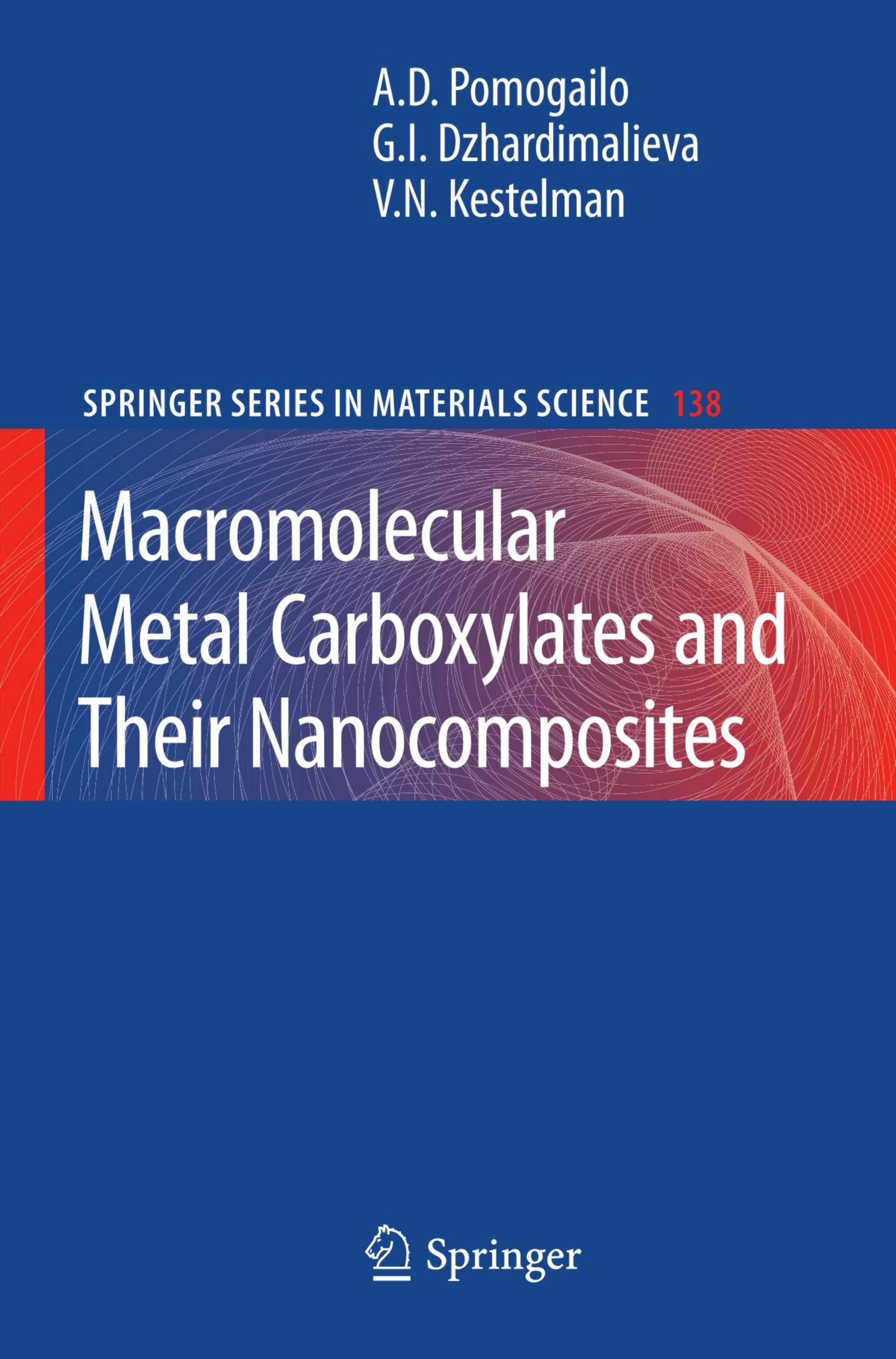

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Preface

This book is devoted to the single functional group, metal derivatives of unsaturated carboxyl ion $RCOO^-$, where R is a radical with multiple bonds. This field embraces a huge number of chemical compounds, among which are new types of monomers and polymers with interesting structures and properties and unusual chemical transformations. This field includes both natural and artificial polymers but mainly various synthetic materials.

Macromolecular metal carboxylates are currently the object of extensive studies due to their unique catalytic, magnetic, optical, and other properties as well as perspective precursors of novel nanocomposite functional materials. These complexes and nanocomposites have attracted scientific interest both from a fundamental point of view and their potential applications. Reactivity of unsaturated metal carboxylates containing metal atoms in immediate proximity to a polymerizable bond is closely related to their molecular structure. It is of essence to reveal the peculiarities of their behavior, which is determined by the metal on the one side and the polymeric backbone on the other.

In this book, the main representatives of unsaturated carboxylic and corresponding polymeric acids as well as the methods of synthesis of metal carboxylates are analyzed. There are no analogs of such monographs devoted to various aspects of synthesis, polymerization, and properties of the monomeric and macromolecular metal carboxylates and nanocomposites in the literature.

Structure of monomer and macromolecular metal carboxylates, the type of coordination of carboxylate ion, the electronic and valence state of metal, and specificity of metal–organic ligand bond were also considered. We want to note the role of kinetic and stereochemical effects on the main stages of polymerization and copolymerization of such metal-containing monomers. Knowledge of these peculiarities allows one to effectively control the structure and properties of metallopolymers.

An alternative way to produce of macromolecular metal carboxylates by the interaction of polymeric acids with metal compounds is also discussed. In this book, the features of complexation of carboxylic macromolecular ligands, the effects of a polymer chain, the constants of formation and stability of macrocomplexes formed are considered.

Special chapters of the book are devoted to applications of metallopolymer and nanocomposites as well as polymer-assisted synthesis of metal nanoparticles.

We think that this book is the first comprehensive analysis of this field of science. We tried to consider the problem as exhaustively as possible, and we hope that missed questions are not principal.

Who is our potential reader? Chemistry of carboxylates, as any interdisciplinary field of science and technique, rapidly develops, and intensive accumulation of experimental data in this field embarrasses not only beginners but also experienced researchers working in this field. First of all, this book can be useful for a wide range of scientists and engineers of research institutes and industry. Then, it can serve as a handbook for students, postgraduate students of universities and colleges that are interested in this field of science. After 25 years of our own researches in this field and analysis of literature, we believe in the necessity of appearance of this book generalizing accumulated data on all aspects of monomeric and polymeric metal carboxylates.

Section 9.2.1 was written together with Professor Aleksander S. Rosenberg who to our great regret deceased untimely.

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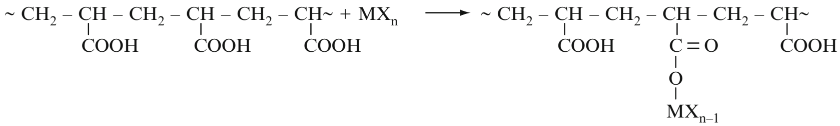
May 2010

Contents

Chapter 1
Introduction

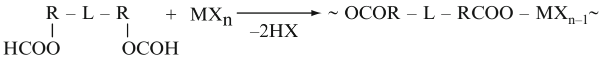
At present, there are three main ways of production of metal-containing polymers on the basis of carboxyl precursors [1]: (**I**) the interaction of metal compounds MX$_n$ with linear functionalized (carboxyl-containing) polymers, when the main polymer chain remains untouched (so called polymeranalogous transformations), (**II**) the polycondensation of proper precursors, when metal ions are incorporated into and removed from the main chain leading to polymer destruction, (**III**) the recently developed method, polymerization and copolymerization of metal-containing monomers.

I



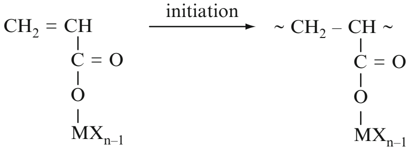
$$\sim \mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}}\sim + \mathrm{MX_n} \longrightarrow \sim \mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{\mathrm{C=O}\\ |\\ \mathrm{O}\\ |\\ \mathrm{MX_{n-1}}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}}\sim$$

II



$$\underset{\mathrm{HCOO}}{\mathrm{R}}-\mathrm{L}-\underset{\mathrm{OCOH}}{\mathrm{R}} + \mathrm{MX_n} \xrightarrow[-2\mathrm{HX}]{} \sim \mathrm{OCOR}-\mathrm{L}-\mathrm{RCOO}-\mathrm{MX_{n-1}}\sim$$

III



$$\mathrm{CH_2}=\underset{\substack{\mathrm{C=O}\\ |\\ \mathrm{O}\\ |\\ \mathrm{MX_{n-1}}}}{\mathrm{CH}} \xrightarrow{\text{initiation}} \sim \mathrm{CH_2}-\underset{\substack{\mathrm{C=O}\\ |\\ \mathrm{O}\\ |\\ \mathrm{MX_{n-1}}}}{\mathrm{CH}}\sim$$

Metallopolymers on the basis of transition metals, obtained by method I, as a rule are characterized by low content of bond metal and are used mainly for ion-exchange extraction, concentration, and isolation of metals. Condensation method II as a rule uses dicarbonic acids, including element – substituted (L), for instance carboran-containing acids [2, 3]. Production of metallopolymers by method III and investigation of their structure and properties is the main content of this book.

Metal carboxylates are widely used in science and technology. They are a part of polynuclear coordination compounds (in catalytic and biomimetic systems) and

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metal-proteins, intermediate compounds of many metabolic processes. Biochemical behavior of metal-enzymes and antibodies is determined in many respects by their carboxyl ate function [4, 5].

Carboxyl ion can serves as mono-, bi-, and even tridentant ligand of metal ions with numerous types of coordination. For instance, 18 structural functions of carboxyl group were found for monobasic carboxylates of transition metals [6] and 15 diverse types of coordination were observed by X-ray diffraction study for homolog of maleate anion $C_2O_4{}^{2-}$ [7].

Oxalate ions bind metal ions by only one or two of four oxygen atoms, and as a rule five-member metallocycles are realized, i.e., potentially tetradentant anion $C_2O_4{}^{2-}$ serves usually as bidentant cyclic ligand. In general case, the type of coordination depends on a large number of factors: the nature of metal atoms and outersphere cations, the system of hydrogen bonds, the presence of competing acidic or electroneutral ligands L'. This permits to consider these compounds as so called “smart” materials. This can be illustrated by the following example. It was shown by IR[1] and EXAFS that coordination of zinc ion in Zn (II)-neutralized ethulene-methacrylic acid ionomer depends on temperature, the presence of adsorbed water, pressure applied to melt at 130 °C [9, 10].

In vacuum, Zn(II) carboxylate has mainly a hexacoordinated structure, which gives IR peaks $\nu_{as}(COO^-)$ at 1,624 and 1,538 cm^{-1}, but at atmospheric pressure ($P = 0.1$ MPa) a tetracoordinated structure is formed with $\nu_{as}(COO^-)$ at 1,585 cm^{-1}.

Donor–acceptor properties of carbonic acids and their anions in aqueous solutions are characterized by the basicity constant pK_a. The value of pK_a can be calculated quantum-chemically [11]. The energy of decoupling of double bond electrons of acrylic acid and its cobalt salt, as well as the ways of formation of the transition state, differs substantially [12].

In principle, the problem of metal carboxylates can be divided into two unequal parts: the larger and long-developed problem of salts of saturated carbonic acids, and the smaller and recently developed problem of unsaturated carboxylates. Fundamental data on synthesis and properties of saturated carboxylates of metals and their application are rather well considered in reviews and books, for example monograph [13], comprehensive in 1983 and still of current importance, and rather complete old and recent reviews [14–17]. Studies of unsaturated carbonic acids are

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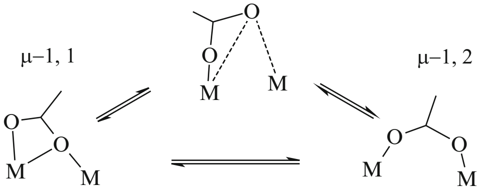
[1] IR spectroscopy is widely used for study of structure of these complexes, because valence vibrations $\rangle C = O$ are sensitive to geometry of COO^- group and its surrounding [8]. In this group the double bond is delocalized and the valence vibration CO splits in asymmetric high-frequency (ν_{as}) and low-frequency symmetric (ν_s) vibrations. Intermediate symmetry is possible depending on the type of coordination (this will be considered in detail in Chap. 4). Other methods of study of structure of metal-containing group are determination of the values of charges on oxygen atoms of carboxyl and hydroxyl groups and the values of chemical shifts of ^{13}C NMR of carbon of carboxylate group, estimation of ionization energy (especially for thermochemical calculations), and others.

practically not generalized. Scrappy data on methods of their synthesis, structure, chemical transformations and numerous applications are dispersed in scientific and patent literature. Sometimes, analysis of some unsaturated carboxylates can be encountered in reviews and chapters in monographs, but they do not give complete presentation of the state of problem.

At the same time, this type of compounds was intensively studied in last years by methods of high-molecular compounds with the aim of obtaining new types of metal-containing materials. Although many attempts of generalization of synthesis methods and polymerization transformations of some specimens of this type of metal-containing monomers are known (see, for example, [18–20]), among them dissertations (for example, [21, 22]), it is enigmatic why unsaturated carboxylates were not thoroughly analyzed like their saturated analogs.

This task is more difficult because the multiple bond affects all aspects – synthetic and structural chemistry (for instance, in many cases the multiple bond can be involved in formation of carboxylate unit), reactivity of these compounds, polymerization ability. Maybe, this can be explained by interdisciplinary character of the problem. On the one hand, synthetic and structural part of carboxylates belongs to inorganic and coordination chemistry where unsaturated ligands are considered traditionally as “ugly ducklings”. On the other hand, methods of synthesis and investigation of these promising exotic monomers are rarely developed in high-molecular chemistry. The interests of specialists in these two fields of science are rarely intersected in this promising and rapidly developing field of chemistry, therefore one of the aims of this book is to draw together these specialists.

Among vast diversity of salts of unsaturated carbonic acids, derivatives of acrylic, methacrylic, crotonic, oleic, fumaric, maleinic, acetyldicarbonic, vinylbenzoic, and some other acids, which are virtually typical metal-containing monomers containing multiple ready-to-open bonds and metal atoms chemically bond to organic part of the molecule [18]. Unsaturated bond affect coordination of carboxylate ligand. Intensive development of this field in last years is caused by practical value of obtained products, polymers with ion metals in each chain. This improves many properties of polymers and their composites. In subsequent chapters we plan to analyze thoroughly transformations of unsaturated metal carboxylates in the course of synthesis, as well as their polymerization and copolymerization with conventional monomers. Here we only give one example of such transformations. Photopolymerization of diacetylene acid $(CH_3(CH_2)_{11}C{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$ was studied in [23] on the interphase air–water in the presence of divalent metal ions Ba (II) (pH 7.7), Cd (II) (pH 6.8), and Pb (II) (pH 6.0). It was found that in the course of the photopolymerization carboxylate group of acetylene acid in monolayer in subphase of ions Ba (II) and Pb (II) changed its coordination from bridge to bidentant, whereas for Cd (II) the bidentant structure was unchanged at the decrease of molar square from 0.8 to 0.18 nm^2/molecule, i.e., the polymerization stimulates more compact packing of carboxyl groups in monolayers. Experimental data and theoretical calculations show that the change of the type of coordination, so called carboxylate shift, is a low-energy process. This plays an important role in catalytic cycles of metal enzymes [24]:



The carboxyl shift of coordination from bidentant-chelate ($\mu - 1, 1$) to bidentant-bridge ($\mu - 1, 2$) is easily observed by $^1H - ^{13}C$ [25] NMR.

Diversity of functions, symmetry of ligands, metal–ligand coordination, various types of bonds in their molecules determine unique possibility for construction of promising materials on their basis. Metal oxo-clusters with unsaturated carboxylate ligands are very promising as nanostructural elements for organic–inorganic hybrid nanocomposites [26]. First of all, these are high-organized objects with strictly determined size and shape which are remained unchanged in final material. Therefore, their distribution in matrix is homogeneous and mono-disperse nanostructures are formed. In other words, mono- and polycarboxylates of metals are objects of supramolecular chemistry, and their polymer films are characterized by improved mechanical [27, 28], adhesion [29], optical [30], electric [31], and other properties.

This book is devoted to a wide range of problems, embracing methods of synthesis, structure, and properties of unsaturated metal carboxylates, features of their polymerization transformations, morphology, as well as properties and characteristics of formed metallopolymers, including polymeranaloguous transformations. The interest to the problem increased substantially when it was found that these materials are effective precursors of metal–polymer nanocomposites [32], in which carboxylate matrix or products of its transformation serve as stabilizing agents and prevent aggregation of nanoparticles of metals or their oxides [33].

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Chapter 2
Monomeric and Polymeric Carboxylic Acids

Our goal was not to analyze known unsaturated carboxylic acids (this problem itself is unrealizable), but only to give a general idea about unsaturated acids and their polymers more often used for obtaining metal carboxylates. Basic attention was paid to those representatives which are a priori capable of polymerization. As data on unsaturated carboxylic acids are dispersed in numerous researches, directories, and catalogs, many of which are not always accessible, their most important characteristics are given below. Other unsaturated heteroacids and their polymers (for example, vinylsulfonic and vinylbenzoic sulfonic acids, thio-, phosphonic, amino-, and other acids) are not analyzed in this book. More detailed information can be found in other available literature [1–4].

2.1 Mono- and Polybasic Unsaturated Carboxylic Acids: Characteristic and Polymerization

These types of monomers traditionally form the material basis of high-molecular compounds chemistry. Polycarboxylic acids and polymers based on its derivatives are large-tonnage products. Unsaturated carboxylic acids are used to a great extent for the preparation of polyethers and polyesters, polynitriles, polyamides, etc.

2.1.1 Monobasic Carboxylic Acids with One Double Bond

The brightest representatives of monobasic unsaturated acids are acrylic and methacrylic acids (and their derivatives) – the extremely important products in high-molecular compounds chemistry. The most widespread commercial syntheses of acrylic acid are oxidative carbonylation of ethylene, vapor-phase oxidation of propylene, butylene, and acrolein, hydrolysis of ethylene cyanohydrin, hydrolysis

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of β-propiolactone, etc. The basic method for obtaining the acrylic acid is the preparation from acetylene, carbon oxide, and water:

$$4\,CH{\equiv}CH + 4H_2O + Ni\,(CO)_4 + 2\,HCl \rightarrow 4\,CH_2{=}CH{-}COOH + NiCl_2 + H_2 \tag{2.1}$$

The reaction proceeds with a high yield both at standard pressure (in this case CO is engaged as nickel tetracarbonyl) and at 30 atm and 170°C with gaseous nickel tetracarbonyl in the presence of catalytic quantities of nickel salts.

Methacrylic acid, $CH_2{=}C(CH_3)COOH$, is obtained by gaseous-phase oxidation of isobutylene, by catalytic gaseous-phase oxidation of methacrolein, and through an intermediate formation of acetone cyanohydrin, etc.

Many homologs of acrylic acid exist in geometrical stereoisomeric forms caused by a different arrangement of substituents at a double bond, for example, crotonic (*trans-*) and isocrotonic (*cis-*) acids, $CH_3{-}CH{=}CHCOOH$. Crotonic acid, contained in the croton oil, is a crystal substance, b.p. 180°C and m.p. 72°C. Isocrotonic acid (b.p. 169°C, m.p. 72°C) is a less stable form and it is transformed partly into crotonic acid by heating up to more than 100°C.

Angelic (*trans-*) and tiglic (*cis-*) acids, $CH_3CH{=}C(CH_3)COOH$, are isomers. The first acid is the labile form (b.p. 185°C, m.p. 45°C), the second is the stable form (b.p. 198°C, m.p. 64.5°C).

(+)-Cytronellic acid, $(CH_3)_2C{=}CHCH_2CH_2CH(CH_3)CH_2COOH$ (b.p. 152°C at 18 mm Hg) is an optical active compound. Undecylenic acid, $CH_2{=}CH(CH_2)_8COOH$, is formed at vacuum distillation of castor oil, b.p. 213°C at 100 mm Hg, m.p. 24°C. Ricin acid, $CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOH$, is also used comparatively often.

Palmitooleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$, is an oily liquid, b.p. 223°C at 10 mm Hg, m.p. +14°C.

Erucic (b.p. 225°C at 10 mm Hg, m.p. 34°C) and brassidic (b.p. 256°C at 10 mm Hg, m.p. 65°C) acids ($CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$) are geometrical isomers.

4-Vinylbenzoic acid has received the most expansion among vinylbenzoic acids.

From unlimited number of characterized polyunsaturated fatty acids with two and three isolated ethylenic bonds in a molecule, used for obtaining the carboxylates, the following acids have been used.

Sorbic acid, $CH_3CH{=}CHCH{=}CHCOOH$, is synthesized by sorbic aldehyde oxidation prepared by condensation of three molecules of acetic aldehyde. Geranic acid is obtained from 2-methylpentene-2-one-6. α- and β-Eleostearic acids with three double bonds ($CH_3(CH_2)_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_4COOH$) are also interesting: α-isomer is a low-melting form (m.p. 47°C) and it rearranges into high-melting β-isomer (m.p. 67°C) at UV-irradiation. Thus, they are *cis–trans*-isomers having especially high abilities to "exsiccation" as well as all acids with three ethylenic bonds.

Linolenic acid, $CH_3(CH_2CH{=}CH)_3(CH_2)_7CO_2H$, is also one of the "exsiccant" fatty acids (b.p. 229°C at 16 mm Hg and 184°C at 4 mm Hg, density 0.905 g/cm^3 (20°C), it is quickly oxidized and solidified in air). Linolenic acid and many unsaturated arachidonic acids are the vital fatty acids. Dehydrogeranic acid, $(CH_3)_2C{=}CHCH{=}CHC(CH_3)_2{=}COOH$, (m.p. 185–186°C) also should be noted.

2.1.2 Unsaturated Dicarboxylic (Dibasic) Acids

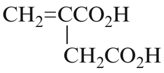
Unsaturated dicarboxylic acids can be mono- or polyunsaturated. The most important representatives of β-dicarboxylic acids are the first members of this row, maleic (m.p. 130°C) and fumaric (m.p. 287°C) acids, $HOOC{-}CH{=}CH{-}COOH$, differed by a spatial structure. Maleic acid has *cis*- and fumaric acid has *trans*-configuration. Both acids are obtained by heating of malic acid but at different temperatures. In industry, maleic acid (as maleic anhydride) is prepared under catalytic oxidation of benzene by the oxygen in the air.

When two electron-seeking carbonyl groups are conjugated with an olefinic system, acceptor character of C=C bond especially increases. Maleic anhydride has the best acceptor properties among derivatives of α, β-unsaturated dicarboxylic acids. Maleic acid is stronger than fumaric acid: hydrogen atom of the first carboxyl group dissociates more easily, than in case of fumaric acid, and conversely for the second carboxyl group. Ionization constants at 18°C are:

- For maleic acid $\mathrm{p}K_1 = 2.0$, $\mathrm{p}K_2 = 6.23$
- For fumaric acid $\mathrm{p}K_1 = 3.03$, $\mathrm{p}K_2 = 4.38$

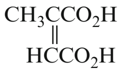
For comparison we shall note that for oxalic acid (saturated analog of maleic and fumaric acids), $\mathrm{p}K_1 = 1.46$ and $\mathrm{p}K_2 = 4.40$.

Citraconic, methylmaleic (m.p. 91°C), mesaconic, and methylfumaric (m.p. 202°C) acids have the same relationship among themselves as well as with maleic and fumaric acids: the first of them is a *cis*-form, second is a *trans*-form.



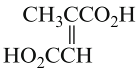
$$\begin{array}{l} CH_2{=}CCO_2H \\ \qquad | \\ \qquad CH_2CO_2H \end{array}$$

(1)



$$\begin{array}{l} CH_3CCO_2H \\ \qquad \| \\ \quad HCCO_2H \end{array}$$

(2)



$$\begin{array}{l} \quad CH_3CCO_2H \\ \qquad \| \\ HO_2CCH \end{array}$$

(3)

Itaconic, 2-methysuccinic (1), acid and their isomers, citraconic (2) and mesaconic (3) acids, are more often than other acids used for the binding of metal ions as well as their polymeric analogs. Besides, itaconic acid is the perspective candidate for obtaining the high-functionalizated copolymers. It is connected with the low cost of itaconic acid received from renewable sources under fermentation by *Aspergillus terrus* microorganisms.

Unsaturated tribasic propene-1,2,3-threecarboxylic (aconitic) acid, $HOOC{-}CH_2{-}C(COOH){=}CH{-}COOH$, is obtained by water elimination from citric acid. It is rather distributed in flora and contained in sugar-cane and beet; it is extracted from *Aconitum* poisonous plants of the buttercup family. Unfortunately, these acids have not yet found practical application in the metal carboxylates synthesis.

2.1.3 Unsaturated Carboxylic Acids with Triple Bond (Acetylenic Acids)

Interaction of sodium derivatives of acetylenic hydrocarbons with carbon dioxide facilitates the preparation of acetylenecarboxylic acids in which triple bond is localized near a carboxyl group as depicted in the following scheme:

$$C_nH_{2n+1}C{\equiv}CNa + CO_2 \rightarrow C_nH_{2n+1}C{\equiv}CCOONa \qquad (2.2)$$

This type of acids has received the name of propiolic acid series because of the simplest representative of this series, propiolic acid, $HC{\equiv}CCOOH$. Propiolic acid is a liquid with a pungent smell (b.p. 83°C at 50 mm Hg, m.p. 9°C). The peculiarity of propiolic acid (as will be shown in the subsequent chapters) gives the possibility of the replacement of hydrogen atom by metal not only in the carboxyl group but also in the acetylenic residue. Methyl-propiolic ($CH_3C{\equiv}CCOOH$, b.p. 203°C), 2-octynoic acid ($CH_3(CH_2)_4C{\equiv}CCOOH$), and phenyl-propiolic ($(C_6H_5)C{\equiv}CCOOH$) acids are the most commonly used for the preparation of corresponding carboxylates among numerous higher homologs of propiolic acid.

Carboxylic acids in which triple bond is far from the carboxyl group can be synthesized from the corresponding dibromodirevatives of fatty acids by hydrogen bromide elimination upon alkali, for example, stearolic acid, $CH_3(CH_2)_7C{\equiv}C(CH_2)_7COOH$, and its isomer – 6-octadecynoic acid, $CH_3(CH_2)_{10}C{\equiv}C(CH_2)_4COOH$. A set of strongly unsaturated acids containing acetylenic and ethylenic bonds was extracted from plants and prepared synthetically.

Derivatives of acetylenedicarboxylic acids are less important for the problem under consideration, although 10,12-penta-cosadiynoic acid ($CH_3(CH_2)_{11}C{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$) forms Langmuir–Blodgett films easily [5].

Some properties of unsaturated carboxylic acids considered are summarized in Table 2.1.

The composition and structure of unsaturated carboxylic acids determine the basic approaches to their carboxylates, on the one hand, and to their polymerization, on the other hand.

2.2 Peculiarity of Polymerization of Unsaturated Carboxylic Acids and their Polymers Structure

Unsaturated carboxylic acids can be classified as polymerized (most often by the radical mechanism) ionized monomers as well [8]. In turn, obtained linear water-soluble polymers are ionomers – ion-containing polymers with a carbon-containing main chain and relatively small number of partly or completely ionized acidic groups of carboxylic, sulfonic, phosphoric, and other acids in a side chain [9–11].

Table 2.1 Composition and characteristics of unsaturated carboxylic acids

Acid	Formula	B.p. (°C/mm Hg^a)	M.p. (°C)	pKa (°C)	d^4 20 (g/mL)	n^D20
Monobasic unsaturated carboxylic acids						
Acrylic acid	$CH_2{=}CHCOOH$	139;142/760	13	4.25(25)	1.051; 1.045 (25°C)	1.4242; 1.4185
Methacrylic (2-methylpropionic) acid	$H_2C{=}C(CH_3)COOH$	163	12–16	4.66	1.015	1.431; 1.4288
Crotonic (*trans*-2-butenoic)) acid	$CH_3CH{=}CHCOOH$	185(760) 180–181°C	71.5 (70–72°C)	4.69(25)	1.027 (25°C)	
2-Ethylacrylic acid	$H_2C{=}C(C_2H_5)CO_2H$	176			0.986 (25°C)	1.437
2-Pentenic (*trans*-2 pentenic) acid	$C_2H_5CH{=}CHCO_2H$	106°C/20	9–11		0.99 (25°C)	1.452
4-Pentenic (3-vinylpropionic, allylacetic) acid	$CH_2{=}CHCH_2CH_2COOH$	83–84/12	−22.5		0.981 (25°C)	1.428
2-Propylacrylic acid	$CH_3(CH_2)_2({=}CH_2)CO_2H$	165–188			0.951 (25°C)	1.441
2-Octenoic acid	$CH_3(CH_2)_4CH{=}CHCO_2H$	154/22	5–6		0.944 (25°C)	1.4588
3-Vinylbenzoic acid	$H_2C{=}CHC_6H_4CO_2H$		91–95			
4-Vinylbenzoic (styrene-4-carboxylic) acid	$H_2C{=}CHC_6H_4CO_2H$		142–144			
2-Carboxyethyl-acrylate	$CH_2{=}CHCO_2(CH_2)_2CO_2H$	103°C/19 mm Hg			1.214 (25°C)	
trans-3-Benzoylacrylic (4-oxo-4-phenyl-2-butenoic) acid	$C_6H_5COCH{=}CHCO_2H$		94–97			
2-Bromoacrylic acid	$H_2C{=}C(Br)CO_2H$		62–65°			
2-Bromomethyl-acrylic acid	$CH_2{=}C(CH_2Br)COOH$		70–73°			

(continued)

Table 2.1 (continued)

Acid	Formula	B.p. (°C/mm Hg[a])	M.p. (°C)	pKa (°C)	d^4 20 (g/mL)	n^D20
Ricinoleic acid, (R)-12-hydroxy-*cis*-9-octadecenoic, 12-hydroxyl-oleinic acid	$CH_3(CH_2)_5CH(OH)CH_2$ $CH{=}CH(CH_2)_7COOH$				0.940	
10-Undecenoic acid	$CH_2{=}CH(CH_2)_8COOH$	137/2	23–25		0.912 (25°C)	1.449
cis-5-Dodecenoic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_3CO_2H$	135/0.4			0.906 (25°C)	1.454
Palmitoleinic (*cis*-9-hexadecenoic) acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	162/0.6	0.5		0.895	1.457
trans-Oleinic (*trans*-9-octadecenoic, *trans*-Elaidic) acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	288/100	42–44			
cis-Oleinic (*cis*-9-octadecenoic, elanoic) acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	194–195/1.2	13–14		0.887 (25°C)	1.459
cis-11-Eicosenoic (gondoic) acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_9CO_2H$		23–24		0.883 (25°C)	1.4606
Nervonic (*cis*-15-Tetra-cosenoic) acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOH$		42–43			
α-Linoleic (*cis*, *cis*, *cis*-9,12,15-Octadecatrienoic acid	$CH_3(CH_2CH{=}CH)_3(CH_2)_7CO_2H$	230–232/1	−11		0.914 (25°C)	1.480

(continued)

Table 2.1 (continued)

Acid	Formula	B.p. (°C/mm Hg[a])	M.p. (°C)	pKa (°C)	d^4 20 (g/mL)	n^D20
γ-Linolenic acid (*cis*, *cis*, *cis*-6,9,12-Octadecatrienoic) acid	$CH_3(CH_2)_3CH_2CH{=}CHCH_2$ $CH{=}CHCH_2CH{=}CH(CH_2)_4COOH$					
cis-5,8,11,14,17-Eicosapenta-enoic acid	$CH_3(CH_2CH{=}CH)_5(CH_2)_3CO_2H$		−54 − 53		0.943 (25°C)	1.4977
Acetylenic carboxylic acids						
Propynoic (Acetylenecarbo-xylic, Propinoic) acid	$HC{\equiv}CCOOH$	144/760; 83/50; 102/200	18; 9, 16–18	1.84 (25)	1.138 (25°C)	1.431
2-Butynoic (tetrolic, 1-Propynecarboxylic, 3-Methyl-propiolic) acid	$CH_3C{\equiv}CCO_2H$	203/760	78–80	2.50		
2-Pentynoic acid	$CH_3CH_2C{\equiv}CCO_2H$		47–53			
4-Pentynoic (Propargylacetic) acid [6, 7]	$CH{\equiv}CCH_2CH_2COOH$	110/30	54–57			
2-Hexynoic acid	$CH_3(CH_2)_2C{\equiv}CCO_2H$	230			0.992 (25°C)	1.460
2-octynoic (2-Octyn-1-oic) acid	$CH_3(CH_2)_4C{\equiv}CCO_2H$	148–149/19	2–5		0.961 (25°C)	1.46
Phenylpropynoic acid	$C_6H_5C{\equiv}CCOOH$	135–137	137	2.23(25)		

(continued)

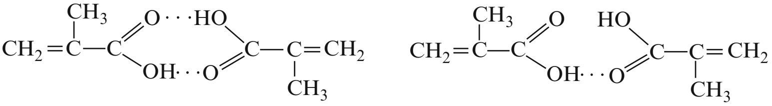
Table 2.1 (continued)

Acid	Formula	B.p. (°C/mm Hg[a])	M.p. (°C)	pKa (°C)	d^4 20 (g/mL)	n^D20
Unsaturated dicarboxylic acids						
Fumaric (*trans*-1,2-Ethene-dicarboxylic acid	$HOOCCH{=}CHCOOH$		298–300°C (субл)1659 субл.)/1.7	3.02, 4.38		
Maleic (2-Butenedioic, *cis*-1,2-Ethylene-dicarboxylic, Toxilic) acid	$HOOCCH{=}CHCO_2H$		137–140	1.92, 6.23	1.59 (25°C)	
Itaconic (2-propene-1,2-dicarboxylic; Succinic acid, methylene-) acid	$HO_2CCH_2C({=}CH_2)CO_2H$		165–168	3.85, 5.45	1.573 (25°C)	
cis, *cis*-Muconic (*cis*, *cis*-2,4-2,4-Hexadienedioic) acid	$HOOC{-}CH{=}CH{-}CH{=}CH{-}COOH$		194–195			
Acetylendicarboxylic (2-Butynedioic) acid	$HOOCC{\equiv}CCOOH$		180–187 (разл.)			
2-Acetamido-acrylic acid; Acetyl-dehydroalanine	$CH_2{=}C(NHCOCH_3)COOH$		185–186 (разл.)			
Maleic acid monoamide (maleamic) acid	$H_2NCOCH{=}CHCO_2H$		158–161			

[a] 1 mm Hg = 133.322 n/m^2

Among carboxylic acids, polyacrylic (PAA) and polymethacrylic (PMAA) acids have found an application as macroligands for the binding of the metal ions. PAA is a weak polymeric acid and it is similar to the polybasic saturated acids in its chemical properties. The average value of pK_a in aqua solutions (concentration 0.1 mol/L, alkali titration, 25°C) is equal to 6.4.

Polyacids are obtained usually in water solutions in the presence of potassium, sodium, or ammonium persulfate or by initiating systems of "ammonium persulfate – ascorbic acid" type – and also under the action of metal chelates ($M^{-} \approx 50,000$) [12]. As a rule, these monomers exist in a form of cyclic or linear dimers, in which double bonds are considerably removed from each other.



PAA, synthesized in the presence of peroxide initiators, is characterized by branching and rather low molecular weights; the reason is the reactions of chain transfer to a monomer or to a polymer due to hydrogen atoms of CH_2 group. Thus, the ratio of the growth rates to the termination rates of polymer chains upon bulk polymerization of methacrylic acid (44.1°C), initiated by azobis(isobutyronitrile), is equal to $k_p/{k_t}^{0.5} = 0.278,\ \Delta H = 13.5\,\text{kcal/mol.}$ [1]

Kinetics of free-radical polymerization of the nonionized methacrylic acid in water solutions has a lot of peculiarities (see, for example [13]).

Unsaturated carboxylic acids can enter into the polymerization reaction both in protonic (below pK_a) and in deprotonic (anionic) (over pK_a) forms:

$$\text{RCOOH} \xrightarrow{pK_a} \text{RCOO}^{-} + \text{H}^{+} \tag{2.3}$$

Deprotonation results in the appearance of electrolytic repulsion between polymerized groups. It depends on many factors, the main of which are solvent nature, pH, and an ionic strength of a solution. They determine also molecular-mass (MM) characteristics of the polymers formed [14, 15]. Concentration of the ionized carboxyl groups $[\text{COO}^{-}]$ is αc, where α is the average dissociation degree, $c$is the total concentration of carboxyl groups. The curve of the potentiometric titration of the polymeric acids is described by the Henderson-Hasselbach equation:

$$\text{pH} = pK'_a - m \lg\left[\alpha/(1-\alpha)\right], \tag{2.4}$$

where pK'_a is the characteristic constant, equal to pH value at $\alpha = 0.5$; m is the empirical parameter considering influence of electrostatic effect – deviation of system behavior from the law for low molecular weight analogs (for polyelectrolytes $m > 1$, whereas for monomeric electrolytes $m = 1$). The ratio of the ionization constant of a polymeric acid to the ionization constant of an analogous monocarboxylic acid is approximately equal to 10^{-4}. It is important that the acidity of the carboxyl group having two nonionized acidic groups in the neighborhood should be more than the acidity of the carboxyl group with one or two ionized carboxyl groups; the neighboring groups should not be necessarily the same type. It is illustrated by this typical example. Carboxyl group and phenolic fragment influence mutually on their acidic properties because of the intramolecular hydrogen bond formation. It is very important under the action of ribonuclease [16]. Values of $\mathrm{p}K_{\mathrm{a}}'$ and m of polyacids depend on the ionic composition of the solution. Thus, $\mathrm{p}K_{\mathrm{a}}'$ of carboxyl groups in polymeric acids can be approached to $\mathrm{p}K_{\mathrm{a}}'$ of their monomeric analogs with an increase in the ionic strength of the solution; $\mathrm{p}K_{\mathrm{a}}'$ and $m$can change from 6.17 to 4.60 and from 2.0 to 1.44 [17]. In other words, PAA is a weak polyelectrolyte and pH increasing induces the rise of the number of negative charges. Besides, $\mathrm{p}K_{\mathrm{a}}'$ value is essentially influenced by the neighboring groups and by the cross-linking degree of polymer chains, degree of a coil convolution. Characteristic viscosity $[\eta]$ of the ionized acids is higher than that $[\eta]$ of the initial acids because of the electrostatic repulsion between ionized groups and extension of polymer chains. It confirms the rod-like form of the short chains of the ionized PAA in water. The chain length and the solvent nature determine the solution concentration at which polymeric coils start to interact. Polymeric coils can be considered as relatively isolated in a good solvent of 1–2 mass% concentration and at the molecular mass of PAA $\sim$100,000. PAA macromolecule is unfolded in water to a greater extent than in the organic θ-solvent (dioxane). Its hardness is characterized by the value of Kuhn segment equal to 17 Å and can be compared with the flexibility of the noncharged polymers. Hydration numbers are equal to 4.9–5.4 at 25°C and 5.6–6.0 at 35°C per one PAA unit.

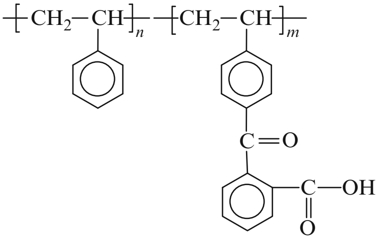
PMAA is the nearest chemical analog of PAA but it has a series of anomalous properties in aqueous and alcoholic solutions which are given below. The first property is the more compressed and compact structure stabilized by hydrogen bonds which results in the formation of the cyclic secondary structures. The second one is the hydrophobic interactions of methyl groups (at $\alpha < 0.15$). Hydrophobic areas stick together aspiring to avoid contacts with water (like surface-active substances (SAS) which consist of polar and nonpolar groups and form micelles at dissolution in water. Nonpolar groups in the micelles are turned inside). Besides, replacement of $CH_3 \ldots CH_3$ to $H_3C \ldots H_2O$ contacts induces additional structuring of water, decreasing the solvent entropy and exceeding the entropy increase of macromolecules at their structure destruction. Addition of organic solvents or ionization induces the cooperative polymer unfolding, and methanol forms the intramolecular hydrogen bonds worse than water. It is also necessary to take into account that PMAA itself shows pH-induced transfers especially in the diluted aqueous solutions at pH equal to 4–6 [18].

The contact structures formed in polyethylacrylic acid molecules are more stable than PMAA structures. It is seen from the comparison of free energy of their conformational transfer ($\Delta F = 0$ for PAA, $\Delta F = 150$ for PMAA and $\Delta F = 1{,}000$ cal/mol for PEAA) [19]. Polymonomethylitaconate behaves similarly to PMAA.

Among other polyacids, we shall note poly-4-carboxystyrene, prepared by polymerization and more often by copolymerization of 4-vinylbenzoic acid and polymaleic acid and polymers based on polymaleic anhydride. These polyacids can also be obtained by polymeranalogous reactions. Formation of the copolymer of maleic acid and vinyl alcohol under copolymerization of maleic acid with vinylbutyl ester at 60°C followed by hydrolysis of the precipitate formed [20] can be given as an example. Copolymerization of unsaturated carboxylic acids is also characterized by a lot of peculiarities. Without going into details we shall note only that $k_p/k_t^{0.5}$ value decreases, as a rule, with an increase in their concentration in a monomeric mixture (by the example of copolymerization of styrene with itaconic acid [21]).

Lastly, we shall note that many representatives of carboxyl containing polymers are the so-called "smart" polymers having such a feature as the temperature influence on the chains conformation [22]. Thus, the ability of the linear macromolecules of a heat-sensitive poly(*N*-vinylcaprolactam-co-methacrylic acid) to swell is the function of pH and temperature of a solution and MAA unit's quantity [23].

2-Carboxybenzoyl- and 3-carboxyl-2-naphthoyl-substituted derivatives of styrene and 4-vinylbenzoyl-2′-benzoate [24] are able to form polychelate complexes due to O,O-functional knots.



The number of such examples can be increased essentially without doubt.

2.3 Stereoregular Polyacids

Stereoregular polyacids, especially PAA and PMAA, are the most interesting macroligands. Isotactic PAA is obtained by hydrolysis of polyisopropenylacrylate which, in its turn, is synthesized at −78°C with use of $BrMgC_6H_5$ as a catalyst [25]. Isotactic PMAA is prepared by methods of polymeranalogous reactions such as hydrolysis of isotactic PMMA (it is the methyl methacrylate polymerization initiated by ethylmagnesiumbromide). Isotacticity degree of this polymer is approximately equal to 90% and molecular weight is equal to 4.8×10^4 [26]. Radiation polymerization of acrylic acid (initiated by γ-irridation of ^{60}Co at −78°C in polar solvents) gives syndiotactic PAA as a product [27]. Another approach is the transformation of syndiotactic anhydride of PAA, obtained by cyclopolymerization, into syndiotactic

PAA. After that syndiotactic PAA is transformed into isotactic polyanhydride (at heating with Py) and into isotactic PAA [28].

The isotactic polyelectrolyte has a local spiral conformation (degree of helicity is equal to 0.72) because of strong electrostatic repulsion between the fixed charges, while atactic and syndiotactic chains have a flat zigzag conformation. Flexibility of PAA depends on tacticity and nature of a solvent and is in the following order: isotactic > atactic > syndiotactic (in organic mediums) and syndio- > iso > atactic (in water).

Iso-PMAA also has a local spiral conformation, and syndio-PMAA has a flat zigzag conformation. The flat zigzag conformation is favorable for the formation of contacts between hydrophobic methyl groups that realized in the nonionized molecules of PMAA in water; formation of $C{=}O\ldots..H{-}O$ hydrogen bonds between the neighboring monomer units are preferable in the organic solvents. Stereoregular structures influence essentially on the nature of the conformational transfer from compact globules to more unfolded solvated chains [29]. Addition of the organic solvents containing nonpolar groups weakens the interaction of methyl groups and promotes the transfer of a macromolecule into more unfolded conformation. It will be shown in the subsequent chapters that stereostructure of polyacids influences essentially on their ability to carboxylate formation.

2.4 Cross-Linked Polyacids

Cross-linked polyacids have been produced by the industry of ion-exchange resins for several decades. Usual subacid cation-exchange resins include groups of aliphatic carboxylic acids and contain ~3.5–5 mg-eqv of an acid per 1 g of a material.

Cationites consisting of the cross-linked PMAA, obtained directly under suspension copolymerization of MMA with a mixture of divinylbenzenes, contain a high number of carboxyl groups (9–10 mg-eqv/g) that correspond to the polymer in which almost 100% of side groups are acidic. The comprehensive description of such synthesis for obtaining the ion-exchange resins is given in numerous guides.

Most often, ion exchangers are converted into necessary forms: deprotonated ($\alpha \to 0$), completely protonated ($\alpha \to 1$) and partly protonated ($1 > \alpha > 0$). For obtaining a deprotonated form, an ion exchanger is treated with 5% aqueous solution of NaOH. A protonated form is prepared under washing out an ion exchanger with a solution of 1 N HNO_3. A partly protonated ion exchanger is formed under the treatment of the protonated and deprotonated forms by the calculated quantity of an alkali or an acid. The most typical examples are saponified copolymer of methylmethacrylate and divinyl benzene and aminated dimethyl ester of iminodiacetic acid and chloromethylated styrene copolymer with divinyl benzene; the other ion exchanger is obtained under condensation of pyridine, polyethylenepolyamine, and epichlorohydrin, modified by a chloracetic acid.

Micronetwork polymers are divided into *microporous* (pores size less than 2 nm), *mezoporous* (pores size is 2–5 nm) and *macroporous* (pores size more than 5 nm). These polymers provide more successful isolation of carboxyl groups than gel polymers under the same conditions. However, micronetwork polymers also have some drawbacks. For example, concentration of carboxyl groups approx. equal to 1 mmol/L can be considered as the limiting concentration. At the concentration of carboxyl groups, more than 1 mmol/L effects of intrapolar interaction are revealed, and significant amount of anhydride cycles is formed. The nature of these particles and also their pores elasticity allow them to be used both in gaseous- and liquid-phase reactions in aqueous and in nonaqueous mediums, maximal operating temperature for subacid resins being about 125°C.

Significant attention to this class of polymers is given in literature (see, for example, monography [30]) because of wide spread and systematical researches of carboxylic cation exchangers (the saponified copolymer of methylmethacrylate and divinyl benzene type) and ampholytes.

2.5 Graft- and Block-Copolymers with Carboxyl Fragments

Copolymers on the basis of graft and block-copolymers satisfy the basic requirements for designing the macroligands of the new type with polymer-bearing functional groups. And though these types of copolymers are used for obtaining composite materials with the improved physicochemical properties and imparting new properties to the modified polymers [31, 32], such “bilayer” materials with carboxyl groups appeared to be an interesting object for the formation of the macromolecular metallocomplexes – metal carboxylates. Graft- and block-copolymers are macroligands and their properties are determined in many respects by the type of a polymer-substrate, by the quantity and length of a graft carboxyl fragment, and by the character of their distribution in a material: whether they localize only on a polymer-substrate surface forming an external covering, form a layer with some diffusive extension into the depth of a polymer to which they are grafted, or distribute evenly in the whole volume of the polymer (Fig. 2.1).

The general scheme of obtaining such carboxylcontaining macroligands in a reductive view can be shown as follows [33, 34]. The polymer to which carboxylated fragments are grafted (most often, PE, PP, CEP, PVC, PTFE, PS, cellulose, etc.) is subjected to mechanical, chemical (induced initiation, ozonolysis, oxidation-reduction systems, etc.), and radiochemical (γ-irradiation of ^{60}Co; accelerated electrons; low-temperature gas-discharge plasma of low pressure; plasma of glow low-, high-, and ultrahigh-discharge; corona discharge; UV-irradiation, etc.) initiation in the presence of a grafted acid (or by the post-effect). Such initiation results in the formation of active centers (free radicals, ion-radicals, ions on which graft polymerization takes place) on the surface or in the near-surface layer of the initial polymer. Graft polymerization of unsaturated acids can be homophase (graft is in a solution of polymers) or heterophase (suspension or gaseous-phase). The last type of processes can be presented by Scheme 2.1.

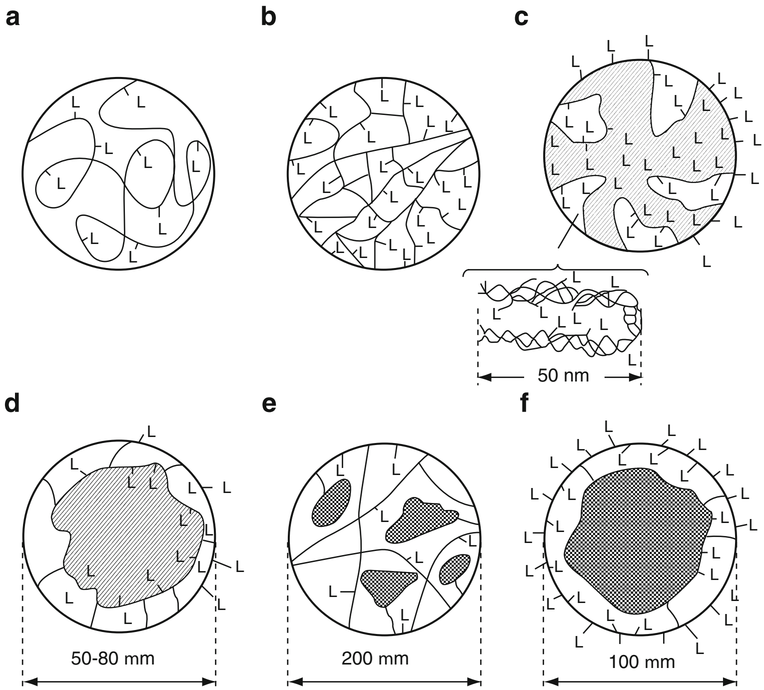
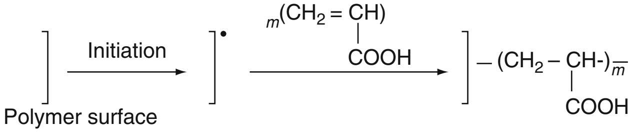


Fig. 2.1 Schematic diagram of the distribution of functional groups in polymers of various types. The type of polymer: (**a**) a linearic or branched polymer, (**b**) a slightly cross-linked (swelled) polymer, (**c**) a highly cross-linked polymer (macroporous) polymer, (**d**) a polymer with a grafted functional layer, (**e**) a polymer with microencapsulated particles, (**f**) the material of hybrid type



Scheme 2.1 Graft polymerization of unsaturated acids on the surface of polymer

The most effective technique of graft polymerization of unsaturated acids is the gaseous-phase graft polymerization of acrylic and methacrylic acids on the surface of HDPE under plasmochemical treatment. For example, formation of a monolayer from carboxyl groups on a polymer-powder surface ($S_{sp} = 10\,m^2/g$) is equivalent to a graft of 1% mass of acrylic acid. As a rule, thickness of a grafted layer does not exceed 10–30 nm. For acrylic or methacrylic acids graft polymerization on the surface of HDPE not only penetrating radiation, but also low-temperature HF-gas-discharge plasma can be used (Fig. 2.2) A contribution to the total action of such plasma is introduced by electrons, ions, radicals, excited particles, and electromagnetic radiation; elementary act of monomer insertion into polymer structure is catalyzed by electron-ion bombardment of this surface (Table 2.2) [35].

Fig. 2.2 Scheme of the setup for high frequency grafting of monomers into a surface of polymer (powder): 1 – reservoir for polymer (powder), 2 – vacuum seal, 3 – quartz discharge tube, 4 – high frequency generator, 5 – reactor with stirring, 6 – reservoir for a grafting monomer

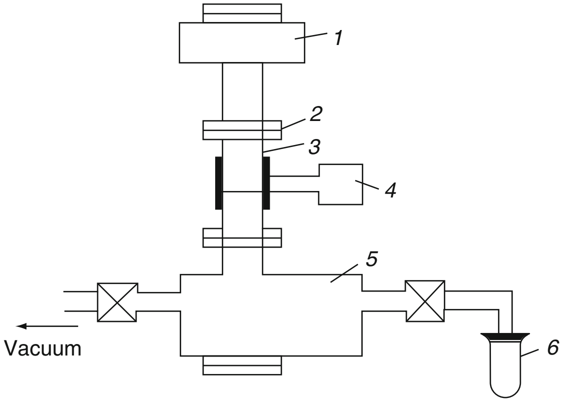


Table 2.2 Graft polymerization of acrylic and methacrylic acids on HDPE initiated by high frequency discharge[a]

		Degree of grafting	
Polymer substrate	Grafting monomer	wt%	10^4 mol/g
PE	$CH_2{=}CHCOOH$	2.0	2.8
PE	The same	9.1	12.6
PE	The same	13.5	18.8
PE	$CH_2{=}C(CH_3)COOH$	2.7	3.7
PE	The same	7.0	9.7
PE	The same	12.0	16.7
PE[b]	$CH_2{=}CHCH_2OH$	2.0.	2.76

[a] Power 1 W/cm^3, residence time in discharge is 1 s, the temperature for monomer and substrate 20°C

[b] To compare the data of grafting of allylic alcohol are given

From the peculiarities of gaseous-phase graft polymerization of AA and MAA to a powdered HDPE, we shall note high values of radiochemical yield under initiation by γ-irradiation (G_{-M} more than 2,000 molecules/100 eV of absorbed energy at 20°C) and also high effectiveness of high frequency grafting (Table 2.2): achievement of 5–10 mass% is not difficult experimentally because of sufficiently high vapor pressure of these monomers at graft temperature. A characteristic feature of graft polymerization of AA on the oriented PE-films is a formation of stereoregular (isotactic) structures in graft fragments [36]. As the thickness of a graft layer increases, ordering in a graft PAA connected with oriented character of monomeric molecules in adsorbed layer, has become apparently worse. The most important factors determining stereoregularity of graft copolymers is the structure of those areas on which graft occurs: pore size, supramolecular structure, etc. By an example of gaseous-phase graft copolymerization of vinylidene chloride and acrylic acid grafted on stretched polyamide fibers of nylon-66, the opportunity of the matrix synthesis of macromolecules with monomers distribution specified by a substrate was found [37]. The effect of matrix copolymerization is caused by a selective sorption of acrylic acid molecules on peptide groups of a fiber. It results in the formation of a sorption layer on a polymer-substrate; composition of this layer reflects an alternation of structural elements of polymer-substrate. This order also remains in macromolecules of a copolymer forming in the sorption layer. In case of a graft of acrylic acid to a powdered HDPE, stereoregular structures were not revealed [38].

Graft polymers are copolymers with the peculiarity in a reactive groups' location; almost all reactive groups are on the surface and are accessible for the reagents (including metal salts) at suspension technique of binding together. By a graft of acrylic and methacrylic acids ion-exchange membranes are obtained (see, for example, [39]).

2.6 Natural Polyacids

2.6.1 Polysaccharides

In the last years, special attention has been paid to modification of natural polymers properties including imparting a functional carboxyl groups to them. Especially it has been referred to the most widespread natural polymer, cellulose, which forms the basis of cell walls of the highest plants. Sufficient mechanical strength, good rheological properties, and possibility of application in fibers, filters, membranes, powders, or woven materials expand the areas of use of a macroligand which connects ions of various metals.

Chemical properties of cellulose are determined by presence of one primary and two secondary OH-groups in each elementary unit and also by acetal (glucoside) bonds between elementary units. High reactivity of cellulose allows to carry out numerous chemical transformations with the purpose of obtaining various macroligands, including carboxyl groups (see, for example [40])), on the basis of cellulose.

Among other polysaccharides suitable for these purposes, we shall note starch, dextrans, chitin, their dezacetylated derivatives, chitozane and pectins, and also alginic acids. Alginic acids are polysaccharides of algae which consist of D-mannuric acid residues [41].

Carboxymethyl cellulose (CMC) is the most often used polymer for obtaining the metal containing polymers among natural polymers. CMC is a homogeneous powdery fine-dispersed polymer containing only carboxyl groups (up to 5×10^{-3} mol/g) which can participate in ionic binding at moderate pH (up to 10).

2.6.2 Humic Acids

Humic and fulvic acids are the most important natural macroligands. These acids are the main organic producers of biogeocomplex, they are a mixture of the same type of macromolecules of variable composition (Fig. 2.3) [42].