unit.

Among promising trends in the synthesis of polymeric supramolecular structures, note intercalation of acrylate ions followed by their polymerisation *in situ* in molecules of layered double metal hydroxides (LDH) as inorganic 'hosts'.[277, 278] Using this approach, acrylate and polyacrylate nanocomposites containing $Ni_{0.7}M_{0.3}$ carboxylate fragments (M = Fe, Co, Mn) were obtained.[279, 280] In the case of Fe intercalates, it is possible to isolate monomeric (Fig. 19 *a*) and polymeric (see Fig. 19 *b*,*c*) systems in successive synthetic stages, whereas for Co- and Mn-containing nanocomposites, intercalation and polymerisation take place in one stage to give polyacrylate

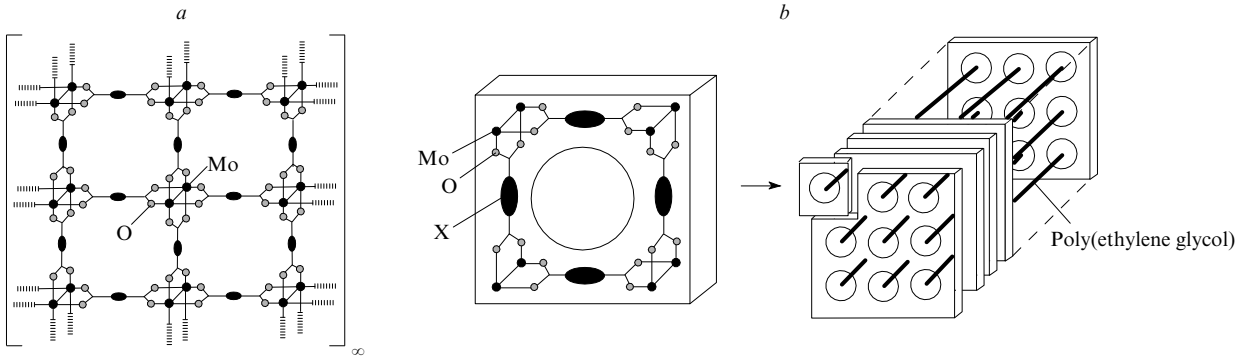



**Figure 18.** Structure of coordination polymers based on dimetal carboxylates (*a*) and scheme of formation of linear micropores, which can accommodate poly(ethylene glycol) chains (*b*).[272]

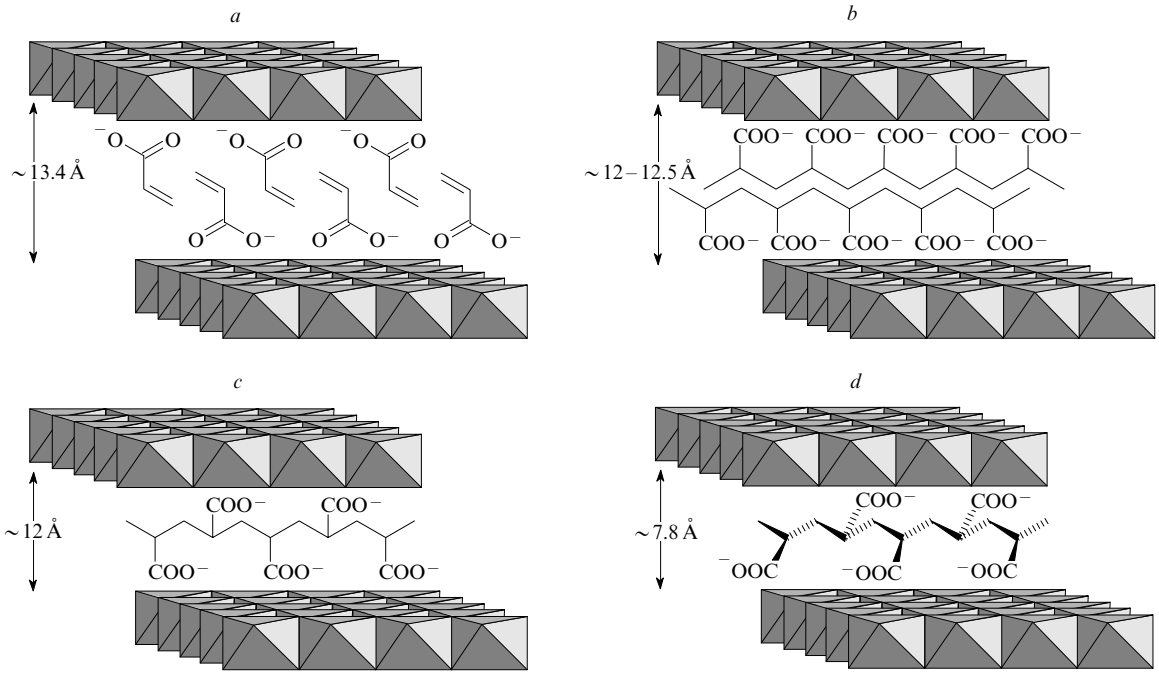
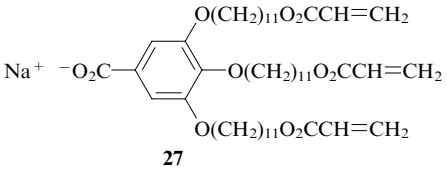



**Figure 19.** Schematic view of intercalated nanocomposites: LDH($Ni_{0.7}Fe_{0.3}$ acrylate) (*a*), bilayer LDH($Ni_{0.7}M_{0.3}$ polyacrylate) (M = Fe, Co) (*b*) and monolayer LDH($Ni_{0.7}M_{0.3}$ polyacrylate) [M = Fe or Co (*c*), Mn or Co (*d*)].[279]
The layered double hydroxides were obtained by solid-phase synthesis (*b*, *c*) and coprecipitation (*d*).

structures (see Fig. 19 *c*,*d*). Depending on the conditions of synthesis, the interlayer distances in these materials are 7.8–12.5 Å.

In addition to micro- and mesoporous compounds, liquid and organic crystals, micelles, bilayer lipids and so on are often used as highly organised media for the preparation of supramolecular systems.[281] Thus mixing of poly(*p*-phenylenevinylene) (PPV) with amphiphilic acrylate monomers or their precursors, for example, salt **27**,[282, 283]




**27**

affords a reverse lyotropic liquid-crystalline phase in which the polymer, poly(*p*-phenylenevinylene), pierces the hexagonal structure and is oriented parallel to the *c* axis (Fig. 20).

Photopolymerisation of the acrylate salt **27** and subsequent heating of the cross-linked matrix lead to the formation of a hybrid material with more intensive fluorescence compared to the bulk poly(*p*-phenylenevinylene). Note that in the case of similar Eu(III) salt,[283] a new intense band appears in the emission spectrum at 670 nm, indicating the interaction of the metal cation with PPV chains with possible energy transfer between the components.

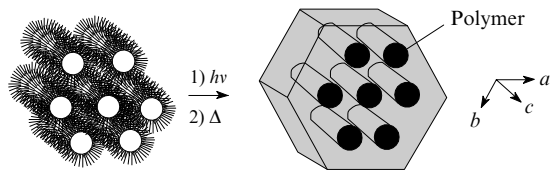
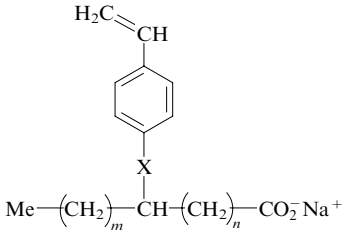



**Figure 20.** Scheme of stabilisation of lyotropic liquid-crystalline phase by polymerisation of an acrylate monomer.[282]

The dimensions of the reverse hexagonal phase depend on the nature of the metal and type of metal–carboxylate interaction,[283, 284] and for amphiphilic mesogenic metal-containing monomers, *p*-styryl (**28**) and *p*-styryloxy octadecanoates (**29**), also on the length and structure of the aliphatic chain.[285]




**28**, **29**

X is none (**28**), X = O (**29**); $m + n = 15$.

For systems containing liquid-crystalline salts of mesogenic metallomonomers and nanostructured polymers and composites based on them, the interplanar spacings ($d_{hkl}$) in the crystal lattice of the hexagonal mesophase were found by powder X-ray diffraction; these spacings are determined by the charge and the size of the metal ion (Table 19).[283, 284] Salts of triply charged lanthanide ions have smaller unit cells than similar salts of doubly charged transition metals, which is consistent also with the data from IR spectroscopy on the coordination mode of the carboxylate ion (see Section II.2). Stronger chelation of the carboxylate group with lanthanide ion ($\Delta\nu = 96-97$ cm$^{-1}$) results in a decrease in the overall size of the amphiphilic molecule and ensures closer packing of the

**Table 19**. Powder X-ray diffraction data for nanostructured polymers based on liquid-crystalline salts of mesogenic metallomonomers **28** and **29**.[283, 284]

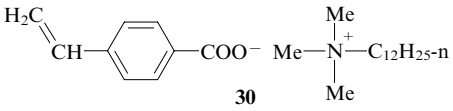
| Metal ion | Compound **28** [a] | | | Compound **29** [b] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | monomer mixture | | | | | after polymerisation | | | | |
| | $d_{100}$ | $d_{110}$ | $d_{200}$ | $d_{100}$ | $d_{110}$ | $d_{200}$ | $r$ [c] | phase [d] | $d_{100}$ | $d_{110}$ | $d_{200}$ | $r$ [c] | phase [d] |
| $Na^+$ | 34.5 | 20.2 | 17.5 | 36.7 | 21.1 | 18.3 | 42.1 | RH | 35.7 | 20.5 | 17.7 | 41.0 | RH |
| $K^+$ | – | – | – | 38.2 | 19.5 | 13.0 | 38.8 | L | 38.2 | 19.2 | 13.0 | 38.6 | L |
| $Ca^{2+}$ | – | – | – | 30.9 | 18.1 | 15.7 | 36.1 | RH | 30.4 | 17.7 | 15.4 | 35.4 | RH |
| $Mg^{2+}$ | – | – | – | 28.9 | 16.9 | 14.6 | 33.6 | RH | 28.1 | 16.5 | 14.2 | 32.9 | RH |
| $Ni^{2+}$ | 35.8 | 20.8 | 18.2 | – | – | – | – | – | – | – | – | – | – |
| $Co^{2+}$ | 35.6 | 20.3 | 17.7 | 27.7 | 15.9 | 13.8 | 31.9 | RH | 28.2 | 15.6 | 13.6 | 31.5 | RH |
| $Cd^{2+}$ | 35.0 | 20.6 | 18.0 | 30.0 | 17.4 | 15.3 | 34.9 | RH | 29.5 | 17.2 | 15.1 | 34.5 | RH |
| $Cu^{2+}$ | – | – | – | 23.0 | 13.3 | 11.5 | 26.7 | CH | 22.6 | 13.1 | 11.4 | 26.2 | CH |
| $Eu^{3+}$ | 30.2 | 17.6 | 15.7 | – | – | – | – | – | – | – | – | – | – |
| $Ce^{3+}$ | 30.9 | 17.8 | 15.5 | – | – | – | – | – | – | – | – | – | – |

**Note**. The $d$ values are in Å. [a] After polymerisation of the system **28** (85 mass %) – $H_2O$ (10 mass %) – 2-hydroxy-2-methylpropiophenone (HMP, 5 mass %); [b] after polymerisation of the system **29** (87 mass %) – DVB (7 mass %) – $H_2O$ (5 mass %) – HMP (1 mass %); [c] $r$ is the interchannel distance (Å); [d] phase designations: RH is reverse hexagonal, L is lamellar, CH is columnar hexagonal.

molecule. Larger metal ions, the charge being the same, are more prone to form lamellar or regular hexagonal structures. For example, potassium salts form lamels with an interchannel distance of 38.9 Å, whereas sodium *p*-styryloctadecanoate (**28**) tends to form a clearly defined reverse hexagonal phase with $r = 41.9$ Å.[284]

Among analogous salts, the size of the mesophase formed by copper *p*-styryloctadecanoate is the smallest. Powder X-ray diffraction data attest to the formation of a thermotropic columnar-hexagonal phase, which is related to specific features of binuclear structure typical of copper carboxylates (see Section II.2.a). It is noteworthy that the microstructure of the liquid-crystalline phase is not changed much during polymerisation and chain cross-linking (see Table 19).

A similar approach to the synthesis of highly organised systems was applied to prepare polymeric micelles based on the 4-vinylbenzoate monomer **30**.




**30**

The rod-like shape of molecule **30** is retained during radical polymerisation and the product is thermally stable and is not changed on dilution.[286]

The directing influence of the 'parent' polymer chain and non-valence interactions favour the formation of ordered polyelectrolyte complexes during matrix polymerisation of sodium methacrylate [287] or acrylate [288] in the presence of poly(allylamine) hydrochloride as the template polymer molecule (Fig. 21 *a*). The kinetic effects (high initial rate of polymerisation and dependence of the rate on the molar ratio of the template units and the monomer) are consistent with the predominant growth of the daughter chains according to the so-called zip-mechanism, which implies that the monomer molecules are initially adsorbed on the template macromolecule and then growth takes place. However, deviations from the ideal zip-mechanism are also possible: for example, in those cases where the growing radical reacts with the monomer of another template chain or where non-adsorbed monomer molecules are involved during the chain growth and then another template chain is added. In this case, polymerisation becomes diffusion-controlled and its rate decreases. This gives rise to a network product (see Fig. 21 *b*).

These data imply that the molecular organisation of metallopolymers can be different: from linear polymers to two- and three-dimensional networks and supramolecular structures. The structural and chemical control of polymerisation at all levels of metallo(co)polymer organisation, *i.e.*, molecular,

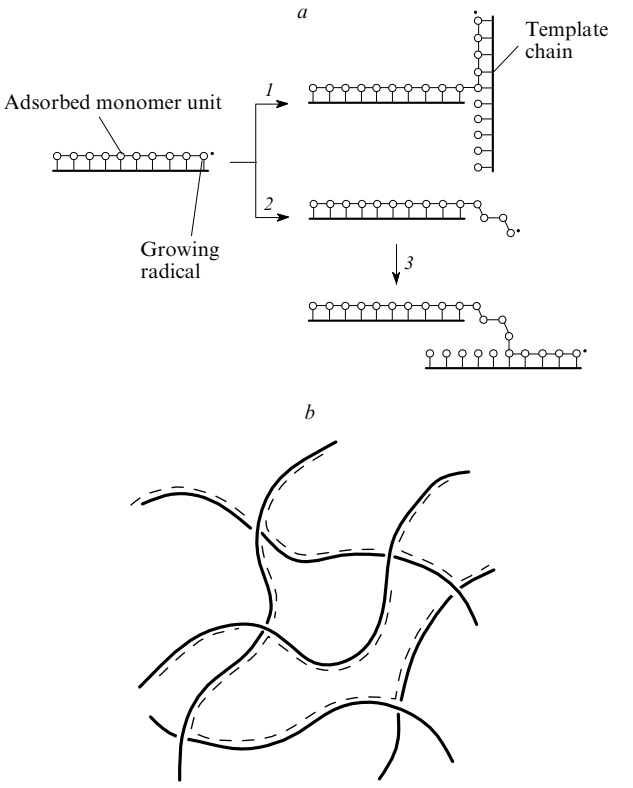
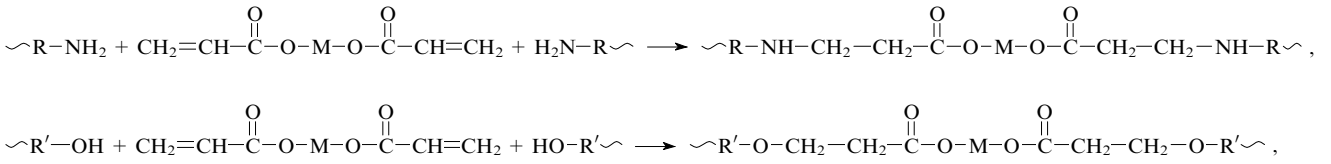



**Figure 21.** Mechanism of template polymerisation of sodium methacrylate in the presence of poly(allylamine) hydrochloride (*a*) and schematic view of the network structure of the resulting polymer (*b*).[287]
(*1*) Formation of network nodes, (*2*) attachment of non-adsorbed monomer, (*3*) linear chain formation.

Scheme 1



R, R′ — gelatine macromolecules

topological and supramolecular levels, allows the production of new materials with a set of valuable properties.

## V. Properties and applications of metallo(co)polymers

The properties of metallo(co)polymers and traditional polymers modified by means of metal carboxylates are largely determined by the ability of metal ions to form ionic and coordination bonds, the possibility of electronic transitions in the metal atoms induced by both an electric field and high-energy radiation, by cohesion and adhesion interactions, and by geometric and configurational features of metallocomplexes.

### 1. Enhancement of the properties of polymeric materials by cross-linking using monomeric and polymeric salts

As shown above, polymer cross-linking involving metal carboxylates may follow different mechanisms: (co)polymerisation of monomeric salts; cross-linking through additional interchain coordination of a metal ion to an electron-saturated heteroatom; polymerisation of the residual double bonds in the polymers; the use of aggregates and multiplets in the ionomer molecules as the nodes of physical network, *etc*. For example, photopolymerisation of metal acrylates in a gelatin matrix is accompanied by chain cross-linking through addition of the gelatin $NH_2$ and OH groups to the acrylate double bond (Scheme 1).[289, 290]

The cross-linking of metallocarboxylate (co)polymers increases considerably their thermal stability as compared with the metal-free analogues. The destruction temperatures ($T_d$) of metal-containing macromolecules usually exceed 300–400 °C. Thus for lithium and sodium polymethacrylates $T_d$ are equal to 457 and 491 °C, respectively.[31] At high temperatures, cobalt(II), nickel(II) and zinc(II) polyacrylates also decompose (Table 20).[291] The decrease in the weight of these polymers during heating to 210 °C is due to evolution of methanol (the solvent used most often for polymerisation) occluded in the polymer. The second endothermic peak refers to decomposition of polymer salts. The thermal stability of polyacrylates depends on the nature of the metal ion and varies in the series $Zn^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}$.

The cross-linking effect of metal carboxylates is manifested in the preparation of copolymers based on them. Thus an increase in the content of lead methacrylate from 5 mass % to 25 mass % in terpolymers of lead(II) methacrylate, styrene and methacrylic acid [292] increases the initial temperature of their destruction corresponding to a 5% loss of mass in a nitrogen atmosphere from 350 to 380 °C; simultaneously, the glass transition temperature increases from 126 to 148 °C. The addition of only 0.5 mol % of the cluster monomer $Zr_6O_4(OH)_4[O_2CC(Me)=CH_2]_{12}$ to the copolymerising system results in an increase in the $T_d$ by 50 °C for polystyrene and by 110 °C for PMMA.[293, 294] The cross-linking density in the cluster-containing copolymers of this type increases even more upon polymerisation of the remaining double bonds, for example, upon post-thermal treatment of methacrylate $Mn_{12}O_{12}(O_2CC(Me)=CH_2)_{16}(H_2O)_4$ copolymers with MMA.[295] Typically, the metal-containing copolymers formed are distinguished by composition uniformity, as indicated by the DSC data, namely, the only $T_g$ value depending on the content of cluster units in the copolymer.

For ion-containing copolymers obtained at low degrees of transformation of monomers, the role of ionic cross-links is quite significant. This is indicated by the increase in $T_g$ of copolymers with an increase in the concentration of the ion-containing component (Table 21).[242, 296, 297]

Good agreement was established [298] between the experimental $T_g$ values and those calculated from the equation

$$T_g = \frac{m_A T_{gA} + K_g m_B T_{gB}}{m_A + K_g m_B} + q\, m_A m_B, \qquad (12)$$

where $T_{gA}$ and $T_{gB}$ are glass transition temperatures of homopolymers A and B, $m_A$ and $m_B$ are the mass fractions of

**Table 20**. Results of investigation of the thermal decomposition of metal polyacrylates in a nitrogen atmosphere.

| Metal | Process | DTGA [a] | | TGA [a] | | DTA [b] | |
|---|---|---|---|---|---|---|---|
| | | temperature peak /°C | region /°C (see [c]) | mass loss (%) | total mass loss in the 25–500 °C range | temperature peak /°C | region /°C (see [c]) |
| Zn(II) | loss of MeOH | 84 | <210 | 14.5 | 51.5 | 90 | <210 |
| | decomposition | 418 | 360–460 | 35.0 | | 416 | 397–440 |
| Co(II) | loss of MeOH | 96 | <210 | 18.0 | 60.5 | 110 | <210 |
| | decomposition | 410 | 370–480 | 39.4 | | 413 | 403–450 |
| Ni(II) | loss of MeOH | 93 | <210 | 22.0 | 65.5 | 102 | <210 |
| | decomposition | 368 | 300–415 | 40.0 | | 374 | 360–415 |

[a] (D)TGA is (differential) thermogravimetric analysis; [b] DTA is the differential thermal analysis; [c] the temperature region is indicated.

**Table 21**. Glass transition temperatures of styrene copolymer with metal acrylates.[296]

| Metal | Acrylate content (mass %) | $T_g$ /°C | |
|---|---|---|---|
| | | experiment | calculated |
| None | 0 | 87 | |
| Zn(II) | 7.05 | 103 | 102 |
| | 10.41 | 107 | 109 |
| | 13.07 | 114 | 114 |
| | 22.77 | 134 | 133 |
| | 29.84 | 146 | 146 |
| | 100 | 423 | – |
| Co(II) | 1.76 | 94 | 91 |
| | 4.20 | 97 | 95 |
| | 8.53 | 103 | 104 |
| | 11.26 | 109 | 109 |
| | 17.06 | 115 | 119 |
| | 100 | 368 | – |
| Ni(II) | 2.04 | 95 | 92 |
| | 3.80 | 98 | 96 |
| | 6.01 | 102 | 100 |
| | 11.29 | 109 | 111 |
| | 13.74 | 114 | 116 |
| | 100 | 410 | – |

components A and B in the copolymer, $K_g$ is the copolymer constant ($K_g = T_{gA}/T_{gB}$), the parameter $q$ takes into account the specific interactions in the system and can be used to estimate the efficiency of cross-links.

The glass transition temperatures of zinc, cobalt and nickel polyacrylates (see Table 21) determined by extrapolation of glass transition temperatures of copolymers to a zero styrene content are close to $T_g$ of other metal poly(methacrylates), *e.g.*, of sodium (363 °C) and lithium (359 °C),[31] and $T_g$ of chromium polyacrylate was much lower (254 °C).[167]

Unsaturated metal carboxylates are widely used as cross-linking agents on curing of unsaturated polyether resins and in rubber vulcanisation. In addition to the considerable improvement of mechanical characteristics of these composites, their thermal stability also increases relative to the initial materials.[299–302] For example, the tensile strength of a composite based on magnesium dimethacrylate and vinyl acetate rubber is 22.5 MPa, and the elongation at break exceeds 300%, this value being retained even when the content of the methacrylic sal is $< 50$ mol %.[300] Epoxy resins based on bisphenol A and epichlorohydrin obtained in the presence of chromium(III) acrylate have enhanced thermal stability.[43] Thus modified epoxy polymers have high electrical conductivity: $(4.6–6.1) \times 10^{-10}\ \Omega^{-1}\ cm^{-1}$. Previously, similar properties were revealed for block copolymers of chromium,[42] copper[216] and nickel[218] acrylates.

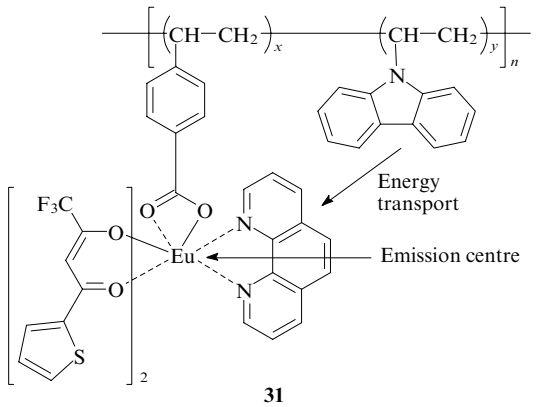
## 2. Radiation stability, photophysical and optical properties of metallo(co)polymers

Exposure of a metal ion or atom to ionising radiation usually gives rise to low-energy electrons; their transition from one level to another is accompanied by various radiation effects of the polymer matrix. The metal content in the polymer is an essential factor: at low metal concentrations, the polymer matrix undergoes destruction or cross-linking and at higher content (30 mol % – 50 mol %), copolymers acquire protective properties from various types of radiation. This is characteristic of homopolymers of magnesium, zinc, strontium, cadmium, copper, mercury and lead (meth)acrylates and for their copolymers with MMA and tetra(ethylene glycol) diacrylate.[303] Good protective properties of these polymers are combined with the optical transparency of the material. Thus light transmission of optical resins based on copolymers of Pb, Ba, Sr, Zn, Ti, Zr, Th vinylbenzoates or methacrylates acid with vinyl monomers exceeds 80%.[304] The relative transparency of lead (meth)acrylate copolymers with alkyl acrylates reaches 88%. This material was used to manufacture transparent X-radiation filters.[305]

The same type of optical properties was found for the St – MAA – lead(II) methacrylate terpolymers.[292] They are transparent in the visible region. The refractive index ($n_D$) decreases with an increase in the content of methacrylic acid and, conversely, increases upon an increase in the fraction of the metal salt in the terpolymer up to 40 mass %. These data together with high (compared to other comonomers) $n_D$ value for the $Pb(O_2CC(Me)=CH_2)_2$ homopolymer (1.622) suggest that lead(II) methacrylate additives to the system of monomers can change substantially the refractive index and increase the radiation stability of the optical resins. Even low content of $Pb(O_2CC(Me)=CH_2)_2$ ($\sim 5$ mass %) results in fairly high X-ray absorption by its terpolymer with styrene and MMA (97.2% for the radiation energy $E_X = 8.04$ keV); the salt content of 25 mass % ensures complete absorption of the radiation. Copolymers of lead mono(alkyl) itaconates are also used as radiation protective materials.[306] Cadmium methacrylate – alkyl methacrylate copolymers are lusterless transparent materials; these are used for protection from neutrons.[306]

On exposure to non-ionising radiation, metallopolymers behave in an unusual way. The polymeric nature of the ligand accounts for the specific luminescence and photochemical properties of macromolecular complexes. This can be demonstrated especially clearly in relation to lanthanide salts the photoluminescence properties of which is well known. For example, on passing from europium and terbium methacrylates to their homopolymers, fluorescence intensity considerably decreases: almost by an order of magnitude for $Eu^{3+}$ ions and fourfold for $Tb^{3+}$ ions,[117,307] which is due to the effective concentration luminescence quenching caused by high content of the metal (up to 50 mass %) in the metallopolymer. Similar phenomena can also be induced by slight radiation absorption by the metal ion and the absence of effective intramolecular energy transfer from the levels of the macromolecular ligand to the levels of the emission centre.

There are two approaches to the increase in the fluorescence intensity of the considered metallopolymers. One of them consists of introduction into the macromolecule of an organic ligand able to transport the absorbed energy to the rare earth ion. The second method implies an increase in the absorption capacity of the metal ion due to a change in its steric environment. Ligands such as dibenzoylmethane,[308,309] 1,10-phenanthroline,[70,310] salicilylate[311] and naphthoate anions for unsaturated rare earth salts[312] can be used as chromophore groups that enhance the electron transport. If necessary, it is possible to introduce several such groups into the metallopolymer. For example, copolymerisation of the monomeric complex based on europium(III) 4-vinylbenzoate[70] (or methacrylate[310]) with *N*-vinylcarbazole gave bifunctional copolymers **31** containing two energy transfer channels (the carbazole and phenanthroline fragments transport holes and electrons, respectively).




**31**

This combination of different functional groups in the macromolecular chain results in pronounced enhancement of the luminescence properties, first of all, an increase in the luminescence intensity of metallocopolymers with respect to the monomeric rare earth salts. Thus the luminescence intensity for europium(III) bis(naphthoate)acrylate copolymer with methyl methacrylate at the excitation energy $\lambda = 300$ nm is almost eightfold higher than for the corresponding monomeric complex.[312]

The excitation energy transfer from the chromophore group to the lanthanide ion is proved by the luminescence excitation spectra. Indeed, these spectra[308] of the europium(III) acrylatebis(dibenzoylmethanate) metallocopolymer with MMA exhibits, in addition to the discrete lines caused by intraconfigurational $f$–$f$ transitions of the $Eu^{3+}$ ion, also broad diffusion bands at 350–500 nm related to the electron transitions in the ligands. For example, in the spectrum of europium polyacrylate is a set of narrow discrete lines (Fig. 22), the most intensive band corresponds to the

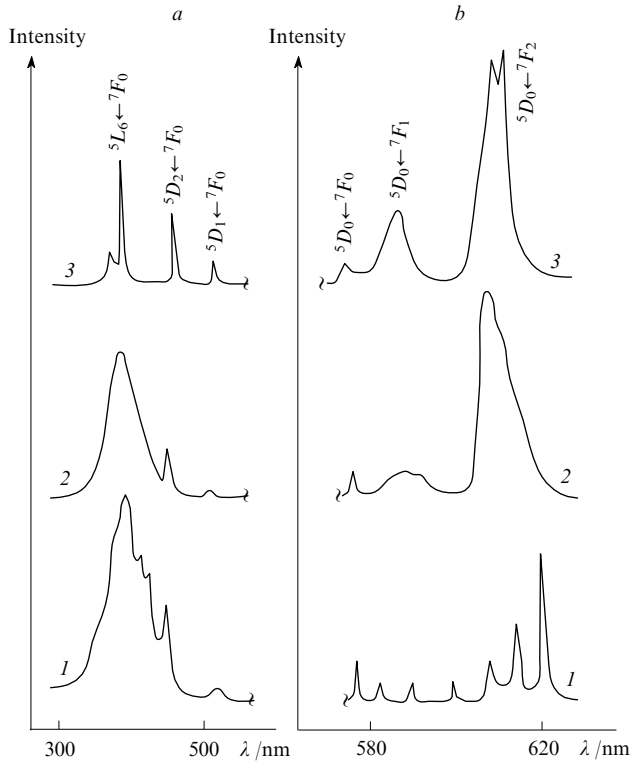



**Figure 22.** Luminescence excitation ($\lambda = 612$ nm, 77 K) (*a*) and luminescence (77 K) spectra of europium(III) acrylatebis(dibenzoylmethanate) (*1*), its copolymer with MMA (*2*) and europium polyacrylate (*3*) (*b*).[308]

$^5L_6 \leftarrow {}^7F_0$ transition (at 395 nm), which increases the probability of radiationless energy loss at $Eu^{3+}$ higher excited levels. The spectral pattern attests to the absence of excitation energy transfer from the polyacid levels to the resonance levels of the metal, which is in line with the relatively low luminescence of this metallopolymer.

The dependence of the fluorescence intensity on the metal ion content in the metallocopolymer is, most often, nonlinear. Thus terbium acrylatebis(salicylate) copolymers with MMA and styrene[311] show maximum luminescence intensity at a metal content of 3.8 mass % and 2.8 mass %, respectively. Analogous dependences were found in another study.[312] Note that polymeric systems in which Eu and Tb acrylate complexes function as chemically non-bonded doping agents are prone to concentration emission quenching. The luminescence spectra of the polymeric systems that contained a saturated rare earth carboxylate additives have been studied.[313] As comonomers, methacrylates of the same metals were used. It was found that their introduction into a macromolecular chain as comonomers results in an increase in the intensity of the characteristic emission bands (almost 10-fold for europium methacrylate and 3-fold for terbium methacrylate) compared to the intensity of this band in the systems containing octanoates of these metals.

It is noteworthy that there exist different views on the mechanism of luminescence deactivation in the systems considered. For many lanthanide polymers, deactivation is related to an increase in the efficiency of excitation energy cross-relaxation with an increase in the local concentration of the metal ions in multiplets and ionic aggregates.[247, 314–316] A considerable contribution to the emission quenching processes can be made by electrostatic multipolar interactions [311, 317] and by migration of ligand excitation energy in macrocomplexes.[311, 312, 318, 319]

Thus, stabilisation of the luminescent centre through the covalent binding of the metallocomplex to the polymer chain and its homogeneous distribution in the macromolecular chain during copolymerisation of the unsaturated salts allows one to change efficiently the photophysical and fluorescence properties of metallopolymers. In addition, this modification helps to avoid phase separation and ion aggregation observed in the systems obtained by physical mixing of the polymer and the rare earth complex. For example, the photoluminescence quantum yield of the terpolymer poly(*N*-vinylcarbazole)–MMA–bis(benzoylacetonate)(1,10-phenanthroline) europium methacrylate was 40.28%, which is severalfold (in some cases, by an order of magnitude) larger than the corresponding value for low-molecular-mass complexes and doped polymeric systems.[310]

On the basis of materials that combine the functions of charge carrier and emission layers able to emit monochromatic radiation and to form films, one can design various electroluminescent devices, for example, polymeric light emitting diodes. Thus a one-layer monochromatic diode was obtained from the copolymer of the bis(thenoyltrifluoroacetonate)-(1,10-phenathroline)europium 4-vinylbenzoate complex with *N*-vinylcarbazole.[70] Its key characteristics are comparable with or even exceed, the parameters of analogous devices based on other $Eu^{3+}$ complexes.[320, 321]

The prospects of using metallopolymers as fluorescent materials and laser-active media stimulate studies into their thermal and photochemical stability. The photochemical behaviour of metallopolymers is affected by various factors, in particular, the composition and structure of the macrocomplex, the microstructure of the polymer chain, the coordination state of the metal ion, and so on. On UV irradiation of the polymeric $Eu^{3+}$ and $Tb^{3+}$ complexes, the intensity of the

principal absorption bands in the IR spectra decreases and the electronic absorption spectra develop a band at 270–280 nm corresponding to vibrations of the carbonyl chromophores, which is indicative of photodestruction of the macromolecular ligand.[322] The luminescence intensity of terbium polyacrylate almost does not change during UV irradiation, whereas for macromolecular $Eu^{3+}$ and $Tb^{3+}$ complexes based on copolymers of acrylic acid with alkyl methacrylates, the fluorescence intensity of ions markedly increases. In the authors' opinion, the efficiency of luminescence build-up of metallocopolymers is related to a decrease in the degree of dissipation of the metal ion electronic excitation energy on high-frequency vibrations of macroligands during photolysis, to a greater number of coordinatively unsaturated structures in copolymers, to an increase in the degree of asymmetry of the nearest environment of lanthanide ions. The electrodipole $^5D_0-{}^7F_2$ transition (for $Eu^{3+}$) is especially sensitive to the effect of the last-mentioned factor, whereas the $^5D_4-{}^7F_5$ transition (for $Tb^{3+}$) has a partly magnetodipole nature.

The terpolymers of methacrylic acid, cobalt or copper methacrylate (1 mass %) and fluoroalkyl methacrylates [323] or MMA are stable against UV irradiation.[324] The invariability of spectral characteristics allows one to use these polymers as band and cut-off light filters.

Hhigher photostability compared to MMA–methacrylic acid copolymers is inherent in rhodamine 6G-coloured metal-containing terpolymers comprising MMA, methacrylic acid and metal methacrylates. Their photostability depends on the nature of the cation and increases in the sequence $Na^+ < Ba^{2+} < Pb^{2+} < Er^{3+}$. The photodestruction of copolymers and dyes is usually estimated by monitoring the relative changes in the viscosity of their solutions ($\eta/\eta_0$) and absorbance at the absorption peak wavelength ($D/D_0$) before and after the irradiation of the mixture with the light of a mercury lamp (Table 22).[193] The initial photodestruction ($w_\eta$) and photobleaching ($w_D$) rates are used to characterise the system. In addition to the direct photostabilising effect of the carboxylate groups in metallocopolymers, one can follow a tendency for pronounced decrease in the parameters $w_\eta$ and $w_D$ on passing from linear copolymers to network structures with different degrees of cross-linking and with an increase in the degree of polymer stereoregularity. Hence, the metallocopolymer morphology determines more favourable conditions for the dissipation of the photoexcitation energy of the macromolecule to the metal ion.

An important photophysical feature of some metallopolymers is the selective light absorption. For example, neodymium (meth)acrylate copolymers with MMA or hydroxyalkyl (meth)acrylates show the light absorption at 580 nm typical of compounds of this metal.[325, 326] When these copolymers are used as light filters for a metal halide or mercury lamp, this absorption coincides with the emission spectrum, resulting in brightness suppression.

**Table 22**. Photoageing parameters of rhodamine 6G-coloured terpolymers of methyl methacrylate with methacrylic acid and metal methacrylates (0.1 mol %).[193]

| Metal | Cation radius /Å | Cation polarisation coefficient | Parameter change $/10^{-2}$ rel.u. $h^{-1}$ | |
|---|---|---|---|---|
| | | | $w_\eta$ | $w_D$ |
| Na | 0.98 | 1.02 | 7.4 | 2.3 |
| Ba | 1.43 | 1.40 | 7.0 | 2.0 |
| Pb | 1.32 | 1.52 | 2.0 | 1.0 |
| Er | 2.04 | 2.88 | 1.8 | 0.5 |
| – | – | – | 7.8 | 2.8 |

## 3. Water absorption and sorption properties of metallopolymers

Owing to the large number of ionogenic groups, metallocopolymers based on alkali metal (meth)acrylates can swell under appropriate conditions and behave as superabsorbing materials. The volume of absorbed water can exceed by hundreds of times the proper volume of the sorbent. Water absorption is monitored by gravimentric analysis, while swelling kinetics is studied by calorimetry and video and television recording.[327] The distribution of water of diffusion in sodium polyacrylate was studied successfully by the magnetic resonance visualisation in low fields or scattered fields.[328]

For example, the sorption capacity for sodium acrylate copolymers with *N*,*N*′-methylenebis(acrylamide) and *N*,*N*′-dimethyl(acrylamidopropyl)ammoniumpropanesulfonate equals 992 (Ref. 329) and 721 g of $H_2O$ per g of polymer (g $H_2O$ $g^{-1}$) [330] in deionised water and 106 and 83 g $H_2O$ $g^{-1}$ in a 0.9% solution of NaCl, respectively.

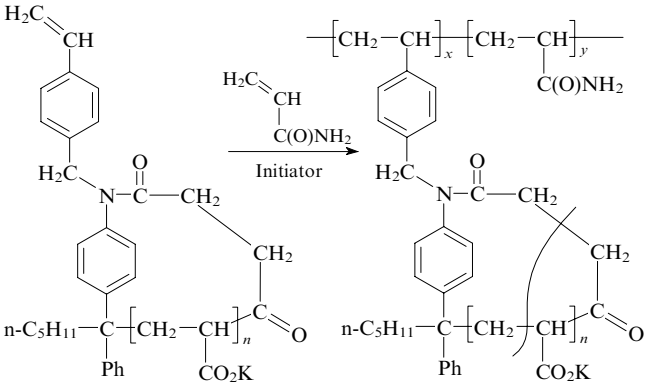
In the case of cross-linked acrylamide–calcium(II)methacrylate copolymer,[331] the equilibrium swelling of the polymeric gel increases with an increase in the methacrylate content in the initial monomer mixture. The driving force of water penetration into a polymer is the chemical potential gradient between the external water and the drops of absorbed (internal) water. This gradient is higher for a metallopolymer solution in distilled water than for a salt solution, which results in water absorption by macromolecules. The swelling properties of materials based on sodium acrylate are determined by characteristics of the external salt solution, *e.g.*, concentration, metal valence, pH of the medium. An increase in the ionic strength of the solution leads to a decrease in the osmotic pressure difference between the copolymer gel and a solution of a singly charged cation salt [332] and, finally, to a decrease in water absorption. However, in the case of polyvalent cations, the type of swelling can also depend on the degree of their complexation with carboxy groups of the polymeric chain.[329, 332, 333] It was found that upon immersion into a 0.01 M solution of a polyvalent salt, the xerogel of sodium acrylate with *N*,*N*′-dimethyl(acrylamidopropyl)ammoniopropyl sulfonate first passes into the swollen state and then absorption of water ceases, which may be due to diffusion of the absorbed water into the polymeric network and subsequent cation exchange.[332] Similar effects were observed also in the case of sodium acrylate copolymer with hydroxyethyl methacrylate.[334]

It is worth noting that, according to the data from $^{23}Na$ NMR spectroscopy, water absorption by sodium polyacrylate results in a more pronounced downfield shift of the $^{23}Na$ resonance (−6.6 ppm) than for usual hydrated sodium ions. This indicates that water molecules surrounding the sodium ions form intermolecular hydrogen bonds with the polyacrylate carboxy groups and that a gel structure is formed.[328] Moreover, a fairly narrow (the line width at a half-height is 1.2 kHz) and symmetrical $^{23}Na$ NMR signal attests to the presence of mainly isolated sodium ions in the polymer. Meanwhile, in the ionomeric zinc acrylate copolymer, water molecules (up to 6.5 $H_2O$ molecules per $Zn^{2+}$ ion) are located in ion domains.[242] The absorbent gels under study also tend to show a high initial water absorption rate; for example, for sodium acrylate–*N*,*N*′-methylenebis(acrylamide) copolymer, this value is 208 g $H_2O$ $g^{-1}$ $min^{-1}$ (Ref. 329).

The recently obtained sodium polyacrylate composites and mineral clay-based nanocomposites have enhanced sorption characteristics.[35, 335] The effective water absorption properties of the metal acrylate copolymers dictate the fields of their application. These materials are used to produce absorbents for water and blood as well as diapers, bandages, medical sponges, water evaporation retardants in water-storage ponds, as water-shutoff agents in petroleum production, as filtration loss agents of drilling fluids, *etc*. Data on the use of such agents can mainly be found in patents.

In recent years, the interest in hydrogels, including those based on alkali metal (meth)acrylates has markedly increased. Their ability to phase transition depends on solution temperature, pH and ionic strength, the nature of the solvent, *i.e*., on the external factors.[336–340] Most of these hydrogels are prepared by chemical[341] or physical[342, 343] cross-linking of water-soluble polymers. The mechanically cross-linked hydrogel based on terpolymer comprising acrylamide, potassium acrylate and cyclic macromonomer **32** was prepared by the *in situ* formation of a polymer network.[344]

The polyelectrolyte **33** thus formed (the curved line shows the linear chain of another macromolecule that penetrates the macrocycle) has a higher swelling ability (the initial particle diameter $d_0 = 7.0$ mm) than the chemically cross-linked gel ($d_0 = 1.9$ mm) and a higher volume shrinkage ($d/d_0 < 0.25$) in a 0.2 M solution of copper(II) chloride.




**32** **33**

In hydrogels, metal cations are efficiently exchanged with protons to form dimeric carboxy groups through hydrogen bonding. This was demonstrated in sodium polyacrylate cross-linked by the aluminium ion, which was placed into water and water was replaced by a fresh portion at intervals.[343] The non-monotonic swelling of the gel was accompanied by two relaxation processes: the first stage was fast swelling and the second stage was shrinkage to a state with a lower degree of swelling than the initial gel. The temperature-sensitive swelling–shrinkage transition was also observed for *N*-isopropylacrylamide (NIPA) copolymer with sodium acrylate or methacrylate (Fig. 23).[341] As can be seen from this Figure, the experimental points corresponding to shrinkage on heating and the data obtained on cooling are in good agreement with one another, *i.e*., a change in the volume of the gel is thermally reversible. The minimum in the differential curve $dr/dT$ ($r = m_h/m_x$, where $m_h$ is the weight of the swollen gel plate, $m_x$ is the weight of the dry gel plate) corresponds to the lower critical temperature of hydrogel swelling. It is important that the $r$ values for NIPA copolymers with sodium acrylate and methacrylate proved to be higher than for NIPA copolymers with their metal-free analogues, acrylic and methacrylic acids.[345] Thus, the incorporation of strong electrolytes, (meth)-

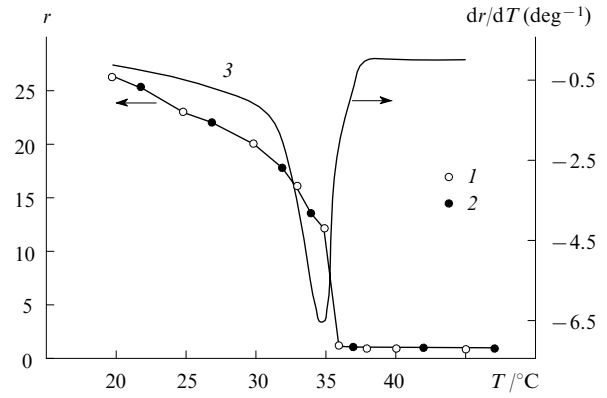



**Figure 23.** Degree of swelling ($r$) of the hydrogel of *N*-isopropylacrylamide–sodium methacrylate (1 mol %)–*N*,*N*′-methylenebis(acrylamide) (0.5 mol %) *vs*. temperature in direct (*1*, *2*) and differential (*3*) coordinates.[341]
Data were obtained during heating (*1*) and cooling (*2*).

acrylic salts, into a hydrogel favours enhanced water absorption by the polymer.

Cross-linked metallocopolymers are also of considerable interest for metal ion sorption and preconcentration. The ability to form the polymer–metal ion complex was found for sodium acrylate copolymer with maleic anhydride and diethylenetriamine. During adsorption and separation of trace amounts of metal ions from aqueous solutions, rather high sorption capacity of this copolymer with respect to $Au^{3+}$, $Ru^{3+}$, $Bi^{3+}$ and $Hg^{2+}$ ions was found (220, 105, 155 and 176 mg $g^{-1}$, respectively).[346]

The molecular recognition method is most promising for the preparation of this type of sorbents.[347–350] Metallo(co)-polymers are known, for example, to have high substrate selectivity but can have low adsorption capacity. In view of the former factor, metal-containing monomers provide additional possibilities for template binding of metal ions or organic molecules.[40, 213, 351, 352] (Co)polymerisation of metal (meth)acrylates in the presence of cross-linking agent followed by removal of the metal with an appropriate eluent results in the formation of cross-linked copolymer (the so-called 'metal-tuned' copolymer) that retains the macromolecule conformation of the initial metallocopolymer favourable for the complexation with these ions. This scheme was used to prepare, for example, cross-linked macroporous copolymers of copper(II) methacrylate and their macromolecular templates based on ethylene glycol dimethacrylate, which exhibit selective sorption properties with respect to $Cu^{2+}$ ions (Table 23).[40]

**Table 23**. Effective sorption capacity (in μmol $g^{-1}$) of 'copper-tuned' and analogous 'untuned' polymers cross-linked by ethylene glycol dimethacrylate with respect to the metal cations.[40]

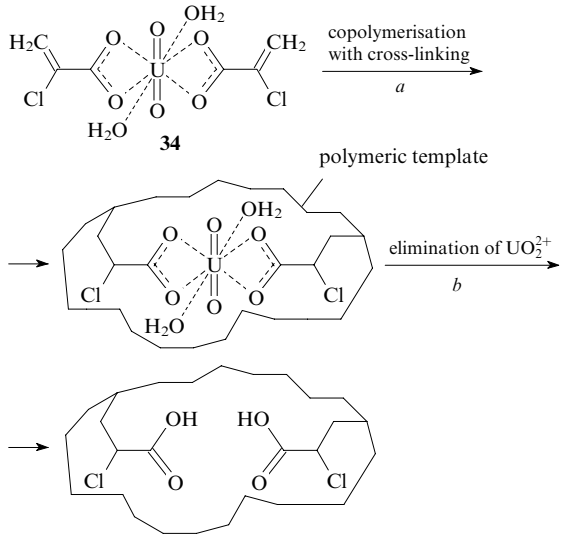
| Comonomer | $Zn^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ | $Cu^{2+}$ |
|---|---|---|---|---|
| $[Cu(O_2CC(Me)=CH_2)]_2 \cdot H_2O$ | 10.3 | 7.4 | 15.5 | 45 |
| $NH_4(O_2CC(Me)=CH_2) \cdot H_2O$ | 4.6 | 4.6 | 16.5 | |
| $[Cu(O_2CC(Me)=CH_2)]_2 \cdot Py$ | 9.7 | 7.8 | 15.2 | 49 |
| $[Cu(O_2CC(Me)=CH_2)]_2 \cdot 4\text{-VPy}$ | 12.4 | 5.7 | 6.7 | 52 |
| $NH_4(O_2CC(Me)=CH_2) \cdot 4\text{-VPy}$ | 3.2 | 4.1 | 12.6 | 30 |

**Note**. Sorption capacity: salt concentration, $4.08 \times 10^{-3}$ mol litre$^{-1}$, pH 4.7, 25 °C, 2.5 h.

The bound 'domestic' ions make 60% – 70% of their initial content in the copolymer and they are selectively adsorbed from rather dilute solutions ($10^{-3}$ – $10^{-5}$ mol litre$^{-1}$), which is important for preconcentration and recovery of metal ions where their content, for example, in contaminated waters, is below the detection level.

A practically important application of metallocopolymers is the design of selective sorbents for radionuclides. Using the above-described approach and starting from the corresponding monomeric salts, it is possible to prepare cross-linked copolymers 'tuned', for example, for $Sr^{2+}$ (Ref. 351) or $U^{4+}$ (Ref. 353) ions.

The template terpolymer of 2-chloroacrylic acid, ethylene glycol dimethacrylate and salt **34** shows high selectivity with respect to $UO_2^{2+}$ ions in the presence of strong complexing agents.




(*a*) 2-chloroacrylic acid, ethylene glycol dimethacrylate, AIBN, $CH_2Cl_2$, Δ; (*b*) conc. $HNO_3$, sonication (30 kHz), 15 min.

The selectivity factor (the ratio of amount of the 'domestic' ion to the amount of sorbed 'foreign' ion) of uranyl-tuned copolymers is rather high for competing ions:[353]

| Ion | $Cu^{2+}$ | $VO^{2+}$ | $Al^{3+}$ | $Fe^{3+}$ | $Th^{4+}$ |
|---|---|---|---|---|---|
| Selectivity factor | 8.8 | 3.8 | 8.6 | 8.1 | 2.7 |

As the degree of cross-linking increases, the sorption capacity of the material usually decreases. Thus for strontium(II) acrylate – ethylene glycol dimethacrylate copolymers,[351] there is an optimal region of compositions in which the sorption properties of the copolymer are manifested the best: the selectivity factor is 20 – 27 for the content of the cross-linking agent of 4 mol % – 53 mol % (Table 24). Apparently, a decrease in the selectivity at a higher metal concentration in the copolymer is due to the change in the mechanism of ion sorption, which is performed not only by tuned centres but also by other centres, for example ester groups, by a coordination mechanism.

**Table 24**. Sorption properties of the copolymers of $Sr(O_2CCH{=}CH_2)_2$ ($m_1$) with ethylene glycol dimethacrylate ($m_2$).

| Copolymer composition (%) | | Amount [Sr] in the initial sorbent /mg-equiv. g$^{-1}$ | Metal concentration after sorption /mg-equiv. g$^{-1}$ | | Selectivity factor |
|---|---|---|---|---|---|
| $m_1$ | $m_2$ | | Sr | Ba | |
| 61 | 39 | 6.03 | – | – | – |
| 58 | 42 | 5.73 | 2.74 | 0.10 | 27.4 |
| 49 | 51 | 4.84 | 3.07 | 0.14 | 21.9 |
| 46 | 54 | 4.5 | 1.23 | 0.06 | 20.5 |
| 18 | 82 | 1.78 | 0.54 | 0.78 | 0.69 |
| 7 | 93 | 0.68 | 0.80 | 0.96 | 0.83 |

## 4. Metallo(co)polymers as precursors of nanocomposite materials

The interest in metallopolymer nanocomposites is due to the unique combination of properties of metal-containing nanoparticles with mechanical, film-forming and other polymer characteristics, which allows these materials to be used as magnetic devices for data recording and storage, catalysts, sensors and for various purposes in medicine and biology.[354] Homo- and copolymers of acrylic and methacrylic acids and their salts are often used for stabilisation of metal-containing dispersions. For example, PbS nanocomposites with a styrene – methacrylic acid copolymer[355] and with an ethylene – methacrylic acid copolymer,[356] CuS nanocomposite with a poly(vinyl alcohol) – polyacrylic acid copolymer,[357] CdS nanocomposite with copper polyacrylate,[358] Co particles with a polyacrylic acid – polystyrene block copolymer were prepared.[359] The heterometallic ZnS/CdS nanocrystals in a polymeric matrix having unusual luminescence properties were synthesised by treatment with $H_2S$ of the styrene – zinc diacrylate – cadmium diacrylate terpolymer ($M_n = 4.7 \times 10^4$, atomic ratio Zn : Cd = 3.3 : 1).[360]

The aggregate stability of nanoparticles in the polymeric matrix is determined by the possibility of spatial arrangement, flocculation, phase separation, electrostatic interactions, *etc*. It was shown using atomic force microscopy (AFM)[361] that the van der Waals attraction forces act between two polymer-uncoated surfaces of yttrium-stabilised zirconyl (YSZ) nanoparticles at distances of up to 200 nm and cause their aggregation. However, the presence of an adsorbed layer of ammonium poly(meth)acrylate on the surface of YSZ nanoparticles gives rise to repulsion forces between them at a distance of 35 nm from the surfaces. It was found that ammonium polymethacrylate ensures stronger repulsion of nanoparticles (4 nN at a distance of 25 nm) than polyacrylate due to additional steric influence of the methyl group.

The conformation effects of the polymeric chain are especially sensitive to reaction conditions, for example, to the pH of the medium. For example, the radiation chemical reduction of $Ag^+$ ions in aqueous weakly alkaline media in the presence of PAA is accompanied by bright blue colouring of their solutions.[362–364] In alkaline solution, the PAA molecules are rotated outwards due to repulsion of the $CO_2^-$ groups and the $Ag^+$ ions can interact with them. This gives 'blue silver', which is stable in air and can be isolated in a pure state by evaporation of water. The formation and evolution of oligomeric Ag clusters to subcolloid particles upon γ-radiolysis of silver salts in the presence of PAA or the polyacrylate anion are tightly related to the reaction conditions.[365]

Unusual effects of concentration of $Ag^+$ ions and sodium polyacrylate and the molecular mass of the latter were reported.[366] The addition of a slight amount of $Ag^+$ ions (1% – 2% of the amount of bound $CO_2^-$ groups) to a dilute solution (< 0.1 g litre $^{-1}$) of sodium polyacrylate with the molecular mass of 650 kDa induced compression of the polymer coil and UV irradiation of this system resulted in silver nanoparticles. When the polyacrylate molecular mass

was reduced from 650 to 149 kDa, no nanoparticles formed (even upon the addition of a greater amount of $Ag^+$ ions). This means that the formation of nanoparticles requires a rather high local concentration of $Ag^+$ ions, which is dictated by a particular molecular mass of polyacrylate chains. Typically, monomeric acrylate and sodium polyacrylate with lower molecular mass (2100 – 30 000) behave as not only stabilisers, but also as reducing agents in the synthesis of Ag and Au nanoparticles.[367]

The PAA concentration has a substantial influence on the morphology of Ag nanoparticles: a 0.1 mass % content of the polymer resulted in dendrimeric Ag particles with a diameter of 400 – 500 nm.[368] An increase in the PAA concentration to 0.5 mass % gave rise mainly to spherical Ag particles (particle size 160 – 200 nm).

Spherical copper nanoparticles were also produced by reduction of copper polyacrylate films under $H_2$ at temperatures of $> 220$ °C.[369] Note that the nanocomposite films obtained at 220 °C were rather unstable and $Cu^0$ particles were oxidised to $Cu^{2+}$ over several weeks. However, reduction at temperatures above 230 °C was accompanied by appearance of keto groups upon condensation of carboxylate anions and cross-linking of PAA chains, which ensured higher stability of the copper nanoparticles formed.

A promising method for the formation of metal-containing nanoparticles and their polymeric composites consists of thermal transformations of metal-containing monomers in which the *in situ* formation of highly dispersed metal particles and the polymeric matrix stabilising them can be combined.[370 – 375] Using this approach, polymeric nanocomposites based on copper(II),[370] cobalt(II),[376, 377] iron(III) [378] and nickel(II) acrylates,[379] their copolymers,[380] and cobalt(II) [381] and iron(III) maleates [382] were obtained. These composites comprise metal-containing nanoparticles of diameter 5 – 30 nm with a nearly spherical shapes, which are homogeneously dispersed in the polymeric matrix with an average distance between the particles of 10 – 12 nm (Fig. 24).[383] The uniformity of distribution of the metal particles in the matrix and their narrow size distribution attest apparently to the homogeneous nature of decarboxylation and formation of a new phase.

Depending on the nature of the metal-containing disperse phase, the polymeric nanocomposite materials possess unusual magnetic, catalytic, optical and other properties. In particular, owing to the formation of ferrimagnetic $Fe_3O_4$ and $CoFe_2O_4$ nanoparticles or antiferromagnetic CoO oxide, the thermolysis products of co-crystallisates of cobalt(II) and iron(III) acrylates behave as solid magnets with a coercive force of 0.18 T and residual magnetisation of 15.5 mT at room temperature.[383] A twice higher coercive force was found for Co-containing particles (average diameter of 7 nm) composed mainly of CoO prepared from cobalt(II) acrylate in a polymeric matrix.[377] The spinel ferrites $Zn_{0.5}Mn_{0.5}Fe_2O_4$,[384] $CoFe_2O_4$ [385] and $MnFe_2O_4$ [386] and the nanocomposites $MnFe_2O_4/TiO_2$ synthesised by pyrolysis of the corresponding polyacrylate salts exhibit superparamagnetic properties at room temperature and can be used as magnetic and radar absorbent materials.

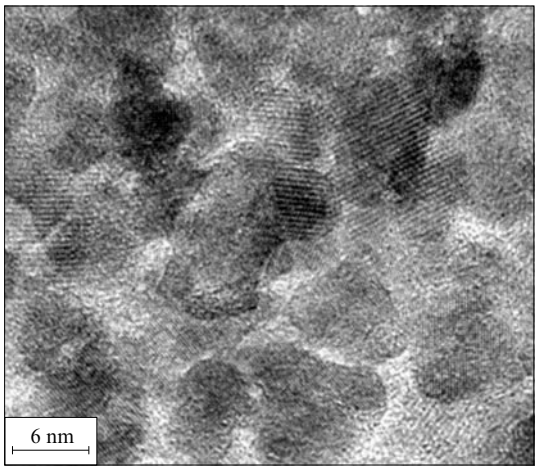



**Figure 24.** Transmission electron microscope image of the product of thermolysis (370 °C) of the cobalt(II) and iron(III) acrylate co-crystallisates.[383]

Unsaturated metal carboxylates are of considerable interest as precursors in the design of multimetallic superconducting ceramics, multicomponent alloys, oxide electrodes, and so on. Traditional methods for batch preparation of high-temperature superconducting (HTSC) ceramics are poorly reproducible, often accompanied by the formation of micro- and macroinhomogeneities, in particular, non-conducting phases. The synthesis of multicomponent ceramics based on polymers allows one to overcome these drawbacks and obtain structurally homogeneous products. This is attained, for example, by the use of a polymeric matrix with metal ions dispersed there down to the molecular level. This method was used to prepare $YBa_2Cu_3O_{7-x}$ HTSC ceramics from polymeric $Y^{3+}$, $Ba^{2+}$ and $Cu^{2+}$ complexes with polyacrylic [387] or polymethacrylic [388, 389] acid.

In another approach, *i.e.*, in the synthesis of polymers in the presence of components of HTSC ceramics, polymerisation of acrylic acid is carried out in a mixture of aqueous solutions of yttrium nitrate or barium and copper acetates.[390] Homogeneous distribution of metal ions can be attained by introducing them into a monomer molecule by copolymerisation of the corresponding unsaturated metal carboxylates. In this case, yttrium, barium and copper acrylates are mixed in a 1 : 2 : 3 molar ratio in a minimum amount of methanol, which is subsequently evaporated, and then solid-phase copolymerisation is carried out.[391, 392] In another version of this method, single-phase stoichiometric films of HTSC ceramics are obtained by spray pyrolysis of solutions of the corresponding methacrylates (aerosol drops are applied onto a heated substrate, the precipitate is dried and twice annealed in an oxygen atmosphere, at 500 and 920 °C).[393, 394] This HTSC ceramics has a superconducting transition temperature of 87 – 92 K and a critical current density of up to 540 A $cm^{-2}$. The pattern of dependences of the electrical resistance and magnetic susceptibility *vs.* temperature attests to a sharp phase transition and to the presence of only one superconducting phase (Fig. 25).[391]

Important applications of nanostructured polymetallic materials produced from unsaturated metal carboxylates include acoustoelectronics and optoelectronics, sensors, electrode materials of fuel cells, and so on.

Ferroelectric $PbTi_{0.6}Zr_{0.55}O_3$ films were obtained using aerosol deposition and pyrolysis of solutions of saturated metal carboxylates in methacrylic acid.[395] Transacylation (replacement of saturated carboxylate ligands in the metal coordination sphere by methacrylates) decreases the annealing temperature (to 650 °C) and essentially improves the film surface quality: no pores or cracks are formed. Sol – gel synthesis also reduces the annealing temperature (to 550 °C) in the preparation of ultradisperse layered $LiMO_2$ oxides (M = Co, Ni, V) (particle size 30 – 50 nm, specific surface area

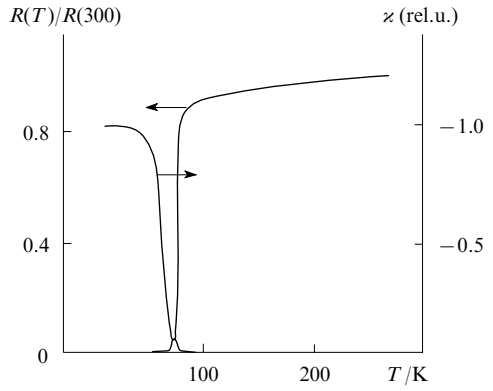



**Figure 25.** Temperature dependences of the reduced electrical conductivity ($R$) and magnetic susceptibility ($\varkappa$) of HTSC ceramics obtained from yttrium, barium and copper acrylate terpolymer.[391]

$2.3-17\ m^2\ g^{-1}$) in the presence of maleic [396] or polyacrylic [397] acid as chelating agents.

In recent years, considerable attention has been paid to material based on unsaturated metal oxo-carboxylates (see Section II.5). Owing to relatively small size ($\sim$1 nm), oxo clusters can be used as structural elements of hybrid organic-inorganic nanocomposites (Fig. 26).[21, 22, 398–400] The synthesis

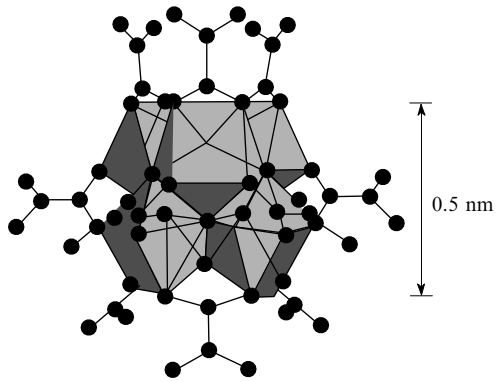



**Figure 26.** Molecular structure and size of a typical metal oxo cluster.[398]

of these systems by traditional methods is often accompanied by phase separation due to the difficulty of control over the size, shape and particle distribution of the inorganic component in the organic matrix.[401] Elimination of these effects is facilitated by the presence of covalent bonding or strong intermolecular interactions (*e.g.*, hydrogen bonds) between the main components of the system.[402]

As the initial component, one can use oxo-carboxylate clusters containing functional groups that accomplish covalent bonding between the metal oxo cluster fragment and the polymer chain. In this case, the inorganic core is connected to the unsaturated fragments of the hybrid molecule through electrostatic interactions and hydrogen bonds, as this is shown for the oxo cluster $[(Bu^nSn)_{12}O_{14}(OH)_6](O_2CC(Me)=CH_2)_2$ (Ref. 403). Its copolymerisation with MMA gives the polymethyl methacrylate–methacrylate copolymer cross-linked by the $[(Bu^nSn)_{12}O_{14}(OH)_6]$ units, which do not change during polymerisation transformations (Fig. 27).

For the preparation of hybrid thin films based on silica gel with inserted hafnium oxo clusters, the oxo cluster $Hf_4O_2(O_2CC(Me)=CH_2)_{12}$ methacrylate (**35**) and 3-methacryloyloxypropyltrimethoxysilane were used (Scheme 2).[404, 405] The chemical binding of the components was performed by photochemical polymerisation of methacrylate groups, the silane alkoxy groups were pre-hydrolysed and pre-condensed to give the oxide network.

These hybrid nanocomposite films have low dielectric constants (1.8 at the atomic ratio Si : Hf = 18); therefore, they could find application in various microelectronic devices, for example, as insulating films.

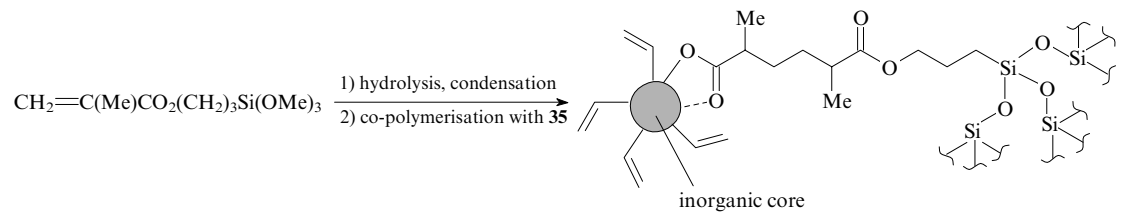
A similar procedure has been used to prepare three-dimensional photonic crystals based on $TiO_2$ nanoparticles in a polymeric matrix: a system containing titanium(IV) alkoxide methacrylate and photopolymerisable urethane acrylic resin was exposed to a laser beam (780 nm) and then hydrolysed and heat treated.[406]

A promising application of these hybrid nanocomposites is immobilisation of molecular magnets. Using the SAXS method, it was demonstrated that the magnetic cluster $Mn_{12}O_{12}(O_2CCH=CH_2)_{16}$ (**36**) copolymerised with ethyl acrylate taken in molar ratios from 25 to 200 in the presence of benzoyl peroxide at 80 °C does not undergo aggregation and is homogeneously distributed in the polymeric matrix.[13] The hybrid polymers thus formed behave as superparamagnets at temperatures above 8 K. It is worthy of note that despite the relatively low content of cluster units (0.1 mol % – 1 mol %), these materials behave as molecular magnets with characteristics similar to those for the initial clusters. For example, field dependences of magnetisation for methacrylate cluster **36** and its copolymer with MMA (MMA : **36** = 200) have a hysteresis loop with a coercive force of 0.8 and 0.1 T, respectively.[295] Thus, polymerisation of magnetoactive clusters in the presence of organic monomers allows one to obtain materials that can be processed as typical polymers with preservation of properties of molecular magnets.

## VI. Conclusion

The research of metal unsaturated carboxylates is an intensively developed field of chemical science. Currently, methods of synthesis of these salts of almost all metals and many polymetallic compounds have been developed and optimised; their structural organisation and methods for its determination are known. However, the polymerisation transformations of these potential monomers have not been adequately studied.

Scheme 2



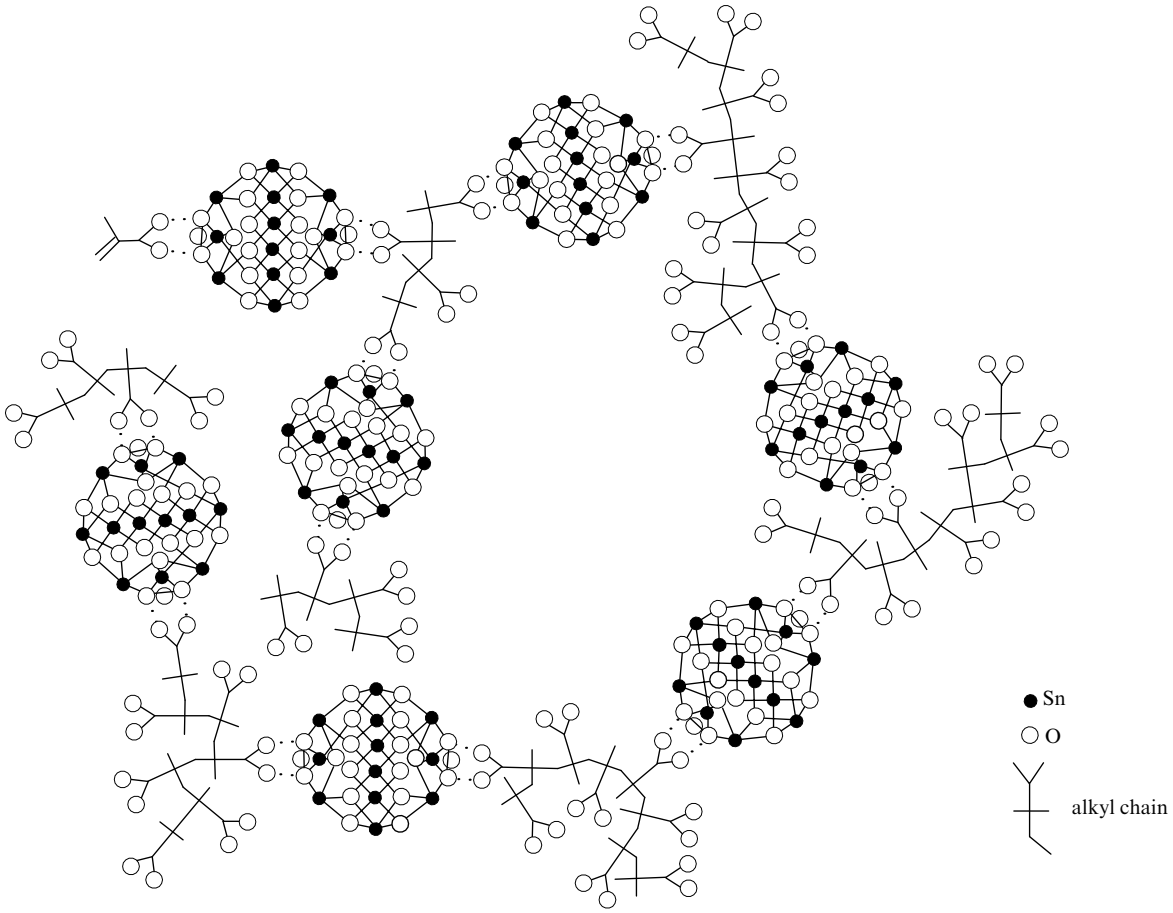



**Figure 27.** Fragment of the structure of hybrid nanocomposite obtained by copolymerisation of $[(Bu^nSn)_{12}O_{14}(OH)_6](O_2CC(Me)=CH_2)_2$ and methyl methacrylate (the butyl groups in the oxo cluster and the methoxycarbonyl groups in the polymer are omitted).[403]

Thus it is virtually unknown what structural changes take place in the coordination unit upon incorporation into the polymer chain, numerous reactions involving initiating and growing radicals in the polymerising metallopolymeric systems have not been fully elucidated. It is beyond doubt that polymerisation of metal-containing monomers proceeds by a complex-radical mechanism;[229] however, elucidation of its characteristic features requires additional studies. First of all, this is due to specific character of these systems for which even determination of the molecular-mass characteristics requires enormous experimental effort. Due to side processes at different stages of polymerisation, the final product can have different units in the chains formed,[407] which also requires special studies. The metallopolymers obtained by these methods, components or precursors of metallopolymer nanocomposites, are objects of a new trend in chemistry related to nanotechnologies.[354]

Finally, polymerisation transformations constitute only one field of application of unsaturated metal carboxylates. These derivatives are potential substrates of hydrogenation, epoxidation, ozonisation, *etc*. In addition, monomeric and polymeric carboxylates can serve as catalysts for various organic reactions. Studies along these lines have been hardly started as yet although their prospects are obvious.

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