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Hybrid polymer-inorganic nanocomposites

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Abstract. Approaches to the preparation of organic – inorganic nanocomposites are considered from a unified viewpoint for the first time. The major problems in the development of this new line of research in materials technology, which has arisen on the border of the science of polymers, colloid chemistry and physical chemistry of the ultradisperse state, are discussed. The main methods for the formation of composite materials and polymer – inorganic cross-linked hybrids with interpenetrating networks are analysed. Primary attention is given to sol-gel procedures for their preparation, including template processes, which occur under conditions of strict stereochemical orientation of reactants, intercalation of monomers and polymers into porous and layered matrices and their intracrystalline and post-intercalation transformations. Methods for the synthesis and properties of metallopolymeric polymolecular Langmuir – Blodgett films, which are peculiar supramolecular ensembles incorporating nanosized metal-containing particles, are discussed. The generality of the processes of formation of organic – inorganic nanocomposites in living and nonliving natural objects is demonstrated and the major fields of application of nanocomposites are considered. The bibliography includes 566 references.

I. Introduction

The science dealing with nanocomposites, which belong to the class of composite materials characterised by nanometer sizes of their structural elements (particles of metals, metalloids, their oxides, chalcogenides, *etc.*), has arisen in recent years on the border of different areas of knowledge. Apparently, the term 'nanocomposites' was proposed for the first time by Theng in 1970.[1] In the literature, the terms 'hybrid nanocomposites,' 'nanohybrids' and 'nanostructural composites' are generally used and the terms 'metallomatrix composites,' 'monophase hybrids,' *etc.* are more rarely used for describing materials consisting of an organic phase (polymer) and a nanodispersed mineral phase. If a polymer of biological origin serves as a component or a precursor of these polymer – inorganic materials, the term 'nanobiocomposites' is used.

An organic phase can capture metal-containing particles into a 'trap' of a peculiar kind, *viz.*, into an oxopolymeric network or a polymeric unit with appropriate parameters. Silicon, aluminium, titanium, zirconium, vanadium and molybdenum oxides, glasses, clays, layered silicates and zeolites, metal phosphates and chalcogenides, iron oxychloride and graphite are used as inorganic precursors. Zeolites (molecular sieves) are of particular interest since methods for control over their pore sizes are well known. Not only carbon-chain but also organoelement (generally, organosilicon) polymers are used as a polymeric component. In the resulting nanocomposite materials, distances between networks and layers formed by polymeric and inorganic ingredients and sizes of particles formed, including metal-containing particles, are nanometric.[2, 3]

Generally, hybrid nanocomposites exhibit a synergism of the properties of the initial components. These compounds are characterised by an enhanced mechanical strength and thermal stability and provide optimum heat transfer.[4, 5] In metallomatrix composites, the strength and hardness of soft metals, for example, of aluminium, are enhanced. These materials possess good thermochemical, rheological, electrical and optical properties.[6 – 8] These compounds are used as chromatographic carriers, membrane materials,[9] optical and magnetic materials, components of polymeric compositions, carriers and catalysts of various reactions (see Section VIII).

Currently, numerous procedures for the preparation of nanocomposite materials are available. Recently, the major synthetic approaches (evaporation of elemental metal with its deposition on polymeric matrices, plasma-induced polymerisation, vacuum evaporation of metals, thermal decompositions of precursors in the presence of polymers and reduction of metal ions using different procedures, including electrochemical, *etc.*) have been surveyed in reviews.[2, 3] However, the uniform distribution of ingredients is generally difficult to achieve when hybrid nanocomposites are prepared with the use of the above-mentioned procedures resulting in the nonuniformity of the properties of the material. The following three principal procedures are most commonly employed: (1) the sol-gel method; (2) intercalation of polymers and nanoparticles into layered structures (including

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polymerisation *in situ*) with the use of approaches applied in the chemistry of intracrystalline structures ('guest–host' systems); (3) a combination of polymerisation and formation of nanosized particles, which provides homogeneous dispersion of an inorganic component (which is often a specific filler) in a polymeric matrix.

In the last decade, these procedures, particularly, the first and second methods, have received primary attention. The properties and procedures for the synthesis of metallopolymeric Langmuir–Blodgett films are being extensively studied. The results of investigations in this field are summarised in a number of monographs and reviews[10–34] as well as in special issues of journals.[35–37] Note that nanocomposites containing not only synthetic but also natural molecules, including biologically active macromolecules, can be conveniently prepared using the above procedures. These procedures have been used for constructing biosensors, enzyme electrodes and other materials based on enzymes. These materials have already found use in biochemistry, medicine, biotechnology and the technology of environmental control.

In the present review, procedures for the preparation of hybrid organic–inorganic nanocomposites are considered from a unified viewpoint and the generality of the processes of their formation in living and nonliving natural objects is demonstrated. Thanks to the help of colleagues from different countries who responded to my requests and sent copies of their latest articles, the review surveys fresh results and the data under consideration were generally published within the last decade.

II. Preparation of hybrid nanocomposites by the sol-gel method

From the ecological viewpoint, optimum procedures for the preparation of composite materials are those without outflow, in particular, the sol-gel method (sol-gel or spin-on-glass process). The latter method allows one to exclude numerous stages of washing because compounds, which are used as the initial compounds, do not contaminate the final product. The sol-gel method is a convenient procedure for the preparation of dispersed materials, which are often called ceramers. This method is based on polymerisation reactions of inorganic compounds (formation of metallooxo polymers in solutions) and involves the following stages: (1) preparation of a solution, (2) formation of a gel, (3) drying and (4) thermal treatment. It is common practice to use metal alkoxides $M(OR)_n$ (M = Si, Ti, Zr, VO, Zn, Al, Sn, Ce, Mo, W, lanthanides, *etc.*; R = Alk or Ar), which are hydrolysed upon addition of water, as the starting compounds. The reactions are carried out in organic solvents. Subsequent polymerisation (condensation) affords a gel. For example, when $n = 4$

$$M(OR)_4 + 4H_2O \longrightarrow M(OH)_4 + 4ROH,$$

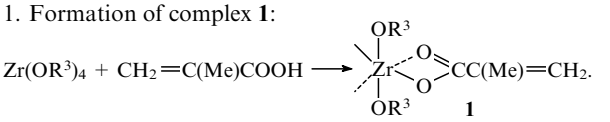
$$mM(OH)_4 \longrightarrow (MO_2)_m + 2mH_2O.$$

This method is sometimes called 'a one-stage procedure' because both reactions, *viz.*, hydrolysis and condensation, are catalysed by the same compound (by acid, base or, sometimes, by a nucleophilic catalyst, such as NaF).[14,38] These reactions with the participation of $Si(OR)_4$ have long been known. Apparently, the preparation of monodisperse TiO_2 particles by hydrolysis of alkoxides has been described for the first time by Barringer and Bowen.[39,40]

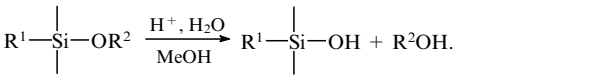
It is needless to say that the real process is much more complicated and occurs according to a multiple-route mechanism. Generally, metal oxoalkoxides $MO_n(OR)_m$, including polynuclear compounds, are formed as intermediates. Thus hydrolysis of $Ti(OR)_4$ proceeds in two stages,[27,41] *viz.*, nucleophilic replacement of the alkoxy group by the hydroxy group and condensation in the course of which oxo and hydroxo bridges are formed. It was demonstrated that the rates of these reactions are comparable.[42] The $Ti_xO_y(OR)_{4x-2y}$ compounds were isolated and characterised.[43] Generally, the controlled synthesis of hybrid nanocomposites based on zirconium alkoxysilanes and alkoxides proceeds according to Scheme 1.

Scheme 1

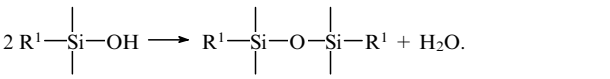
1. Formation of complex **1**:



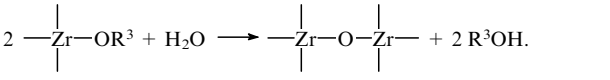
2. Hydrolysis:



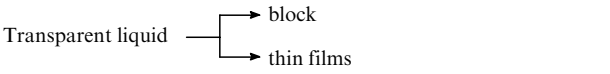
3. Condensation to form latent water:



4. Addition of complex **1** and removal of free and latent water by condensation:



5. Addition of a photoinitiator:



The following reaction conditions are of great importance: the use of catalysts, including polymeric catalysts (for example, polystyrenesulfonic acid[44]); the nature of the alkoxy group and of metal [for example, $Ti(OBu)_4$ is hydrolysed almost 150 times more slowly than $Ti(OEt)_4$ (see Ref. 45)]; the use of alkoxides of a mixed type, particularly, with chelate ligands (β-diketonate, α- or β-hydroxy acid, polyol, *etc.*); the degree of association of alkoxides {for example, in the case of $[Ti(OEt)_4]_m$ $m = 2$ or 3}; the formation of oxo or alkoxo cluster structures [for example, $Ti_{18}O_{22}(OBu)_{26}(acac)_2$] in the course of hydrolysis. The reactivity of alkoxides $M^{IV}(OR)_4$ increases in the series $Si \ll Sn$ and $Ti < Zr < Ce$.[46] The ionic radius of the M atom (0.04 and 0.06 nm; and 0.064, 0.087 and 0.102 nm, respectively), its coordination number (4 and 6; and 6, 7 and 8, respectively) and the degree of its nonsaturation (the difference between the coordination number and the valence; 0 and 2; and 2, 3 and 4, respectively) increase in the same order.[47] However, the $H_2O : M(OR)_4$ ratio (γ) is of prime importance. Thus in the case of $VO(OPr^n)_3$, a homogeneous transparent gel with an alkoxide polymer network is formed in *n*-propanol if $\gamma = 3$, whereas if $\gamma > 100$, the resulting gel attains a quite different structure, which prevents the formation of an inclusion compound. Besides, the formation of a gel is affected by the nature of the medium, the concentration of the initial solution of an alkoxide, the presence of a stabiliser and the reaction temperature.[48–50] The thermal effects of hydrolysis of $Ti(OR)_4$ in ROH increase when $\gamma = 0.2–1$, whereupon they remain virtually unchanged. This corresponds to the thermal effect of replacement of one alkoxy group by the hydroxy group.[51] The solid phase with composition $TiO_x(OBu)_{4-2x} \cdot y$BuOH was obtained upon hydrolysis of $Ti(OBu)_4$ in butyl alcohol through intermediate formation of $TiO(OBu)_2$.[45,51] The *x* and *y* values increase as the concentration of titanium alkoxide in a solution increases. Unfortunately, the effect of the nature of the solvent (generally, alcohols) on these processes has received little attention in experimental studies. It is known that hydroxy-containing compounds (for example, AlkOH, HOH or R_3SiOH) can take an active part in transesterification in the systems

$$M(OR^1)_4 + n\,HOR^2 \longrightarrow M(OR^1)_{4-n}(OR^2)_n + n\,HOR^1.$$

The nature of metal and the ligand in alkoxides affects substantially these reactions.[52–54] Thus $Ti(OPr^i)_4$ and $OV(OPr^i)_3$, which are often used as cocondensates in the preparation of nanocomposites by the sol-gel method,[55] act as catalysts in transesterification of tetramethoxy- and tetraethoxysilanes (TMOS and TEOS, respectively).

Therefore, the sol-gel process involves hydrolysis, polymerisation (chemically controlled condensation) of a gel precursor, nucleation and growth of particles followed by their agglomeration.[56,57] TMOS and TEOS are most often used as precursors. They form silica gel structures ('host') about a dopant ('guest'), thus creating a specific cage trap. Nucleation proceeds through formation of a polynuclear complex. Its concentration increases until slight supersaturation, which is determined by the solubility of the complex, is achieved. From this time on, new nuclei do not form and only the available nuclei grow. To put it differently, these processes are analogous to the processes of formation of nanosized particles in polymers.[2] In the stage of formation of a gel (gelatination), it can be impregnated with ions of different metals.

The resulting oxopolymers have structures of ultrathin porous networks with pore sizes of 1–10 nm similar to the structures of zeolites. Their specific surface (S_{spec}) varies in the range of 130–1260 $m^2\ g^{-1}$ depending on the conditions of the synthesis, and the bulk density is 0.05–0.10 g cm^{-3}. Thus molecular sieves based on silicon oxides, which are characterised by different mesopore structures and S_{spec} of $\sim 1000\ m^2\ g^{-1}$, were prepared by the sol-gel method in the presence of surfactants.[58,59] The specific surface of the powder prepared by hydrolysis of $Ti(OEt)_4$ was 200–300 $m^2\ g^{-1}$; S_{spec} of hydrolysis products of $Ti(OBu)_4$ strongly depends on the concentration of the initial solution of alkoxide and attains 490 $m^2\ g^{-1}$ at the concentration of 1.0 mol $litre^{-1}$.[45] Concentrated aggregatively stable hydrosols (containing up to 40 mass % of TiO_2) can be prepared[60] by secondary dispersion of xerogels formed after drying of the sol (the TiO_2 content is $\sim$ 85 mass %) at 100 °C for 2 h. The sol contains crystalline TiO_2 particles of an average size $\sim$ 3 nm. These particles are a mixture of two polymorphic modifications of TiO_2, *viz*., rutile and anatase, with the latter slightly predominating. The third modification (brookite) is formed much more rarely. In these systems, single crystals of the anatase phase are often metastable. Compounds containing labile vinyl, methacrylate, epoxy and other groups can act as cross-linking agents (see Scheme 1). The conditions of drying in the course of which volatile components are removed determine the texture of the product. Thus coarse-dispersion xerogels can form upon prolonged drying in air due to coalescence of gel particles. Under conditions precluding the action of capillary forces, highly dispersed aerogels are formed. The formation of the structure and texture of the product is completed in the stage of thermal treatment.[10,61–65]

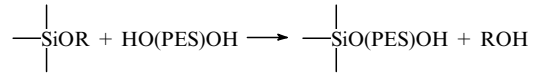
The sol-gel method with the use of highly dispersed silica gel in a polar solvent is applied in microencapsulation of photochromic fluorescent compounds,[66] scintillators[17] and porphyrins. A sol-gel matrix for encapsulation is prepared by simultaneous hydrolysis of $Si(OEt)_4$–$Zr(OBu)_4$ and other alkoxides.[67–69] Thermally stable materials, which are used in nonlinear optics, can be prepared by introducing, for example, azo dyes into TMOS by the sol-gel method.[70] Although these systems (except for biologically active systems; see Section IV) are not considered in this review, they are structurally similar to nanocomposites and are prepared according to analogous procedures. Thus the introduction of methyl methacrylate (MMA), in which an organic dye of the perylene type was dissolved, into a xerogel followed by thermal or UV polymerisation, afforded a coimpregnated SiO_2–polymethyl methacrylate–dye system.[71,72] The technique for sublimation dehydration of impregnated gels was developed.[73] This technique allows one to prevent redistribution of labile components in the matrix in the course of drying.

Sol-gel materials are classified by a mode of formation and types of bonds between organic, organometallic and inorganic components.[17] Organic groups introduced into $R^1_nSi(OR^2)_{4-n}$ serve two functions,[74,75] *viz*., modify a network (ORMOSIL, organically modified silicates) and form a network (ORMOCER, organically modified ceramics). However, this classification has not yet received ample recognition. Low-percentage and high-percentage composites contain 2 vol. %–30 vol. % and up to 45 vol. %–75 vol. % of ceramics, respectively. Thus a material under the name 'rubber ormosil' (based on TEOS and polydimethylsiloxane with $M_w = 1700$) contains more than 70 vol. % of an inorganic component.[76,77]

Hybrid nanocomposites are primarily classified by the type of interphase interactions between components. Thus nanocomposites whose macrostructures are determined by the presence of van der Waals, hydrogen or hydrophilic–hydrophobic interactions are known. These are, for example, amorphous inorganic nanocomposites, which are prepared from silicon-, titanium-, aluminium- or zirconium-containing oxopolymers formed *in situ* in a medium of a soluble organic polymer. Formally, this process consists in homogeneous formation of a nanosized filler in a medium of a polymer. Poly(*n*-butyl acrylate), polyphosphazene, polyvinylpyrrolidone (PVPr), poly(*N*,*N*-dimethylacrylamide), *etc*. were prepared according to this procedure.[78–82] An alternative procedure involves the insertion of a polymer (or its precursor) into an oxogel, which is formed by mixing of metal alkoxides or by their impregnation into pores of an oxide xerogel network. Either organic molecules or polymers are inserted as 'guests' into nanocomposites of another type.

The one-stage formation of oxogels and polymers is exemplified by sol-gel polymerisation (including electrochemical polymerisation) of the so-called silanised monomers, *viz*., *N*-[3-(trimethoxysilyl)propyl]pyrrole,[83,84] 2,5-bis(trimethoxysilyl)thiophene[85] and trimethoxysilylferrocene derivatives.[86]

Hybrid network composites in which organic and inorganic components are linked through strong covalent or ionic bonds have received primary attention. These networks are generally prepared according to two procedures: (1) secondary networks are formed in primary networks, which are functionalised as required; (2) two different networks (including interpenetrating networks) are simultaneously formed from molecular precursors of a different nature, which enter into different reactions (polyaddition, polycondensation, metathesis polymerisation, hydrolysis–condensation, *etc*.). This line of investigation is in a primitive state of development and reliable examples of realisation of this approach are few in number.[87–89] Initially, it was attempted to use solutions of polymers. However, the formation of a gel was accompanied by uncontrolled phase separation to yield a heterogeneous material. More homogeneous sol-gel materials were prepared[90] by acid-catalysed hydrolysis simultaneously with condensation of HO(PES)OH [PES is (polyethersulfone)] and TEOS or TMOS in DMF.



Inorganic and polymeric components are linked *via* deep interactions. Thus poly(ethersulfone) chains are linked through $-SiO_2-$ units. Their condensation affords nanoparticles (Fig. 1).[91]

Bonding of TEOS, diethoxydimethylsilane or their mixture with sulfo groups of perfluoroalkylsulfonate ionomers (under the commercial name Nafion) in which the SO_3H^+ groups form clusters with sizes 3–5 nm affords a hybrid heterogeneous material Nafion/SiO_2 (Nafion/ORMOSIL).[92–96] Studies by differential scanning calorimetry demonstrated that a broad endothermic peak of the initial NafionH^+ at 215 °C was shifted to the lower-temperature region as the ratio of the components of the reaction mixture was changed. This is associated with condensation between the sulfo groups of Nafion and the silanol groups. In the course of the sol-gel process with the participation of TEOS and the styrene–maleic anhydride copolymer in the presence of a

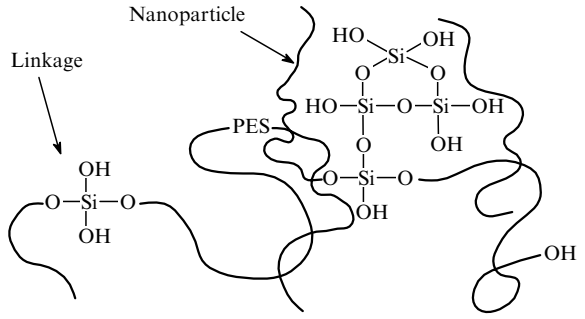
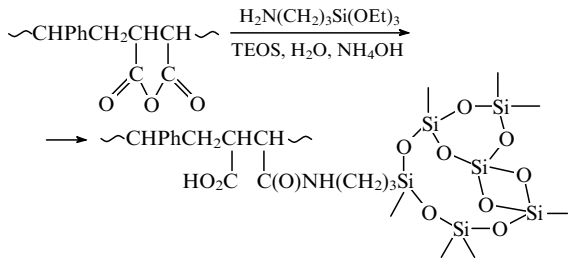


Figure 1. Formation of a hybrid nanocomposite in the reaction of PES with bridging $-SiO_2-$ groups.

binding agent, *viz*., (3-aminopropyl)triethoxylsilane, a covalent bond between polymeric and inorganic components was also formed.[97] In this case, particles with sizes < 20 nm were formed.

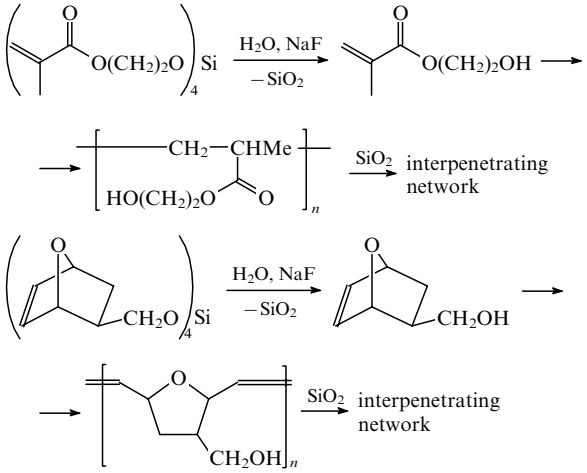


A series of monolithic hybrid materials containing 23 vol. % – 100 vol. % of an inorganic component were prepared by the sol-gel method starting from SiO_2 and the copolymer of methyl methacrylate with 3-(trimethoxysilyl)propyl methacrylate.[98,99]

Polyimide composite materials containing nanosized SiO_2 or TiO_2 particles possess the high mechanical strength due to their ability to form three-dimensional inorganic networks.[100,101] Polyimide – polysilsesquioxane† composites were prepared, for example, by condensation of 1,1-bis(4-aminophenyl)-2,2,2-trifluoro-1-phenylethane with a derivative of pyromellitic anhydride and aminophenyltrimethoxysilane (simultaneously with imidisation at 250 – 350 °C).[104–107] In this case, films of hybrid nanocomposites containing 32% – 70% of homogeneously dispersed SiO_2 with particle sizes of 0.5 – 7 nm were obtained (Scheme 2). Polyamide – SiO_2 compositions were prepared *in situ* by suspending SiO_2 nanoparticles (which were sometimes preliminarily modified with aminobutyric acid) in a polymerised ε-caproamide at high temperature.[108,109] This approach provides homogeneous distribution of SiO_2 owing to which the mechanical properties of nanocomposites are improved, the glass transition temperature rises and the rate of crystallisation is increased.

Analogous nanocomposites were also prepared[17] based on analogues of polyimides, *viz*., polyoxazolines, including those containing triethoxysilane groups.[110–112]

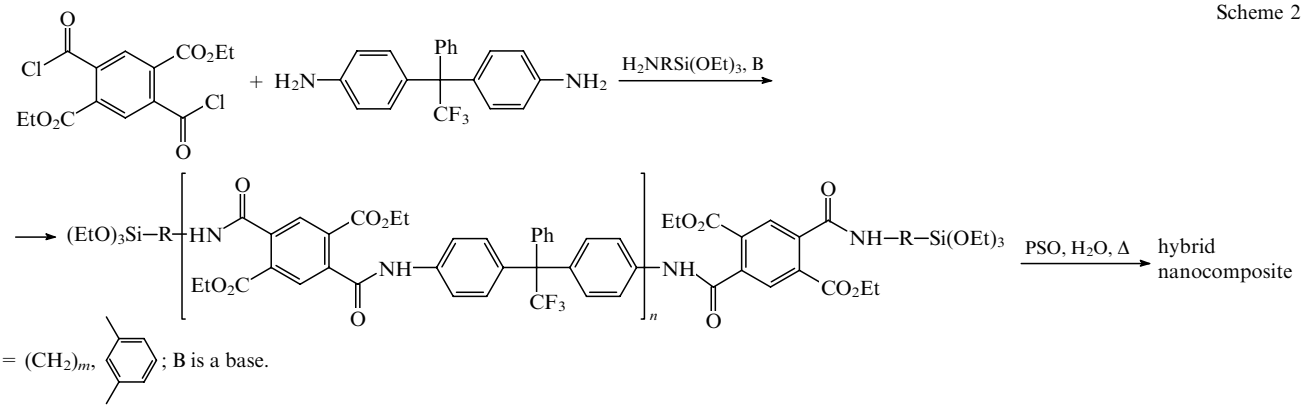
Metathesis polymerisation accompanied by opening of the ring and free-radical addition of cyclic alcohols appears to be the optimum procedure for the synthesis of hybrid SiO_2 – polymer nanocomposites exhibiting the minimum shrinkage.[31,113–115] The synchronous formation of interpenetrating networks occurs as a result of competitive reactions of polymerisation and hydrolysis of silicon alkoxide under the action of the nucleophilic catalyst NaF followed by condensation.



It is known that sols are thermodynamically unstable systems with high surface free energies. It is necessary to stabilise these systems by special techniques, for example, by controlling pH of the system. When the sol-gel method is used, nanosized particles or their precursors are stabilised through adsorption of special monomeric molecules on the sol surface.[116–119] Thus carboxylic acids (including polymeric acids[106,120]) are strongly bound to the surface of SiO_2, ZrO_2, TiO_2 or Al_2O_3 particles. Amines are specifically adsorbed on metallic Pd or Au particles. Thiols are even more specific reagents for Au. Controlled hydrolysis with the use of bifunctional molecules containing a double bond along with hydrolysed silane or ZrOR groups affords the corresponding precursors (see Scheme 1). These precursors incorporate ZrO_2 particles of size ~ 2 nm, which can undergo copolymerisation, for example, with methacrylic acid (MAA). The latter simultaneously acts as a surface modifier due to the presence of a double bond.

† Polysilsesquioxanes (PSO) belong to a class of three-dimensional organosilicon oligomers of the general formula $(RSiO_{1.5})_n$ containing the inorganic cubic Si_8O_{12} nucleus. These compounds have polyhedral structures with different symmetries and are key intermediates in the formation of various nanocomposites (see, for example, Ref. 102). Thus the synthesis and properties of hyperelastic materials, which have been prepared by copolymerisation of 4-methylstyrene and oligomeric silsesquioxane macromers, have been reported recently.[103]

Scheme 2



R = $(CH_2)_m$, ; B is a base.

Alkoxide $Zr(OR)_4$ is readily hydrolysed. Direct hydrolysis of the latter affords a precipitate of $ZrO_2 \cdot nH_2O$, which is unsuitable for the preparation of a homogeneous composite material. In strongly acidic media, a flocculent hydrated gel layer is present on the surface of these particles. This layer contributes significantly to the stability towards aggregation.[121] It is believed[122] that this layer makes it possible to perform repeated peptisation of ZrO_2 from a xerogel. When bound to MAA, $Zr(OR)_4$ is hydrolysed more slowly and hence well-dispersed nanosized ZrO_2 particles are formed in the presence of latent water. Silanes modified with MAA undergo copolymerisation. In this case, the resulting silicon-containing polymer is used as a matrix material for nanosized zirconium particles (Fig. 2).[76] A convenient procedure for the synthesis of these nanocomposites involves dispersion copolymerisation of monomers containing trialkoxysilyl groups.[123–127] Thus statistical copolymerisation of silicon–magnesium monomers affords beads of sizes 100–500 nm from which organic compounds are removed upon heating to 1000 °C in the presence of wet air. The sizes of the final particles are ~ 100 nm.[128]

$$CH_2{=}C(Me)COO(CH_2)_3Si(OMe)_3 + [CH_2{=}C(Me)COO]_2Mg \xrightarrow[65\ ^\circ C]{MeOH,\ AIBN} \text{polymer precursor} \xrightarrow[1000\ ^\circ C]{H_2O} \text{fine ceramic powder}$$

AIBN is an initiator [2,2′-azobis(isobutyronitrile)].

A nanocomposite material was prepared starting from methacryloxypropyltrimethoxysilane.[76] The reaction of equimolar amounts of $Zr(OR)_4$ and MAA yielded a product, which was mixed with silane. The latter was preliminarily hydrolysed and condensed in the presence of 0.5 M HCl, and then H_2O was added. A photoinitiator and alcohol were introduced into the resulting mixture to control the viscosity and then a support was submerged in the mixture thus depositing a thin film of a photosensitive material.

Hybrid nanocomposite materials are prepared from metal-containing monomers, such as alkoxy derivatives of Ti and V of the general formula $Ti(OR^1)_3(OR^2)$[129] or $OV(OR^1)_{3-n}(OR^2)_n$,[130] respectively, where R^2OH is ethylene glycol monomethacrylate, 2-hydroxyethyl methacrylate, furfuryl alcohol, 1,1-dimethylpent-4-en-2-yn-1-ol, propargyl alcohol or other unsaturated alcohols, which are able to undergo polymerisation. Radical polymerisation of metal-containing monomers affords polymers with side chains containing alkoxy groups of titanium[131] or vanadium.[132] The reactions of MAA with alkoxy derivatives of titanium yield metal-containing monomers $[CH_2{=}C(Me)COO].Ti(OR)_3$ (R = Et, CH_2Bu^t or Bu^t).[133] Based on these compounds, nontoxic, self-polished and anticontamination coatings were prepared by free-radical copolymerisation with MMA or by etherification of the resulting polymer and titanium tetraalkoxide.[134]

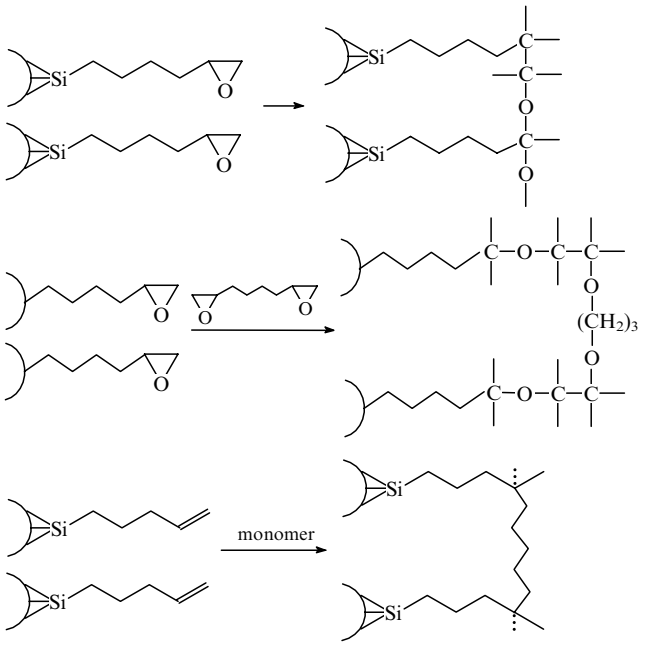


Figure 2. Use of functionalised silanes for cross-linking of organic and inorganic components of the system.

Polytitanosiloxanes are prepared in one stage by simultaneous controlled hydrolysis (actually, cocondensation) of $Si(OEt)_4$ and $Ti(OPr^i)_2(acac)_2$.[134] In this case, a ladder polymer containing Si–O–Si and Si–O–Ti units is formed. Their ratio depends on the conditions of the synthesis and can reach 10 : 1, respectively. This ratio determines the time of gel formation and the possibility of formation of fiber ceramics upon annealing of the material (500–900 °C).[135] The structures, the mechanism of growth and the properties of siloxane composites containing the silicon, titanium and mixed titanium-silicon phases (including those prepared *in situ*) were considered in more detail in the review.[136]

The sol-gel method was used[137] for the synthesis of titanium–silicon nanocomposites based on perfluorosulfonate ionomers as well as for the preparation of nanosized particles with sizes 10–50 nm [from $Ti(OR)_4$ and $Zr(OR)_4$] incorporated into matrices of a copolymer of styrene and 4-vinylphenol,[138] *etc.* These approaches can also be used for the activation of surface polymers, for example, perfluorinated polymers [such as polytetrafluoroethylene (PTFE) or copolymers of tetrafluoroethylene with hexafluoropropylene] by their treatment with $SiCl_4$ followed by controlled hydrolysis.[139, 140]

Metal (primarily, titanium and silicon) alkoxides are used as cross-linking reagents for many natural polymers (polysaccharides, cellulose derivatives, vegetable oils, *etc.*[141, 142]). These polymers contain highly active hydroxy groups, which can form oxopolymers *in situ*. Organic networks are also formed in the reactions of low-molecular-weight compounds containing several hydroxy groups (for example, anthracenobisresorcinol and its derivatives) with $(Pr^iO)_2TiCl_2$.[143]

Cocondensation of macromers containing trialkoxysilyl groups with the best known polymers [modified polystyrene (PS), polyoxazoline, polyimide, polyethylene glycol (PEG), polyetherketones, polymethyl methacrylate and derivatives of polytetramethylene oxide] is a convenient procedure for the preparation of telechelic polymer networks.[106, 144–150]

The insertion of highly dispersed SiO_2 particles into a polymerised system is also widely used for the preparation of nanocomposite materials. Although a survey of this problem is beyond the scope of the present review, let us consider several most prominent, in our opinion, examples. In aqueous media, spherical SiO_2 particles possessing a high specific surface act as peculiar dispersing agents. In this manner, particles of a raspberry-shaped composite with sizes 100–300 nm were formed in polyaniline–SiO_2 or polypyrrole–SiO_2 systems.[151–156] In the course of polymerisation initiated by the redox $FeCl_3 \cdot 6H_2O$–$(NH_4)_2S_2O_8$ system, not only spherical but also fiber-shaped SiO_2 particles were introduced into polypyrrole formed.[157] The particle sizes vary within 80–200 nm as the SiO_2 : polypyrrole ratio changes.

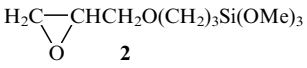
Composites based on SnO_2, which are used in lithography, are prepared by oxidation and cross-linking in films.[158, 159] Tin-containing polymers (for example, poly(4-[(trimethylstannyl)methyl]styrene;[160] its synthesis was reported in Refs 161 and 162) are used as precursors of SnO_2. Photoirradiation of polymers followed by their pyrolysis in air results in simultaneous formation of SnO_2 particles and a polymer network in which the polymers are incorporated. In this case, the C–Sn bonds are cleaved to form radicals of the benzyl and trimethylstannyl types. The former

react with atmospheric oxygen on film surfaces. The latter undergo recombination to form networks.

Hybrid nanocomposites based on nanosized Au[163] and TiO_2 particles[164] were also prepared using reverse micelles. A surfactant (for example, didodecyldimethylammonium bromide) was added to toluene with the resulting formation of revrerse micelles into which $AuCl_3$ and a precursor gel, *viz*., TEOS, were introduced. The $LiBH_4$–THF system was used as a reducing agent. Subsequent hydrolysis and condensation afforded Au particles impregnated into the wet gel. Their sizes depend on the H_2O : Si ratio and the concentration of the surfactant. After immobilisation on the surface of highly dispersed SiO_2 with the use of bifunctional aminosilane $(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$ (see the review[17]), colloidal gold particles were stabilised with dodecanethiol.[165] Subsequent treatment of these particles with thiol resulted in the cleavage of bonds with SiO_2 and the particles became labile. Repeated immobilisation–stabilisation events led to the growth of two-dimensional highly ordered ~ 10 nm thick layers in which particles are linked together (Fig. 3).

It is best to prepare reverse micelles with the use of sodium bis(2-ethylhexyl)sulfosuccinate (SBES).[166] For example, $Ti(OPr^i)_4$ was dissolved in reverse micelles, which were formed from isooctane and SBES and contained a calculated amount of water. In this case, the alkoxide slowly diffused into micelles and then was hydrolysed and condensed in these micelles as in microreactors. This procedure was used for the preparation of TiO_2 nanoparticles, which were extracted and dispersed in a solution of fluorinated polyimide. When a polymer–TiO_2 composite was deposited on a glass plate followed by thermal treatment (at 300 °C under an atmosphere of N_2 for 30 min), an optical film waveguide was formed. Therefore, one of the advantages of the preparation of these nanocomposites in a solution of a polymer is the possibility of formation of transparent films (in this case, yellow titanium complexes are not formed). The thermal stability of the above-described materials (4% of TiO_2) is almost identical to that of the initial polymer. This indicates that the thermal characteristics of the 'host' polymer remain virtually unchanged upon impregnation of TiO_2. In some cases, simple mixing of ingredients, *viz*., a polyimide solution and a sol-gel precursor, which leads to phase separation, is sufficient to form a polymer–inorganic nanocomposite.

Compounds containing epoxysilane groups can form networks as well.[167–170] Thus alkoxysilane (**2**) is a binder providing the compatibility of TEOS with polyacids.[167, 168]



2

The component compositions of hybrid nanocomposites, which were prepared by the gel-sol method based on SiO_2 and an ethylene oxide–epichlorohydrin copolymer, were 71 : 29 – 29 : 71. Acid condensation of TEOS in a THF solution afforded an inorganic network.[171, 172] These networks can also be prepared with the use of alkoxy derivatives of aluminium.

The morphology and fractal structures of these materials were studied. It is known[173] that the structures of aggregates are characterised by the fractal dimension D ($1 \leqslant D \leqslant 3$), which may have a meaning of an exponent in the equation relating the weight of the M particles to their characteristic size R

$$M \approx R^D.$$

For surface fractals with the uniform density, $D = 3$. The self-similarity or scale invariance of the fractal aggregate implies that the structure of the aggregate, on the average, remains unchanged on the interval as extended as is wished and any its portion is similar to the aggregate as a whole. When the surface is dealt with, the D value equal to 2 corresponds to the smooth surface and the D value equal to 3 corresponds to the maximum roughness.

The fractal dimensions of polymeric and colloidal samples of the TiO_2 aerogel with high values of S_{spec} (prepared by the sol-gel method and dried with CO_2 in the supercritical state), which were calculated by different methods, were compared. These values are virtually identical (2.6–2.8). The fractal surfaces of colloidal particles are only slightly less regular than those of polymeric aerogels.[174] This indicates that at the nanosize level, the morphology is determined in the early stages of the process and depends only slightly on the conditions of the synthesis, whereas on the mesolevel, it is the conditions of the synthesis that have a determining effect on the morphology.

Studies of the condensation of TEOS in a polysiloxane network demonstrated[14, 136] that fractal models typical of solutions were not observed upon matrix polymerisation. Owing to large molecular weights of the matrix and the polymer formed, the entropy of the mixture decreases resulting in phase separation. Particular conditions are required to prevent phase separation in the system. However, phase separation always occurs when the concentration of SiO_2 is > 5%, which enhances the mechanical strength of composites. When TiO_2 nanoparticles were precipitated *in situ*, the maximum bulk domains (up to 5% of filling) were formed. These nanocomposites rank below systems with SiO_2 in strengths.[175]

Of special note is the use of the sol-gel method for performing 'template syntheses.' In this case, nanocomposites are formed through 'assembly' from components under conditions of a strictly defined stereochemical orientation of the reagents. These conditions and primarily a small reaction volume (due to which reacting molecules can approach each other more closely than in

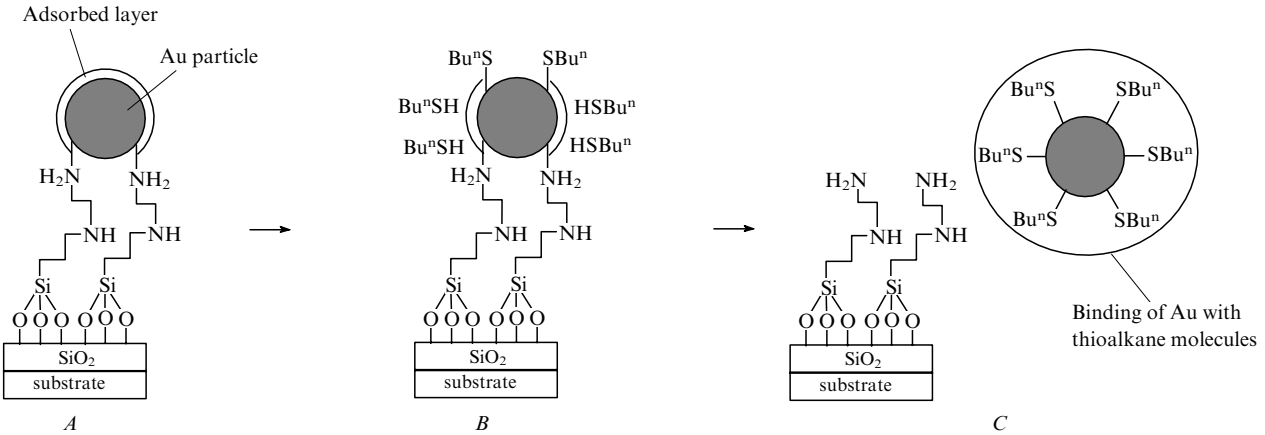


Figure 3. Preparation of hybrid materials with the use of reverse micelles: (*A*) immobilisation of colloidal Au particles; (*B*) exchange of alkanethiol molecules and cleavage of the Au–NH_2 bonds; (*C*) rapid regeneration of the layer on complete binding of Au particles.

solutions or in the solid phase) promote the so-called 'mild' template synthesis in the course of which the 'assembly' occurs under normal conditions (sometimes even at room temperature). For example, this procedure was used [176] for the preparation of tubular semiconducting nanostructures based on TiO_2 [from $Ti(OPr^i)_4$], commercial template membranes based on Al_2O_3 with the pore diameters of 22 and 200 nm [177] and fibrous structures based on ZnO (from zinc acetate [178]) and WO_3.[179] These materials are excellent photocatalysts. The template synthesis is described in more detail below (Section V). The template sol-gel syntheses in fibres, nanotubes or micro- and nanoporous membranes were surveyed in detail in the review.[180] This procedure was used for the preparation of fibrous electrode materials based on V_2O_5 [181] and semiconducting oxide materials, such as MnO_2,[182] Co_3O_4,[183] ZnO, WO_3, *etc*. The template synthesis of tubular nanostructural nanocomposites of the semiconductor–conductor type (as nanotubes or nanowires) was performed [176] starting from TiO_2 in Al_2O_3 pores followed by polymerisation of monomers.[184, 185]

III. Preparation of nanohybrid multimetallic materials by the sol-gel method

Nanocomposites based on heterometallic ceramics, for example, on perovskite with the ABO_3 structure, can be synthesised by the sol-gel method. These materials (primarily, film and epitaxially oriented materials) possess specific ferro-, piezo- and pyroelectric properties and are widely used in electronics and optoelectronics.[186] The naturally occurring mineral perovskite $CaTiO_3$ has the pseudocubic crystal lattice. Perovskites, for example $PbTiO_3$, are generally prepared by calcination of a mixture of PbO and TiO_2, which is ground using a vibrational mill, at temperatures higher than 600 °C (synthesis *exsitu*). However, PbO is toxic and the presence of its phase in the final product is undesirable. The sol-gel technique for the preparation of perovskite $PbTiO_3$ is free from these drawbacks.[187] A mixture of $Ti(OPr^i)_4$, $Pb(AcO)_2 \cdot 3H_2O$, ethylene glycol and citric acid taken in a ratio of 1 : 1 : 40 : 10, respectively, was stirred at 50 °C. Then the resulting citrate metal complexes were subjected to polymerisation at 130 °C and to pyrolysis at 300 °C. The resulting powdered precursor was calcined in air at 400–600 °C for 2 h to obtain thin $PbTiO_3$ films, which retained the properties of a bulk material. Different versions of the sol-gel syntheses of $PbTiO_3$ were described in the literature in detail. Thus polymeric films, which were prepared by mixing $BaTiO_3$ with solutions or melts of polymers, were studied.[188, 189] However, in this case particles were nonhomogeneously distributed and their agglomeration occurred. An alternative hydrothermal procedure for the synthesis of these nanocomposites was proposed.[190] According to this procedure, $BaTiO_3$ particles prepared from $Ba(OH)_2$ and titanium diisopropoxide bis(ethylacetoacetate) at temperatures higher than 100 °C were grown in a polymeric matrix (in a polybutadiene–polystyrene block copolymer, *etc*.[191]). These materials can potentially serve as components of conducting compositions (see, for example, Ref. 192). Structurally homogeneous $BaTiO_3$ nanocomposites can only be prepared using the sol-gel method.[193] One of versions of this procedure involves solid-phase polymerisation of organometallic precursors followed by pyrolysis.[194]

$$Ba + Ti(OPr^i)_4 + CH_2{=}C(Me)COOH \longrightarrow$$

$$\longrightarrow BaTi[OOCC(Me){=}CH_2]_6 \xrightarrow{200\ ^\circ C} \{BaTi[OOCC(Me)CH_2]_6\}_n \longrightarrow$$

$$\longrightarrow BaCO_3 + TiO_2 \xrightarrow{600\ ^\circ C} BaTiO_3$$

Polymerisation was also used for the preparation [195] of $BaSnO_3$ with the perovskite structure. The synthesis was carried out analogously to the synthesis of $PbTiO_3$ (see above) but at a different temperature and with the use of $BaCO_3$, $SnCl_2 \cdot 4.5H_2O$, ethylene glycol and citric acid taken in a ratio of 1 : 1 : 40 : 10, respectively, as the starting compounds. Other multicomponent ceramics of the perovskite type, *viz*., $SrTiO_3$, $NdAlO_3$, $SrBi_2Ta_2O_9$ and superconducting ceramics $YBa_2Cu_3O_{7-\delta}$, were also prepared by the sol-gel method (see below). The application of this method to the synthesis of these materials (the use of metallochelates and decomposition of organometallic precursors) was described in more detail in the study.[196] In the present review, let us note only that single-phase thin $KTiOPO_4$ films, which exhibit remarkable optical properties and high thermal stability, can be prepared according to this procedure; $Ti(OEt)_4$, KOEt and different sources of phosphorus [$(EtO)_2P(O)(OH)$, $(EtO)P(O)(OH)_2$, $P(OH)_2Me$, $P(OMe)_3$, *etc*.], among which $(Bu^nO)_2P(O)(OH)$ is an optimum source, are used as precursors.[197]

Heteropolymetallates of the type of Keggin's acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, which are incorporated into organic–inorganic structures, may be assigned to the group of polymetallic nanocomposites.[17, 117] These materials possess good electrochemical properties and can be potentially used in the holography. Nanocomposites based on these materials can be prepared according to two procedures, *viz*., by mixing polymetallates (spheres of diameter ~ 1 nm) with TEOS [taken in a ratio of (2–6) : 10] and tetraethylene glycol or by introducing polymetallates into organosilanes.

Specific clusters, *viz*., oxometallates containing W–O–Si units, which are inserted into the side chain of the polymer, were synthesised by the reactions of substituted trichlorosilanes $RSiCl_3$ (R = $CH_2{=}CH$, $CH_2{=}CHCH_2$, $CH_2{=}C(Me)CH_2$ or $CH{=}CHPh$) with the polyanion $K_4SiW_{11}O_{39}$. In this case, cluster-containing monomers with composition $[SiW_{11}O_{40}(SiR_2)_2]^{4-}$ were formed.[17] Polymerisation was carried out under the action of radical initiators. The products were characterised by different methods, including ^{13}C and ^{29}Si NMR spectroscopy. The yield of the polymer and the chain length depend on the reactivities of unsaturated groups R and increase in the series $CH_2CH \ll CH_2{=}CHCH_2 < CH_2{=}C(Me)CH_2 < < CH{=}CHPh$. The structure of this polymer is schematically shown in Fig. 4. The syntheses of oxoclusters of transition metals $Nb_4(\mu_2\text{-}OMc)_4(\mu_2\text{-}O)_4(OPr^i)_8$, $Ti_6O_4(OEt)_8(OMc)_8$ (OMc is methacrylate) and $Zr_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OPr^n)_8 \cdot (OPr^n)_{10}(AllylAc)_6$ (AllylAc is allyl acetoacetate) [198] by controlled hydrolysis of different metal alkoxides in the presence of complex-forming agents (OMc or AllylAc) were also reported. These compounds consist of the metal oxide nucleus and peripheral ligands, which can undergo polymerisation. The latter are responsible for the formation of a cluster network. The construction of stable ensembles of nanoblocks requires that clusters possess rather high lability and high reactivity. For example, the thermodynamical stability of titanium oxo clusters and their resistance to hydrolysis depend both on the size and the oxo(alkoxo) group : titanium ratio. With the aim of retaining

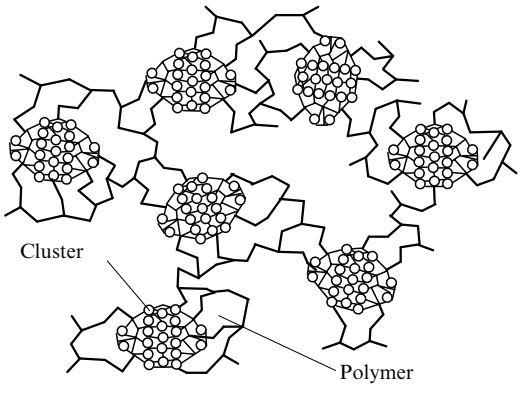
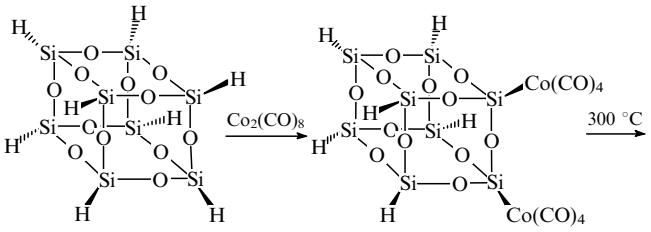


Figure 4. Structure of the hybrid polymer-inorganic material based on the $\{SiW_{11}O_{40}[Si(CHPh{=}CH)_2]\}^{4-}$ polyanion.

their molecular structures, polymerisation should be performed in anhydrous organic solvents.[199]

The syntheses of three-dimensional oxovanadium borophosphates with open frameworks[200–202] and polyboroazinylamines, which are precursors of metal-containing matrix composites containing metal borides and nitrides,[203] are also available.

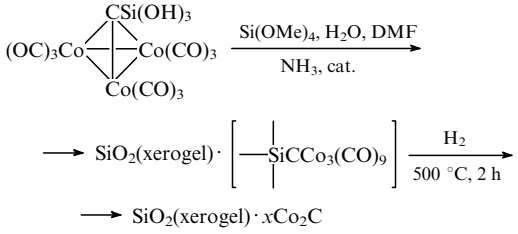
The possibilities of modification of materials prepared by the sol-gel method with different transition metals are being extensively studied (see, for example, Refs 204 and 205). For example, mesoporous materials M41S were prepared based on molecular sieves NCM-41 or MCM-48 modified with solutions of NH_4VO_3 or $ZrOCl_2$ in a mixture with polyoxoethylene stearate. Solutions of NH_4VO_3 or $ZrOCl_2$ acted as precursors of transition metal ions.[206] Nanoparticles (50–60 nm) of cobalt carbide immobilised in a silicon matrix were obtained.[207]



$\longrightarrow Co_2C \cdot SiO_2$

Mesopores of MCM-41 matrices were modified[208] with the *trans*-$[Co(en)_2Cl_2]^+$ or $[Co(en)_3]^{3+}$ complexes (en is ethylenediamine) stabilised by ammonium salts.

Hydrolytic condensation of cyclopentadienyltitanium chloride with silsesquioxane (the product of incomplete condensation of cyclopentyltrichlorosilane) followed by calcination of titanium-containing oligosilsesquioxane afforded microporous titanium–silicon oxides with S_{spec} of up to 780 $m^2\ g^{-1}$.[209] In the stage of sol-gel polymerisation, metal clusters can be introduced into nanocomposites. Thus the trihydrosilyl group was inserted into a cluster with a known composition, *viz*., $(\mu_3\text{-HC})Co_3(CO)_9$, and then it was subjected to heterocondensation.[210]



$\longrightarrow SiO_2(\text{xerogel}) \cdot xCo_2C$

In the resulting xerogel, the unimodal distribution of the particles was observed. The sizes of the particles were 10–46 nm (the average diameter was 25 nm). The Os_3, PtSn, Fe_2P, Co_2P and Ni_2P nanoclusters can be introduced into a composite analogously (by incorporation into a complex with a bifunctional ligand containing the reactive alkoxy- or hydroxysilyl group).[211] The insertion of Pd^{2+} ions,[212] Cu^{2+} ions,[213] *etc*. into poly(ethyltrimethylsilane) formed was described. The structures of organometallic–inorganic diblock copolymers, in particular, the structure of the ferrocenyldimethylsilane–dimethylsiloxane block copolymer, were studied.[214] In a hexane solution, the latter copolymer exists as long rod-shaped cylindrical micelles in which the iron-containing nucleus is placed in a 'case' (crown) formed from polydimethylsiloxane blocks. The micelle of this type comprises up to 2000 polymeric molecules and decomposes under the action of ultrasonics to form short cylinders containing $\sim$ 700 molecules.

To perform heterogenisation of metal complex catalysts (see Section VIII), metal compounds are bound to an inorganic matrix through a bidentate phosphorus-containing ligand of the $[Ph_2P(CH_2)_2CO_2]EO_x(OR)_{3-2x}$ type (E = Ti or Zr; R = Alk).[215] Thus the reactions of such ligands with tungsten carbonyl afforded products $W(CO)_5[Ph_2PXEO_x(OR)_{3-2x}]$, which are potential precursors for the sol-gel synthesis. Cocondensation of these precursors (analogous to the above-described condensation of metal clusters with TMOS) gave[216] xerogel nanocomposites with composition $SiO_2\,(\text{xerogel}) \cdot xM_yP_z$[216–218] (M = Ru, Ga or In, $y = z = 1$; M = Pt, $y = 1, z = 2$; M = Fe, Co, Ni or Rh, $y = 2$, $z = 1$; M = Cd, $y = 3$, $z = 1$; M = Pd, $y = 5$, $z = 2$) and even bimetallic $SiO_2\,(\text{xerogel}) \cdot Zn(Cd)GeP_2$ composites.[217] Immobilisation of the $[\eta^6\text{-PhSi(OMe)}_3] \cdot Cr(CO)_3$ complex in a highly dispersed amorphous xerogel (S_{spec} = 500–1800 $m^2\ g^{-1}$) in the course of sol-gel polymerisation (NH_4F catalyst) made it possible to prepare a single-phase hybrid of inorganic oxide and an organic network polymer containing (1,4-phenylene)siloxane bridges of the 'nucleus–shell' type.[219] Vacuum thermolysis (393 K, 24 h, < 1 Torr) of this composite even at 389 K resulted in elimination of carbonyl groups to form zero-valent chromium nanoparticles of sizes 1.0–10.0 nm in pores of the xerogel (Fig. 5). Under normal conditions, thermal elimination of carbonyl groups of the composite proceeded only at 400 °C. In the latter case, chromium in the low oxidation state was formed.[220]

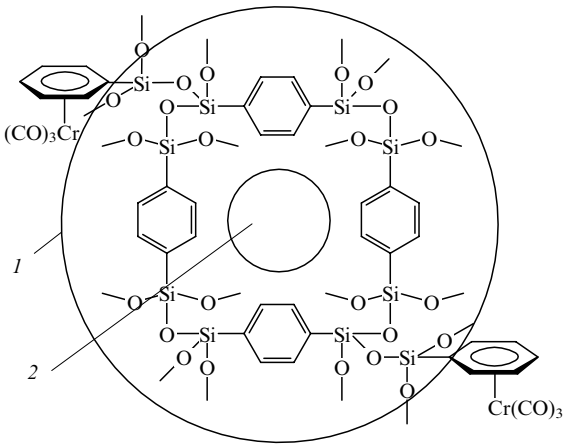
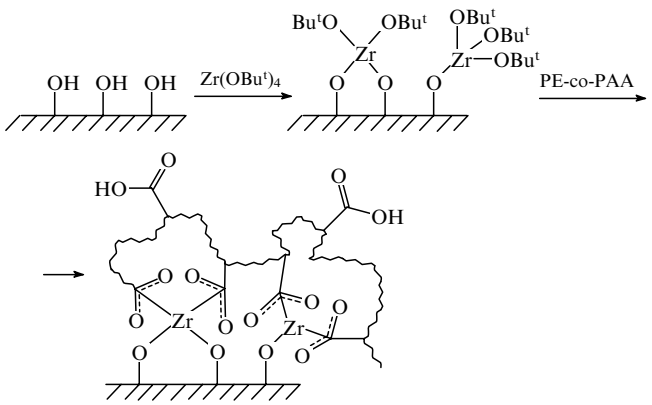


Figure 5. Structure of a single-phase hybrid of the 'nucleus–shell' type; (*1*) a shell, (*2*) a nanoparticle of zero-valent chromium.

Tricarbonylmolybdenum groups were introduced into the resulting polysilane according to the polymer-analogous conversion method. For this purpose, poly(methylphenylsilane) was treated with the $Mo(CO)_3Py_3$ complex.[221]

Nanolayer silanisation of inorganic surfaces of the TiO_2, Al_2O_3 or Fe_2O_3 types, including the introduction of Fe_2O_3 into mesopores of silicates,[222] $CaCO_3$, $BaSO_4$, *etc*., is widely used. Generally,[223–226] a thin layer of silanol derivatives and a dimethylsiloxane oil are deposited on inorganic surfaces and heated to 250–280 °C. In this case, siloxane bonds are cleaved, the terminal groups of the polymer chain react with hydroxy groups of inorganic surfaces and the chains are cross-linked through methylene and siloxane bridges or oligomers. As a result, particles, which are stable to hydrolysis and extraction with different solvents, are formed. For example, $Zr(OBu^t)_4$ modifies the aluminium surface.[227] Zirconium groups are linked upon treatment with the poly(ethylene–acrylic acid) copolymer (PE-co-PAA) containing 5 mass % of units of acrylic acid.[228]



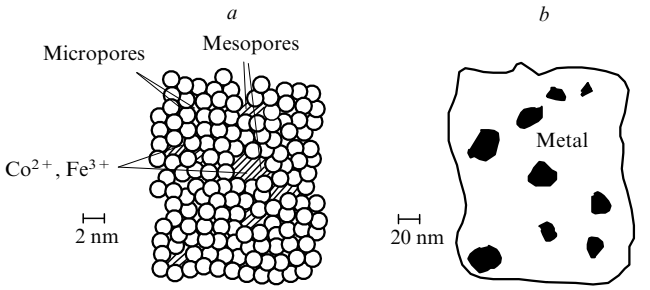


Figure 6. Diffusion and adsorption of metal ions in pores of the 'host' and the structure of the composite before (*a*) and after (*b*) thermal treatment.

The adsorption properties of these materials are changed due to formation of a hydrophobic layer and the material becomes moisture-stable. When Ti and Au layers 5 and 50 nm thick, respectively, were deposted on the activated polydimethylsiloxane surface, ordered structures were formed.[229, 230]

The coating of the surface of inorganic particles (including metals or their oxides) is often used in the technology of powder preparation to form structures of the 'nucleus – shell' type, which possess additional useful properties. Thus SnO_2 or In_2O_3 particles are coated with chelate polymers swelling in water (for example, those containing $In^{3+} - SiO_2$ or $In^{3+} - Sn^{2+} - SiO_2$ as well as Ag^+), which were preliminarily subjected to appropriate treatment. These particles exhibit the surface conductivity and are used for the preparation of thermally stable conducting films possessing antistatic properties, *etc*.[231 – 233]

Therefore, several procedures for the insertion of a polymer into an inorganic material by the sol-gel method are available. Thus silanes containing two different functional groups can be used. One of these groups reacts with a monomeric unit of the macromolecule and the second group reacts with the sol-gel precursor resulting in the formation of a bond between the side group of the polymer and the sol-gel network. Sometimes special binding agents are additionally added. For example, the surface of highly dispersed SiO_2 was modified with aminobutyric acid and the resulting product was dried, dispersed in ε-caproamide and subjected to initiated polymerisation at 90 °C.[234] If the concentration of SiO_2 particles is $\leqslant$ 5 mass % (the distance between the particles is 50 – 110 nm), they are homogeneously distributed in the composite. At concentrations of $>$ 10 mass %, aggregation of particles starts. Layered nanohybrid materials (see Section V) were prepared [235] by the reactions of $Zn(OH)_2$, ZnO or a Zn/Al alloy with carboxylic acids or their oxychlorides. The 'guest' :'host' ratio in these composites varies from 0.75 : 0.25 to 0.9 : 0.1. The morphology of the particles changes from fibrous to platelet depending on the nature of the reacting components, the interlayer distance increasing in the range of 1.61 – 2.01 nm.

Recently, the sol-gel procedures for the preparation of ceramics based on alumoxanes, *viz*., carboxylates of the general formula $[Al(O)_x(OH)_y(OOCR)_z]_n$, have been analysed. [236] At the stage of formation, the $M(acac)_n$ complex ($M = Ca^{2+}$, Mn^{2+}, Y^{3+}, *etc*.) can be additionally introduced into ceramics.[237, 238] Metallic Co and Fe and their alloys, which were formed upon reduction of the corresponding nitrates with hydrogen, were dispersed in an aluminosilicate matrix. The matrix was synthesised by the sol-gel method from $(BuO)_2AlOSi(OEt)_3$ and possesses dielectric properties. In this case, nanocomposites with the particle size of $\sim$ 20 nm possessing magnetic properties were obtained [239] (Fig. 6).

One of new trends today in the field under consideration is to use carbon dioxide in the supercritical state as a solvent in the course of sol-gel polymerisation or in the stage of extraction of the resulting product. To perform the sol-gel process according to this procedure, the initial alkoxysilane is mixed with anhydrous 99% HCO_2H. Then polymerisation of the mixture is carried out in supercritical CO_2 in an autoclave (40 °C, 41.4 – 55.2 MPa). The formation of the gel proceeds over 12 h and then CO_2 is slowly removed (8 h). This is favourable for the formation of highly porous monolithic composites with the meso- and macroarchitecture of the pores.[240] Components, which sharply enhance the ability of SiO_2 to adsorb water, are also introduced at the stage of formation. For example, selective water adsorbents, such as $CaCl_2$ and LiBr, bind up to 53 mass % of H_2O.[241, 242]

Colloidal dispersions of trimetallic Au – Pb – Cd particles (the diameter is 33 nm) containing the gold nucleus with a 18 nm thick lead mantle are formed by γ-irradiation of salts of the corresponding metals.[243] In this case (when nanocomposites contain three or more different metals, *i.e*., they are multimetallic nanohybrids), studies of the structures of these particles is a challenging task. At the same time, these materials have already found use as precursors in the production of superconducting ceramics, special multicomponent steels, *etc*. When traditional approaches are employed, a polymer either is formed in a previously prepared inorganic matrix or is inserted into the latter. Multimetallic nanocomposites are formed either in a polymeric matrix *in situ* or simultaneously with the latter.

It is known that standard methods for the preparation of blends in the production of high-T_c superconducting ceramics (direct mixing of oxides, carbonates, oxalates, nitrates and other metal salts) give rather poorly reproducible results. This is due not only to the heterogeneity of grinding and mixing of the solid initial components but also due to complex physicochemical and mechanochemical conversions that occur in the course of the preparation of samples. As a result, microheterogeneities appear and different phases, including nonconducting phases, are formed resulting in low-quality high-T_c superconducting ceramics with a blurred superconducting transition (Meissner effect). A structurally homogeneous superconducting ceramic of the $YBa_3Cu_4O_8$ type was formed when the initial components [for example, $Y(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$ and $Cu(NO_3)_2 \cdot 2H_2O$] were mixed on the molecular level (in solution). After evaporation of the solvent (congruent evaporation), a homogeneous dispersion of a precursor of a high-T_c superconducting ceramic was obtained. With the aim of preparing composite materials, either a high-T_c superconducting ceramic is introduced into a polymeric matrix or this ceramic is prepared in the presence of a polymeric matrix. For example, in the first case, a dispersed high-T_c superconducting phase, *viz*., $YBa_2Cu_3O_{7-\delta}$ (ceramic Y-123), $(Pb_xBi_{1-x})_2Ca_2.Sr_2Cu_3O_y$ [244] or $Tl_2Ba_2Ca_2Cu_3O_y$ [245] with $T_c \sim 90$, 110 and 125 K, respectively, was introduced into a polymeric polychlorotrifluoroethylene, polyvinylchloride or rubber matrix. The ceramic content is 50% – 75%. The optimum compositions combine advantages of a high-T_c superconductor (high T_c, good magnetic properties and magnetic levitation) and of polymers (mechanical strength, flexibility, simplicity of processing of products and resistance to atmospheric effects, aggressive media, *etc*.). In addition, the preparation of compositions allows one to eliminate drawbacks of a high-T_c superconducting ceramics, *viz*.,

the high porosity, the friability, the susceptibility to degradation, *etc*. However, rather large (micrometer) ceramic particles are inserted into a polymer according to this procedure.

In the second case, polymeric matrices containing metal ions dispersed on the molecular level are used (including the preparation of nanosized particles in the course of polymerisation or polycondensation). For example, citrates of different metals in aqueous solutions of acrylamide are polymerised in the presence of radical initiators and chain carriers (*N*,*N*,*N*′,*N*′-tetraethylenediamine) to form a gelatinous phase.[246] In this case, metal cations were trapped into a polyacrylamide gel much as occurs in the sol-gel synthesis. After calcination, ultrathin multicomponent oxide powders, such as $YBa_2Cu_3O_{7-x}$ or $LaAlO_3$, were obtained. The formation of the $YBa_2Cu_3O_{7-x}$ ceramics was performed with the use of acrylic or methacrylic acid as chelating ligands[247] or with the use of polymer–salt solutions based on polymeric alcohols or acids, PEG or PVPr.[248–250] The sizes of all salt crystals formed in the presence of any one polymer are substantially smaller than those obtained upon crystallisation of pure salt solutions. This is associated with complex formation in solutions as well as with adsorption of macromolecules on nuclei of crystallisation although it is not inconceivable that recrystallisation occurs simultaneously due to the presence of the concentration gradient of the components within the thickness of the film. Homogeneous films are most often formed because their formation occurs not only on the surface but also in the volume. It is essential that the final sizes of crystallites of the ceramics in the resulting powders should be approximately equal to their sizes in films.

The polymer-analogous conversion method was used for the preparation of the Y^{3+}, Ba^{2+} and Cu^{2+} complexes with polymethacrylic acid[251,252] and of the YBC chelates with polyamides[253,254] [gelatinisation with polyvinyl alcohol (PVA) can also be used].[255] The superconducting ceramics based on these metallopolymers has $T_c = 80-92$ K, and the critical current density (J_c) is 150–160 A cm^{-2}. Not only powders but also films and fibres can be prepared from these ceramics. (For this purpose, YBC-epoxy composites prepared from epoxide polymers are also suitable.[256])

For example, long (> 200 cm) fibres 1 mm in diameter were formed from thermoplastic gels based on Y-123 ceramics and PVA.[257] Calcined fibres have $T_c = 92-94$ K. These fibres form materials characterised by different J_c values depending on the degree of saponification (DS) and the content of the Y-123 ceramics in these materials.[258–260] The critical current density has the minimum value when DS = 67 mol. % and the maximum value ($J_c = 3.5 \times 10^4$ A cm^{-2}, 77 K) when DS = 81 mol. %. This parameter is also affected by the conditions of treatment (calcination and pyrolysis) of samples, which is associated with the peculiarities of the distribution of the ceramics over fibres.

Nanocomposite materials based on high-T_c superconductors are also prepared by polymerisation of acrylic acid in a mixture with aqueous solutions of Y^{3+} nitrate and Ba^{2+} and Cu^{2+} acetates.[247]

One of the most promising approaches to the polymer synthesis of high-T_c superconductors involves copolymerisation of metal-containing monomers.[261] If metal ions are introduced into molecules of the monomer before copolymerisation, these ions are distributed in the polymer more uniformly. For this purpose, acrylates or acrylamide complexes of Y^{3+}, Ba^{2+} or Cu^{2+} were mixed in a molar ratio of 1:2:3, dissolved in a minimum amount of methanol, dried and subjected to solid-phase copolymerisation.[262] Acrylamide complexes of Bi^{3+}, Pb^{2+}, Sr^{2+}, Ca^{2+} and Cu^{2+} taken in a molar ratio of 2:0.3:2:2:3 were treated according to the same procedure (copolymerisation was carried out in concentrated aqueous solutions).[263] The organic phase was calcined out from the resulting metal-containing copolymers. The properties of these high-T_c superconducting ceramics are shown in Fig. 7. Analysis of the temperature dependence of the electrical resistance (R) demonstrated that these ceramics behave as metals at $T < T_c$,

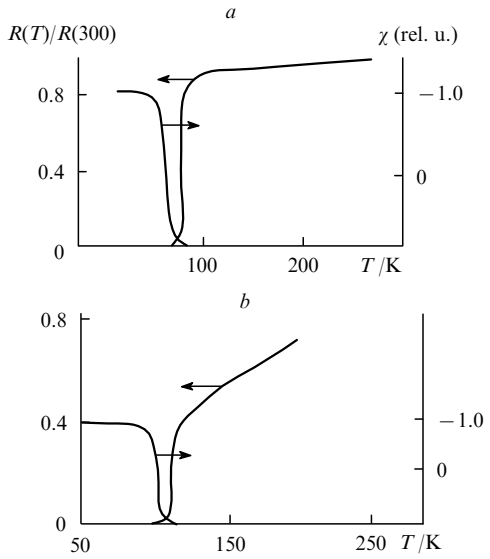


Figure 7. Temperature dependence of the electrical resistance and the magnetic susceptibility of high-T_c superconducting ceramics: (*a*) ceramics from a copolymer of Y, Ba and Cu acrylates; (*b*) ceramics prepared by spontaneous copolymerisation of acrylamide complexes of Bi, Ca, Sr, Pb and Cu.

although T_c of these ceramics are not as high as those of single crystals. It is known that the properties of polycrystalline samples in the normal state depend to a greater extent on the quality of intergrain contacts than on the structure of grains as such. The widths of superconducting transitions in the range of 0.1–0.9 of the value corresponding to complete resistance drop is no more than 2–3 K, which is close to the characteristics of the best samples of high-T_c superconducting ceramics. The character of the temperature dependence of the magnetic susceptibility (χ) is also indicative of the sharp transition and of the presence of the only superconducting phase. In this case, the complete volume of diamagnetic shielding of the phase, which is estimated from a lead reference compound, reaches 100%. The characteristics of superconducting bismuth cuprates are of particular importance. The reproducible synthesis of the latter is a challenging task. Generally, these compounds contain admixtures of a phase with $T_c = 85$ K due to the microheterogeneity of the ceramics and the successive phase transitions $2201 \rightarrow 2212 \rightarrow 2223$. Products prepared by spontaneous copolymerisation are well reproducible single-phase samples with $T_c = 110$ K and a critical current density of up to 240 A cm^{-2}. Apparently, this approach can also be used for the preparation of other single-phase materials in the nanocrystalline state.

The preparation of multicomponent steels of the M50 type (alloys containing 4.0 mass %, 4.5 mass %, 1.0 mass % and 0.8 mass % of Cr, Mo, V and C, respectively, and Fe as the remainder) may become an important field of application of nanostructurised polymetallic materials. These steels are primarily used in aircraft construction for the preparation of supporting bearings, in gas turbine engines, *etc*.[264,265] Generally, M50 steels contain substantial amounts of micron-sized carbon particles, which initiate the formation of fatigue cracks in the material of bearings. The mechanical properties of these structurised materials would be expected to be improved as sizes of grains deposited on defects decrease (healing of microcracks); PVPr is used as a polymeric surfactant; $Fe(CO)_5$, $Cr(Et_xC_6H_{6-x})_2$, $Mo(Et_xC_6H_{6-x})_2$ ($x = 0-4$) and $V(CO)_6$ serve as precursors of the M50 steel. The process is carried out in dry decalin under ultrasonic irradiation (sonochemical synthesis). After removal of the solvent and the gaseous phase, colloidal particles have an average diameter of 7 nm and exist as a homogeneous alloy. Another procedure involves reduction of precursors of the M50

steel ($FeCl_3$, $MoCl_3$, $CrCl_3$ or VCl_3) with lithium triethylborohydride in THF followed by removal of solid LiCl by sublimation *in vacuo* at high temperature. Probably, these approaches will also be useful in the design of magnetic materials, for example, those based on polymetallic nanosized particles of the $LaSrCr_xNi_{1-x}O_{4+\delta}$ type, *etc*. Thus a procedure for the preparation of the $La_{1-x}Sr_xMnO_3$ ceramics ($x = 0$, 0.2, 0.4 or 0.6) has been proposed recently.[266] This procedure involves preliminary polymer synthesis consisting in binding of metal nitrates with a gel precursor from PEG ($M_w = 20\,000$) taken in certain ratios. Autoignition occurred at 300 °C and NO_3 groups served as an oxidising agent. Subsequent thermal treatment of the combustion product afforded a homogeneous perovskite phase (see above). Its morphology and S_{spec} (1–7 $m^2\ g^{-1}$; the sizes of crystallites were 24–150 nm) depended on the reagent ratio and reaction conditions. A ceramic with cadmium and lanthanum additives with composition $Pb_{0.85}Cd_{0.05}La_{0.10}Ti_{0.975}O_3$ was prepared by the sol-gel method from metal acetates and $Ti(OBu)_4$.[267] Thin silicon films can be coated with this material in the stage of concentration of the solution (before drying). Subsequent thermolysis is carried out according to a standard procedure.

IV. Preparation of template synthetic nanobiocomposites by the sol-gel method

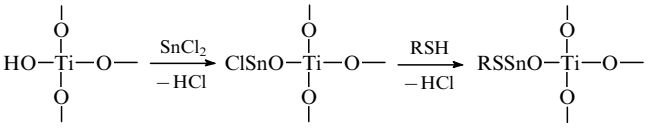
The sol-gel method provides considerable possibilities for the preparation of a series of nanohybrid materials in which biologically active macromolecules can be encapsulated at the stage of formation of ceramics, glasses and other inorganic composites (see, for example, Refs 268 and 269). The biological objects can be enzymes, catalytic antibodies, noncatalytic proteins, polynucleic acids and microbial, plant and animal cells[270–272] used in biocatalysis, for immunodiagnostics, as biooptical agents, various adsorbents, *etc*.[268,273–275]

Biomolecules (active enzymes) were encapsulated into a sol-gel matrix for the first time in 1990.[276] About 40 different types of hybrid bioceramic materials whose inorganic matrices contain silicon, titanium and zirconium oxides, TiO_2–cellulose composites, *etc*. were described.[277] Recently, bioceramic sensors, solid electrolytes, electrochemical biosensors, *etc*. have been surveyed in a review.[278] Moderate temperatures and mild conditions of hydrolysis and polymerisation of monomeric alkoxides make it possible to trap proteins in the stage of formation of the matrix, thus preventing their denaturation. The high stability of the biomolecules trapped, the inertness, the large specific surface, the porosity and the optical transparency of the matrix facilitate heterogenisation because of which the sol-gel method of immobilisation is very attractive. Below are considered the principal approaches.

Proteins, such as copper–zinc superoxide dismutase, cytochrome, myoglobin, hemoglobin and bacteriorhodopsin, were encapsulated into a porous silica gel matrix prepared by the sol-gel method. The matrix effectively retains these biomolecules without loss in their enzymatic activity and changes in their spectral properties,[279] does not preclude the approach of small molecules to the reaction centre and does not hinder transport of the reaction products. Heterogenisation of glucose oxidase and peroxidase, which are used as active solid-phase elements of glucososensors, was carried out according to the same procedure. The spectral characteristics of a gel containing oxalate oxidase and peroxidase are changed upon storage in aqueous solutions of oxalic acid.

Antibodies bound in such a manner are used in medicine, immunochromatography, immunosensors, *etc*. For example, immunoglobulins which are trapped retain their ability to bind external antigens from solutions.[280] Antibodies 14D9 incorporated in sol-gel matrices catalyse different reactions, including hydrolysis of cyclic acetals, ketals, epoxides, *etc*.[281] The ability of the sol-gel matrix containing 10% of PEG and antiatrazine antibodies to bind atrazine was studied.[282] This matrix recognises and binds atrazine and widely distributed herbicides in solutions. In this case, neither leaching of antibodies nor nonspecific physical sorption of atrazine on a ceramic matrix occur. A decrease in the activity was not observed for at least 2 months, while the activity in solutions decreased by 40% in this period. In addition, the use of the sol-gel method excludes the necessity of purifying immunoglobulin. It should be emphasised that these materials have other advantages, such as the enhanced thermal and pH stability, the possibility to monitor easily the enzymatic reactions both in pores and in the body of the matrix by spectral methods, the convenience of storage, the possibility of the repeated use, *etc*.[283]

Enzymes, which act as bioreactors (biodoped polymers), were immobilised according to the above-described procedure.[125–127] For this purpose, chemically active terminal groups of enzymes and active bonds of dopants of the ceramics, for example of Sn–Cl, were used.[284]



R is an enzyme.

For example, alcohol dehydrogenase was immobilised into nanotubes of TiO_2, which was prepared by template synthesis, according to this mechanism. This enzyme retained its ability to oxidise ethanol for more than 4 days (NAD^+ cofactor, phosphate buffer, pH 8).[180] Since nanotubes are open at both ends, this configuration allows one to use them as a flow reactor. These examples are large in number. They involve also covalent binding of antibodies with the aim of functionalising sol-gel films.[280]

Of considerable interest are procedures for the modification of matrices (including surfaces of metal oxides,[285] silicates, siloxanes, hybrid sol-gel polymers) with different polyols (most often with glycerol) and their ethers followed by binding of trypsin, cytochrome *c*, superoxide dismutase, glucose oxidase, phospholipase D, *etc*.[286] Bioencapsulants exhibit activity, which is almost identical to that of nonimmobilised enzymes. Besides, the former possess the high stability and exhibit the substantially better properties than materials prepared by the standard sol-gel method. Vinyl groups are grafted to the surface of SiO_2 particles (by treating aminosilica gel with acryloyl chloride) and copolymerisation of the resulting product with acrylamide and acrylic acid or *N*,*N*-dimethylaminopropylacrylamide is performed in the presence of a cross-linking agent and glucose oxidase.[287] After removal of the protein from these nanocomposites, a molecular impression (template) remains. This template recognises glucose oxidases in protein mixtures.[288] The so-called template approach based on the formation of porous silicate films about a specific reagent, which is then removed, using the sol-gel method was described. Template films prepared based on 3-hydroxytyramine[289] have the higher affinity for this substrate than for structurally related molecules, including serotonin, dihydroxynaphthalene, *etc*., and do not possess the affinity for negatively charged or large molecules, including the Tyr-Gly-Gly peptide. Apparently, the porosity of the film as well as steric, hydrophobic and electrostatic interactions play an important role in controlled penetration of different molecules through this film.

The formation of an organised material by the sol-gel method can be performed according to four procedures:[290] (1) formation of self-assembling organic templates (transcription syntheses); (2) cooperative assembly of ensembles, *viz*., template and building blocks (synergistic syntheses); (3) morphosynthesis in which organised nonlinear chemical environments, *viz*., reaction fields (static, reorganisation, transition) are used for the construction of models;[291] (4) combination of these methods (integrated synthesis). This strategy (reaction ensemble → replication → metamorphism) resembles the general scheme of mineralisation. It can be exemplified by template-directed syntheses of ordered meso-

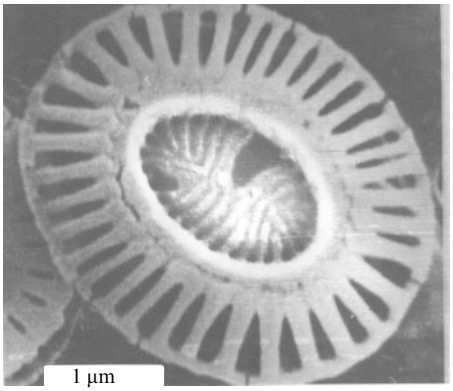


Figure 8. Electron micrograph of a coccus-like coat of the one-celled algae *Emiliania huxleyi*.[292]

forms and organoclays, microframework structures, including those with the use of bacterial templates. In particular, a coat of the one-celled algae *Emiliania huxleyi* consists of radially arranged hammer-shaped single crystals of calcite, which are crystallographically oriented and have a specific species form. The crystallographic orientation is retained in fossil casts, which is indicative of the control over nucleation on the molecular level (Fig. 8). This fact is most pronounced in the reproduction of hierarchic macrostructurised organised silica gels. Multicellular fibres from *Bacillus subtilis* (Fig. 9) can serve as an example of scale organic 3D-templates.[292] Nanosized magnetic (Fe_3O_4), semiconducting (CdS) or TiO_2 particles, which has been preliminarily prepared, were introduced into macroscopic filaments upon swelling in colloids.[293] Dried fibres (the diameter was 500 nm) were coated with a thin (30–70 nm) layer of aggregated colloidal particles. Negatively charged magnetic colloids exhibit the good permeability and reproduce the bacterial superstructure. Neutral CdS particles partially penetrate into the filament, but their major portion remains on the surface of the filament. Positively charged TiO_2 sols form only a surface coating. Removal of a bacterial component from a magnetic composite upon heating afforded structural collapse.

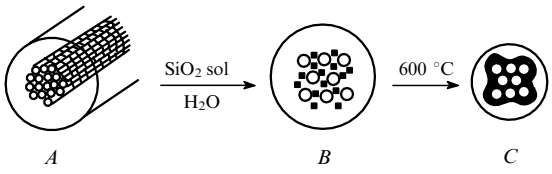


Figure 9. Scheme of formation of an organised macroporous SiO_2 structure with the use of bacterial templates, *viz*., bacterial filaments with the structure of multicellular fibers (*A*), mineralisation of interfibre spaces of filaments (*B*) and the formation of macroporous replica upon drying (*C*).

To summarise, nanohybrid materials are widespread and are of considerable importance both in nonliving and living nature.[2,268,273] Binding and decomposition of different organic compounds, the cycles of compounds and energy in nature and the formation of many useful minerals occur with the participation of nanohybrid materials. Outstanding possibilities are opened up in the field of the design of molecular-organised self-assembled systems, including nanobiomaterials. The protein environment is favourable to the preparation of complicatedly organised (both in form and composition) products. For example, perovskites ($BaTiO_3$, $SrTiO_3$ or $NaNbO_3$) whose synthetic analogues are considered in Section III can be involved in processes of bioaggregation.[294] It is believed[295,296] that finely monodispersed precursors of high-T_c superconducting ceramics could be formed based on bacterial objects.

V. Intercalation of polymers into porous and layered nanostructures

Sometimes products prepared by the sol-gel method or by intercalation can be distinguished only by their past history. No less than 5000 studies dealing with problems of intercalation of organic, organometallic and inorganic compounds as well as with the properties of the resulting products were published up to 1994 inclusive,[297] though the major body of information has been obtained during the last 5–10 years.

Natural layered silicates, the so-called smectites (or smectite clays) are most often used for the preparation of nanocomposites under consideration. Their structures, selected physicochemical properties and the nature of the active surface are considered in a review[298] and monographs.[20,299] These are very widespread minerals to which hectorite and montmorillonite $[AlMg(OH)_2(O)_4]^{5-}[Si_2O_3]^{4+}[Na,nH_2O]^+$ (MMN) with structures of the mica type belong. Crystals of MMN consist of alternating tetrahedral silicate layers of the cations condensed with negatively charged octahedral layers of metal oxides. However, unlike mica, the cations in these minerals are readily exchanged for other ions, including transition metal ions. The exchange occurs predominantly in layers containing solvated sodium cations. Intracrystal cavities can swell when they are filled with organic solvents. The degree of swelling depends on the nature of the cations within the layers and on the negative charge density on the silicate layers. Aluminosilicates and magnesosilicates belong to clays whose nature is determined by the type of the octahedral metal. Within the lattice, Mg^{2+} and Al^{3+} can isomorphically replace Al^{3+} and Si^{4+}, respectively. The cations are hydrated and the layers readily swell and accommodate large cations or a substantial amount of water. In addition, most of inorganic oxides contain surface hydroxy groups, which actively bind metal ions. Crystalline rigid 'host' matrices with a controlled system of percolation nanometer-sized pores, which can be occupied by atomic or molecular 'guest' structures (clusters, nanosized particles, inorganic coordination polymers of the CdS type, large molecules of the C_{60} fullerene type and polymer units synthesised *in situ*[20,300–303]) are rather well studied. Thus intercalation of buckminster fullerene functionalised with ethylenediamine into a mica-like silicate of the fluorohectorite type has been described.[300] Many procedures for the introduction of polymers in 'host' matrices are available. These hybrid nanocomposites are of technological interest because their properties are substantially improved compared to those of materials filled according to a standard procedure.[304–306] For example, these materials prepared by thermal synthesis are generally metastable (in particular, due to flaking of the polymer from the inorganic component).

The properties of intercalated hybrid nanocomposites are determined by a number of characteristics, particularly, by the sizes of their inner open-pore systems. These properties were considered in many reviews (see, for example Refs 20 and 307–311). Intercalation systems are divided into two types according to their architecture and properties.[309] The systems of the first type are characterised by the presence of rigid pores with a constant volume, the parallel isolation of lattice channels and the interrelation between the channels of the network. The location, the concentration and the spatial distribution of 'guests' are governed by the topology, the chemical nature and the reactivity of the inner surface of the 'host'. The matrix of the latter can be additionally dispersed and functionalised or long-chain surfactants can be intercalated into this matrix. In addition, the choice of 'guests' is limited by the minimum size of cross-linked channels, which leads to selective intercalation into induced spatial matrices (of the types of molecular sieves or membrane films). Systems of the second type are characterised by a low dimensionality of the

'host' lattice, *i.e.*, by the structures of the 'layer' or 'chain' types. As a result, the pores are 'flexible' and their sizes can be adapted to the size of the 'guest.' In layered systems, the basal (intralayer) space comprises ~ 5 nm. The thickness of the layer, for example, in perovskite varies in the range of 0.5–2.2 nm. From the viewpoint of the electronic properties, the matrix lattice of the 'guest' may have no effect on the intercalation–deintercalation process (this is true for lattices of dielectrics, *viz.*, of zeolites, layered aluminosilicates, metallophosphates, *etc.*, the intercalation behaviour of which is determined primarily by the acid–base and exchange properties). 'Guest' lattices possessing the electronic conductivity (semiconductors and metals) are a special case. Upon intercalation, redox reactions with electron (ion) transfer occur in these materials resulting in a substantial change in the physical properties of the 'host' matrix.

The inclusion of monomer molecules into pores of a 'host' followed by their controlled conversions into polymeric, oligomeric or hybrid-sandwich products (postintercalation conversions *in situ*) belong to the most interesting group of intracrystalline chemical reactions. This field has been rather well studied (see, for example, Refs 312–314). Intercalation of the appropriate monomer causes delamination and dispersion of 'host' layers, which is accompanied by polymerisation to form a linear or cross-linked polymeric matrix. This procedure was used for the insertion of polyesters,[315] PVPr [316–318] and poly(ethylene oxide) (PEO) [319] into silicates and for the insertion of PVPr,[320] polyimide [321, 322] and poly(ε-caprolactam) [305, 306] into kaolin. (When polymerisation was performed within kaolin, the resulting composites were nondelaminated products.) The most interesting hybrid nanocomposites were prepared from polyconjugated conducting polymers (which are often considered as materials for the preparation of battery plate), such as polyaniline,[323, 324] poly(2-ethylaniline), poly(*p*-phenylene), polythiophene, polypyrrole [323, 325] or pyrolysed polyacrylonitrile [326] in different matrices.[327–329] In this case, a great diversity of procedures can be used, *viz.*, the enclosure of a polymer into a gel,[330] the use of salt solutions of the corresponding polymers [for example, polyaniline hydrochloride in an acid-methanolic solution or a sulfonium salt of poly(*p*-phenylene) soluble in many solvents], *etc.* The results of early studies in this field were summarised in the review.[297] Thus oxidative polymerisation of pyrrole, dithiophene,[331, 332] tetrahydrofuran [333] and aniline [334] in an FeOCl lattice was described. Intercalated aniline forms hydrogen bonds with chlorine atoms of the lattice, and polymerisation occurs along the (101) lattice diagonal. However, the conductivity of the resulting polymer is somewhat decreased. This lattice appeared to be suitable for oxidative polymerisation of aniline introduced from an aprotic solvent.[331, 335, 336] The molecular formula of the resulting product was $(C_6H_5NH_2)_{0.28}FeOCl$.‡ The zigzag polymer chains with $M_w = 6100$, which are comparable with the FeOCl lattice, are extended along the direction of the 'host' crystal and along the hydrogen bonds between the NH groups and the chlorine atoms of the layers of the lattice. The $Fe^{2+}:Fe^{3+}$ ratio is ~1:9. The polymeric intercalate behaves as a *p*-type semiconductor (the conductivity of a single crystal is 1.5×10^{-2} S cm^{-1}). Its prolonged oxidation in air afforded a mixture of polyaniline and β-FeOOH. Recently,[340] it was proposed to use the α-$RuCl_3$ matrix, which is structurally similar to $FeCl_3$, for the preparation of lamellar nanocomposites of this type. The product of oxidative polymerisation of aniline in this matrix has the composition $(C_6H_5NH_2)_xRuCl_3$ ($0.5 < x < 0.6$). Its conductivity at room temperature is ~ 2 S cm^{-1}, which is more than three orders of magnitude higher than that of the initial α-$RuCl_3$.

Postintercalation polymerisation of aniline was carried out in air at 130° in phosphate layers of α-$Zr(HPO_4)_2\cdot H_2O$,[341–343] $VOPO_4$,[344] $HUO_2PO_4\cdot 4H_2O$,[342, 345] layered acidic zirconium–copper phosphates,[19] layered double hydroxides [346] as well as in layers of $HM^1M^2O_6\cdot H_2O$ (M^1 = Nb or Ta; M^2 = Mo or W [347–349]), molybdenum sulfide,[350] porous zeolites of the mordenite type,[351, 352] MCM-41,[351] in layers of perovskite,[353] mica-like silicates,[354] *etc.*[355] The resulting products are generally dielectrics. Polyoxometallates as 'host' matrices can serve as ideal models of 'molecular batteries' because they contain a small number (generally 6–8) of W or Mo atoms linked through oxygen bridges. Their spatial and electronic structures were adequately characterised.[356] Chemical (electrochemical) polymerisation of pyrrole in Keggin's structures $H_3PM_{12}O_{40}$ (M = W or Mo) was described.[357, 358] Sometimes additional chemical reactions are carried out with the aim of converting these products into nanocomposites. For example, $(Bu_4N)_5Na_3[(1,5\text{-COD})M\cdot\cdot P_2W_{15}Nb_3O_{62}]$ (M = Ir or Rh; 1,5-COD is 1,5-cyclooctadiene) was reduced with hydrogen in acetone.[359, 360] These hybrid nanocomposites can be completed with phosphomolybdate anions (Scheme 3). The composition of the product corresponds to the formula $C_6H_5N\cdot(PMo_{12}O_{40})_{0.116}$. Photochemical polymerisation of a diacetylene, *viz.*, 3,5-octadiyne, in layers of Mg, Mn or Zn phosphates was also reported.[311]

It can be suggested that under the appropriate conditions, monomers occupy virtually the entire space of pores or the whole interlayer space. Subsequent oxidative polymerisation ('redox-intercalation polymerisation') [351] was carried out in the presence of molecular oxygen (as an electron acceptor) and a redox-active 'host' (a catalyst of electron transfer). In this connection, layered silicates containing metal ions, which initiate polymerisation of an intercalated monomer, are of particular interest. Thus when Na^+ ions in hectorite are replaced by Cu^{2+} (sometimes by Fe^{3+}), styrene undergoes polymerisation [163] both in pores and on the surface. The polymer has a 'brush-like' structure, which indicates that the inorganic surface possesses an orienting effect. This effect decreases as the chain grows and moves away from the surface.

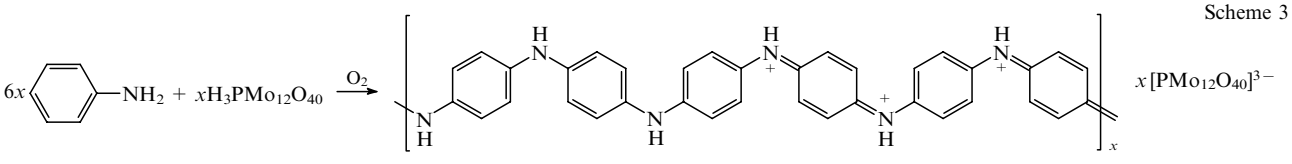
N-Vinylcarbazole is polymerised in MMN at 64 °C (in a benzene solution at 50 °C) due to the presence of cations in MMN.[361, 362] The thickness of the intercalated layer of 'guest–host' particles is 33±10 nm and the conductivity of this nanocomposite (10^{-6} S cm^{-1}) is 10 orders of magnitude higher than that of polyvinylcarbazole.

Intercalated polystyrene exists in two forms.[175] One of them possesses the enhanced rigidity due apparently to a higher degree of ordering of the polymer. The improvement in physicochemical properties of intercalated polystyrene was observed also in the model PS–MMN system.[363]

Redox intercalation polymerisation of aniline, pyrrole and dithiophene with the use of a V_2O_5 xerogel affords polyconjugated

‡ The method consisting in quantitative removal of a polymer from an inorganic 'host,' its repeated dissolution and investigation could be an important technique for the analysis of polymers in these hybrid materials. However, although studies on the extraction of polymers from layered nanocomposites have been reported,[6, 336, 337, 338] this field is poorly understood. Recently, rapid and quantitative extraction of PEO from the $K_x(C_2H_4O)_4M_{1-x/2}PS_2$ composite (M = Mn or Cd) with an aqueous tetraethylammonium salt under normal conditions has been carried out.[339] This process was analysed in detail and the kinetic regularities were revealed.

Scheme 3



anisotropic polymers.[364–366] Intercalation is accompanied by polymerisation. In this case, the chain growth initially occurs within the xerogel and is associated with transport of molecular oxygen.The V_2O_5 xerogel acts as a catalyst. A conducting polymer with different polyaniline : V_2O_5 ratios is formed with the participation of mixed-valence (V^{4+}/V^{5+}) 'host' lamellae ordered along one direction. The material consists of alternating layers of vanadium oxide and the polymer. Physicochemical studies demonstrated that polyaniline was formed as a salt. Ageing of the material in air facilitates partial oxidation of the inorganic framework and oxidative binding of polyaniline in the intralamellar space. The resulting polymer is 'frozen' due to the formation of a NH···OV hydrogen bond. A detailed analysis[351,367] of the insertion of aniline, its competitive polymerisation into MoO_3 and the formation of the nanocomposite $(C_6H_5NH_2)_{0.24}\cdot MoO_3$ structures, including those with the use of a low-temperature intercalation procedure,[367] was carried out. It was found that polyaniline chains expand layers and change the potential surface thus decreasing the polarisability of the lattice.§ The polyaniline chains intercalated in MoO_3 oxidise $(NH_4)_2S_2O_8$.[197] Oxidative polymerisation of aniline, pyrrole or thiophene monomers intercalated in layered aluminosilicates affords highly oriented 'host–guest' layers. It was found [32] that radiation polymerisation of acylonitrile and acrylic acid in MMN inclusion compounds afforded stereoregular (which are most likely syndiotactic) polymers.

Let us consider the most interesting procedures for the synthesis of one-dimensional nanocomposites based on intercalation into a matrix. An aqueous Au colloid (the particle size was 12 nm) stabilised with citric acid was introduced into pores of a Al_2O_3 filtration membrane (the average pore diameter was 20 nm) and oxidative polymerisation of pyrrole was performed *in situ* in these pores by adding an aqueous $Fe(ClO_4)_3$ solution.[369,370] After dissolution of the membrane in 0.5 M KOH, a suspension of one-dimensional colloid-polypyrrole nanostructures was obtained (Fig. 10).

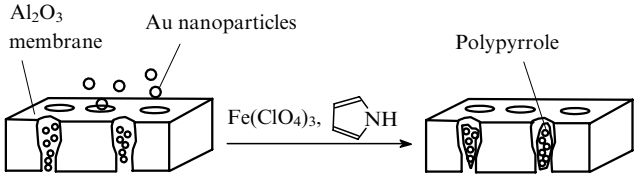


Figure 10. Template synthesis of one-dimensional Au–polypyrrole nanostructures in a Al_2O_3 membrane.

To construct solid light-sensitive solar cells, TiO_2 particles of size ~ 20 nm (prepared from $TiCl_3$, pH 2.5) are obtained at the surface of a photochemical electrode. Simultaneously, polypyrrole, which is formed upon electrochemical polymerisation of pyrrole adsorbed in electrode pores, precipitates on these particles.[371,372] These structurally controlled 'templates' are analogues of self-assembling supramolecular ensembles. Note that the procedure for the preparation of supramolecular systems for molecular recognition comprising chromophores, semiconductors and cluster aggregates, which perform special optical and electronic functions, is analogous to the above-considered preparation of nanobiocomposites.[311,373,374]

One-dimensional parallel polyaniline chains prepared *in situ* can be encapsulated into structures with wide pores and large (the diameter is ~ 3 nm) channels. In this case, the chains take a fibre shape and exhibit microwave conductivity.[351,375,376]

An alternative to polymerisation *in situ* involves direct intercalation of macromolecules into layered structures, most often into silicates. The insertion of polymer molecules into layered 'host' lattices is of interest from different points of view. First, the construction of organic–inorganic polylayered composites becomes possible. Second, the intercalation physical chemistry by itself and the role of intercalation in the fact that the system gains electronic conductivity (for example, in the construction of reversible electrodes [308]) or improved physicomechanical properties (nylon-layered silicate nanocomposites,[377,378] hybrid epoxide-clay composites,[322] nanomaterials based on hectorite and polyaniline, polythiophene or polypyrrole ,[379] *etc.*) are of interest.

The insertion of PEO into layers of mica-like sheet silicates in the reactions of a melt of the polymer with the 'host' Na^+- or NH_4^+-exchange lattice is one of a few examples of direct intercalation of polymers.[380] Poly(ethylene oxide) is also inserted into lamellar networks of $V_2O_5\cdot nH_2O$, MoO_3,[337,338,381–383] $MnPS_3$, $CdPS_3$,[381,384] *etc.* Thus an aqueous solution of PEO ($M_w = 10^5$) reacts with an aqueous gel of $V_2O_5\cdot nH_2O$ to form a composite after removal of water. In this case, the interlayer distance increases from 1.155 to 1.32 nm. Alkali metal ions react with PEO to form inclusion compounds, which can also be inserted into layers of ionic silicates, for example, into MMN. The distance between the layers of the PEO–Li^+ salt complexes intercalated in MMN is 0.8 nm, and the PEO chain adopts a slightly strained helicoid conformation.

Poly(ethylene oxide)–LiX systems find wide application as polymeric electrodes and solid electrolytes. However, these questions are beyond the scope of the present review and were considered in detail, for example, in the monographs.[385–387] These systems are rather often used in combination with ceramic fillers (of the $LiAlO_2$, Al_2O_3, TiO_2, *etc.* types). Let us give only one example.[388] Thus 10% of nanosized TiO_2 (13 nm) or Al_2O_3 (5.8 nm) particles were dispersed in acetonitrile with $LiClO_4$ and then PEO was added (the $LiClO_4$: PEO molar ratio was 1 : 8). The conductivity of the resulting polymer-inorganic nanocomposite is 10^{-4} and 10^{-5} S cm^{-1} at 50 and 30 °C, respectively. Recently,[389] the preparation of a series of new hybrid polymer-inorganic electrolytes, which contain the aluminium atom in the main chain and Li^+ ions, by cocondensation of $LiAl(OR)_2H_2$ with organosilicon precursors has been reported.

The intercalation of polymers [390] (PS,[391] PEO,[380] polypropylene,[392–394] *etc.*) from their melts into a silicate lattice is also a promising procedure. A molecular-dynamic model, theoretical calculations and the kinetics of formation of these intercalates were considered in the study.[390] A new line of investigation involves direct hydrothermal crystallisation of silicate layers from a polymer gel.[395,396] This approach extends the range of intercalated polymers because it allows one to use compounds, which do not contain functional groups.

Activation of surfaces, layers and 'host' pores, including activation under the action of ultrasonics, is of importance in the processes under consideration. Thus Ni particles (10–40 nm) are deposited on submicrospherical silica gel.[397] When a solution of $Ni(CO)_4$ in decalin was irradiated with ultrasonics, the Ni–C bonds were cleaved simultaneously with activation of the SiO_2 surface (the removal of adsorbed water, the cleavage of Si–O–Si bonds and the formation of free Si–O bonds). An alternative procedure involves the reaction of metallic nickel with activated silanol groups of the surface to form Si–O–Ni bonds. These centres serve as nuclei for further growth of Ni particles. Amorphous superparamagnetic Ni clusters were converted at 400 °C into a crystalline ferromagnetic material. This mechanism is realised to some extent for other dehydrated surfaces as well. For example, Al_2O_3 and metal carbonyls $M(CO)_n$ form Al–O–M structures. [398] In such a manner gold nanosized particles were stabilised in a silica gel monolith.[399] Thermolysis

§ Recently, the geometric structures and vibrational properties of complexes of polyenes with aluminium atoms as a constituent were studied by the *ab initio* quantum-chemical method in the Hartree–Fock approximation.[368]

of rhodium carbonyl on the Al_2O_3 surface afforded small Rh clusters.[400]

Nanocomposites self-assembled as $(M/P)_n$ multilayers (M and P are nanosized oppositely charged layers of an inorganic component and a polymer, respectively) are worthy of special notice. These nanocomposites possess a variety of valuable properties, which makes it possible to use them, in particular, in the optical engineering for the production of displays.[401–407] A great variety of procedures for the layer-by-layer assembly of polyelectrolytes and clays,[408–413] lamellar zirconium phosphates[414] and colloidal metal particles[415,416] were proposed. Using anionic MMN and positively charged poly(diallylmethylammonium chloride) (PDAMAC) as an example, the mechanism of formation of these materials on the surface of nanoplates from glass, quartz, silver, gold and even Teflon was considered in detail and the processes of defect formation were studied.[417] Successive submersion of plates into a solution of the P component or in a suspension of M leads to an increase in the number of layers (n). Each event is accompanied by an increase in the thickness of the P and M layers by 1.6 and 2.5 nm, respectively. The formation of multilayers involves several stages. First, adsorption on the substrate surface occurs, which is determined by electrostatic and van der Walls interactions. In this case, the structural hierarchy of the M layers provides limitless possibilities of their application as templates for a great variety of molecules and clusters,[24,418–422] which can be inserted between swollen layers or inside the M plates and can also be located on their surface. Second, the M component is strongly and irreversibly (which was confirmed by physicochemical studies) adsorbed on the oppositely charged polymeric electrolyte to form a very closely packed plane-oriented layer. Irregular M layers cannot provide complete coating of intercalated layers due to which overlapped stacks are formed. Interphase irregularities, which are independent of the nature of the substrate, exceed the thickness of the M/P layer. The control over the process can be performed by applying an external stress to the system in the course of self-assembly. In practice, a wide variety of these procedures were realised. For example, the PDAMAC polyelectrolyte and SiO_2 nanoparticles (the diameter was 25 nm) were successively deposited on the surface of a polystyrene latex. As a result of adsorption, a three-component polylayered material is formed (Fig. 11) in which the thickness of one, two and four SiO_2–polymer layers are 60, 120 and 240 nm, respectively. The method of self-assembling of multilayers was also used for the preparation of nickel phthalocyaninetetrasulfonate–PDAMAC nanocomposites in which the average thickness of the M/P layer was 1.05 nm.[423]

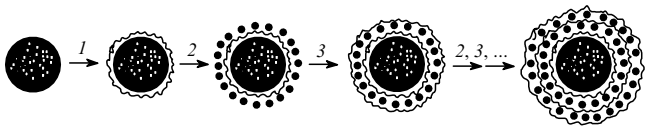


Figure 11. Scheme of self-assembly of a polylayer composite based on PS latex, SiO_2 and PDAMAC; (*1*) adsorption of polyelectrolyte, (*2*) adsorption of SiO_2, (*3*) adsorption of a polycation.

Layered nanostructures were prepared[424] with the use of liquid-crystalline polymers containing ionic groups; MMN or hydrotalcite $[AlMg_2(OH)_2(OH)_4]^+[0.5\ CO_3, OH, Cl]^-$ was used as an inorganic component. According to different estimates, the average thickness of the M/P pair is 4.9 nm. It is believed that the electrostatic self-assembly promotes tight contacts between the components and the establishment of this molecular organisation, which allows one to prepare new types of liquid-crystalline structures with unusual properties. Apparently, the layer-by-layer assembly of aluminosilicate–polyelectrolyte nanocomposites is a promising procedure for the design of new membrane materials.[425] In this review, hybrid nanocomposites, which were prepared, for example, by emulsion or gas-phase polymerisation of traditional monomers (most often, styrene, MMA, aniline, ethylene, propylene, *etc*.) in the presence of different organophilic minerals, are not considered although these approaches are undoubtedly of interest by themselves (see, for example, Ref. 426). Thus emulsion polymerisation of the epoxy prepolymer (a product of condensation of equimolar amounts of bisphenol A with epichlorohydrin) in the presence of Na^+–MMN was accompanied by the insertion of the polymer into the basal space of the smectite clay, which expanded from 0.96 to 1.64 nm.[427] A micelle with the monomer rather than the monomer as such was inserted into the body of the 'host,' which swelled in aqueous media. The resulting composite exhibits a higher thermal stability than that of the corresponding homopolymer. A hydrogel containing 3.5 mass % of MMN,[428] which possesses the lower critical solution temperature ($\sim 32\ ^\circ C$) than that of the nonmodified product, was prepared according to the same procedure (copolymerisation of *N*-isopropylacrylamide and *N*,*N*′-methylenebisacrylamide as a cross-linking agent in aqueous suspensions of MMN).[429]

Layered graphite inclusion compounds (LGC) were studied in detail. Graphite can be considered as an aromatic macromolecule. The number of aromatic rings in this molecule is ~ 1000 and the period of identity (the distance between the parallel planes) is 0.335 nm. Since the bonds between the parallel carbon layers in graphite are virtually absent (the energy of the interlayer interaction is only 16.8 J mol^{-1}), monomolecular layers of different compounds, including metal ions, can be inserted into graphite to form layered (laminated) compounds.[430] Graphite inclusion compounds are generally prepared by the reactions of graphite with vapours or solutions of metals in strongly ionising solvents, with low-boiling chlorides or with cationic metal complexes. These compounds are divided into products of the first, second and subsequent stages of insertion depending on the number of carbon layers separating two adjacent layers of the metal inserted. The nature of bonds in these LGC depends on the nature of the metal. For example, in the cases of Fe, Co, Ni, Mn and Cu, van der Waals interactions exist. Sometimes when the π-electron density of graphite is transferred to the inserted metal layer, the carbon network of graphite becomes a peculiar polymeric ligand. In the case of alkali metals, this bond is formed as a result of electron transfer from the metal atoms to the conduction band of the adjacent graphite layer, *i.e*., due to electrostatic interactions between the positively charged metal ions and free electrons of the conduction band of graphite (this problem was considered in more detail in Ref. 431).

In the course of reduction of inserted metal ions, they may partially leave layered stacks and reduction may occur on the outer surface of graphite. In such a manner nanosized particles, for example, of titanium are inserted into the imperfect lattice of graphite.[432] Many metals are inserted into graphite under high pressure in combination with shift deformation.[433] Nanosized cobalt particles inserted into the graphite lattice according to this procedure exhibit the unusual magnetic and thermal properties.[434]

Therefore, intercalation chemistry provides virtually limitless possibilities for the construction of hybrid nanocomposites. Presently, the major effects attendant on the processes of formation of these materials are revealed. The structural organisation and the principal properties of these materials have been studied. The number of studies in this field is gradually increasing, which allows one to predict the design of materials of new types. For example, the synthesis of nanocomposites of a new interesting class, *viz*., of hybrid materials containing azamacrocycles (gallium phosphates, *etc*.), has been reported recently.[435] A start has been made on studies on intercalation (by the ionic exchange method) of nitrate groups of biomolecules, *viz*., of nucleosidemonophosphates and DNA, into layered double hydroxides of the $Mg_2Al(NO_3)_2 \cdot H_2O$ type ('anionic clays').[436] Nanocomposites containing metal chalcogenide as a structural element ('host') are of special interest.

VI. Metal chalcogenide – polymer inclusion nanocomposites

Metal chalcogenide – polymer inclusion nanocomposites are rather well studied. The results of studies were surveyed in the monographs.[437, 438]

Apparently, intercalation in the CdS structure has received much attention.[439] Film composites are most generally prepared with the use of a solution of the corresponding precursor followed by the synthesis *in situ*.[440] For example, $Zr(OPr)_4$ in propanol was hydrolysed with an aqueous solution of acetic acid, and solutions of cadmium acetate and ammonium thiocyanate were added.[441] The composition was coated onto a glass support and treated as in the case of the sol-gel method (see Section II). The cryochemical treatment of gels impregnated with Cd^{2+}, Pb^{2+} or Zn^{2+} salts followed by sulfiding with hydrogen sulfide in the gaseous phase, afforded nanoparticles of sulfides with sizes from 3–7 to 30–100 nm in a SiO_2 matrix.[73] The formation of the dispersed CuS phase in a polyacrylic acid – polyvinyl alcohol polymeric matrix proceeds through the stages of formation of sulfur-containing copper complexes, associates, amorphous clusters and, finally, crystalline CuS nanoparticles.[442] The specific structure of the interfacial layer and limitations imposed by diffusion in the swollen polymeric matrix are responsible for the characteristic features of formation of small (~ 4 nm) particles, the character of their distribution in the matrix and the aggregative stability.

If the anion is readily polarised and the cation possesses strong polarising properties, the compounds with composition MX_2 have layered structures. The distinguishing feature of these layered materials (of the MoS_2 or TaS_2 types) characterised by the low charge density of the layer is their ability to decompose into nanosized building blocks under appropriate conditions and to form colloidal solutions. In molybdenum dichalcogenide, a layer of molybdenum atoms is located between layers of chalcogen atoms, and packs are formed from these triple layers. In this case, bonds within the packs are substantially stronger than those between two packs linked only through van der Waals forces.[443] The exfoliation procedure has been developed in sufficient detail.[444, 445] Plastic superconducting electromagnetic materials can be prepared based on nanocomposites.[446] Intercalation of PVPr, PEO and PEG from aqueous solutions into monolayers of suspended $NbSe_2$ [it is known that the latter is of one the best superconductors among layered dichalcogenides ($T_c = 7.2$ K)] was reported.[447] The compositions and the selected properties of the resulting nanocomposites are given in Table 1.

$$NbSe_2 + x LiBH_4 \xrightarrow[-0.5xH_2]{-xBH_3,} Li_xNbSe_2 \xrightarrow[-0.5xH_2]{xH_2O,\ -xLiOH,} NbSe_2\ (\text{monolayer}) \xrightarrow{\text{polymer}} \text{polymer}-NbSe_2$$

A polymer is inserted into the WS_2 phase according to the same mechanism.[448]

Table 1. Properties of intercalated polymer – $NbSe_2$ nanocomposites.

Composite	d /nm	Thermal stability in N_2 /°C	Conductivity /S cm^{-1}	T_c /K
$(PVPr)_{0.14}NbS_2$	2.40	310	140	7.1
$(PEO)_{0.94}NbS_2$	1.96	224	250	6.5
$(PEG)_{0.80}NbS_2$	1.88	233	240	7.0

In the case of delamination, the insertion of a polymer can occur according to the 'host – guest' mechanism. Then intercalated systems are deposited by removing the solvent or by increasing the concentration of the electrolyte. Direct intercalation of polyalanine into the interlayer space of MoS_2 ($d = 1.037$ nm) through formation of colloidal suspensions has been described.[351]

The polypyrrole – MoS_2 nanocomposite, which is a product of oxidative polymerisation *in situ* under kinetically restricted conditions, is a *p*-type conductor. Its electronic conductivity is three orders of magnitude higher than that of the initial MoS_2 compound.[449] Intercalation of PEO into a delaminated suspension of TiS_2 or MoS_2 was carried out.[450] In aqueous solutions, nanocomposites of linear polyethyleneimine in layers of MoS_2, $MoSe_2$, TiS_2 or MPS_3 (M = Mn or Cd)[451] as well as composites of polyethyleneimine or poly(styrene 4-sulfonate) in TiO_2 – PbS layers possessing semiconducting properties were prepared.[452]

Nanocrystals of semiconductors based on metal chalcogenides immobilised into polymeric matrices exhibit luminescent properties. This is primarily true for nanocrystals of CdSe,[453, 454] CdS – Ag,[455] ZnS and ZnS – CuS.[456, 457] Composites based on ZnS – CuS, which contain crystals with dimensions ~ 2 nm in a polymeric matrix, were prepared by copolymerisation of acrylates of the corresponding metals with styrene followed by treatment of the solution of the resulting copolymer with hydrogen sulfide in chloroform.[458] These composites possess good photo- and electroluminescent properties. It should be noted that a precipitate did not form from the resulting almost colourless organosol even after one year.

Metal chalcogenides with more complex layered structures, for example, $PbNb_2S_5$ and $SmNb_2S_4$, can also be decomposed and subjected to intercalation.[459] In polar solvents, one-dimensional 'host' phases form colloidal systems with MMo_3Se_3 (M = Li, Na or In). These systems contain monodisperse negatively charged condensed cluster chains $(Mo_3Se_3^-)_n$. The structures of these systems (which are also called pseudo-one-dimensional metals) have been described in sufficient detail.[460] They are of interest in the design of materials with nanowire (or molecular-wire) morphology. For this purpose, block radical polymerisation of dilute (10^{-3}–10^{-4} mol litre^{-1}) solutions of these 'rigid rods' in a solvating monomer (vinylene carbonate) is performed in the presence of a cross-linking agent.[461, 462] The system rapidly solidifies, and the polymeric matrix provides capture, association

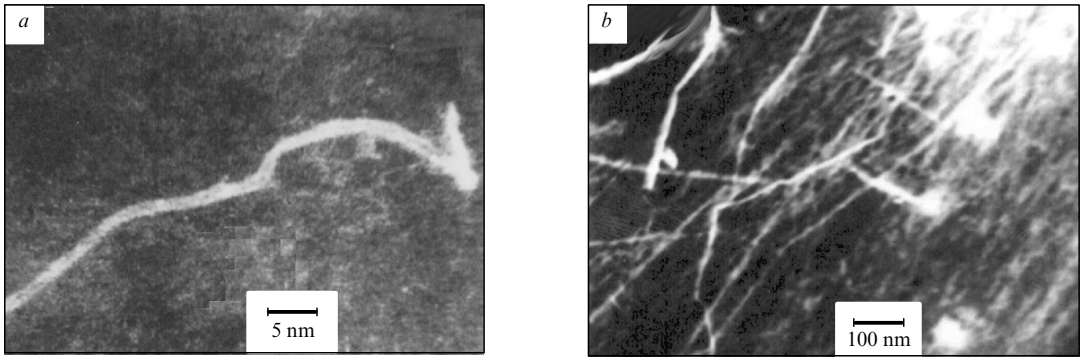


Figure 12. Electron microphotograph of a 'nanowire' (*a*) and 'nanocable' (*b*).

and isolation of the inorganic phase. The nancomposite contains individual isotropic nanowires 0.6–2 nm in diameter and 5–10 nm in length. Polymerisation of more concentrated solutions (10^{-2} mol litre^{-1}) affords nanocomposites as oriented multiwires ('nanocables') 2–4 nm in diameter and $\sim$ 500–1500 nm in length. Each 'nanocable' contains 5–20 'nanowires' (Fig. 12 *a*, *b*). The molecular weight of the inorganic chain (wire) is estimated at $\sim 10^5$. The conductivity is 10^2–10^3 S cm^{-1}, *i.e.*, it is approximately equal to the conductivity of the $(LiMo_3Se_3)_n$ film.

Therefore, intercalation of polymers into the interlayer space of chalcogenides is an extensively and fruitfully developing field of the technology for the preparation of nanocomposites, although many problems, particularly, those associated with the mechanism of insertion and 'guest–host' interactions are still not completely understood. In conclusion, let us give several more examples of these nanocomposites. Polymeric films based on nanosized particles (10–16 nm) of chalcogenides ZnS,[463] as well as of $Cu_2S-CdS-ZnS$ and different polymers, CdS [464] and β-cyclodextrin were described. The inner diameter of the cavity of the latter is 1.53 nm,[465] which is substantially smaller than the sizes of the nanosized particles. Nevertheless, monodisperse complex structures with the participation of β-cyclodextrin are formed. It was suggested [464] that these structures are formed as a result of binding of monodisperse complexes with excess sulfide anions and cadmium cations to form CdS–β-cyclodextrin–S^{2-} aggregates.

VII. Metallopolymeric Langmuir–Blodgett films — self-organised hybrid nanocomposites

Metal-containing nanoparticles inserted into Langmuir–Blodgett films (LBF) belong to yet another promising class of materials for the preparation of nanocomposites. Procedures for the synthesis of self-organised inorganic component–surfactant composites, which have been developed in recent years, made it possible to prepare new two-dimensional composite materials.[58, 466, 467] Generally, the sizes of the elements of these materials are no more than 2–10 nm.

Polymolecular LBF are used for the preparation of highly oriented ultrathin films possessing the special properties, which are determined by their supramolecular structures. Different sensor groups or their precursors possessing nonlinear optical properties can be inserted into these self-organised layers (in some cases, metal complexes, clusters or nanosized particles are inserted). Finally, LBF are used for modelling surface and biological processes (see, for example, Ref. 468). Supramolecular ensembles with mesosized periodicity (intermediates between materials of atomic and macroscopic sizes) are subjects of supramolecular chemistry, *viz.*, constructional chemistry of intermolecular bonds.

Although this line of investigation is still in a primitive state of progress, its methodology has already been developed. The technique for the preparation of Langmuir–Blodgett films was modified, when applied to this methodology. Heterogeneous polar nanolayers are prepared on the surface of a subphase (deionised water) at a given constant surface pressure π, which has the dimensionality mN m^{-1}. The pressure is measured using a Wilhelmy balance in a specially designed apparatus with two-section baths controlled by microprocessor electronic units and a computer with the use of the constant automated monitoring of the technological process.[469] Successive transfer (by methods of Langmuir–Blodgett's vertical lift or Langmuir–Scheffer's horizontal lift) of these layers in the liquid-crystalline state to a solid support allows one to design sufficiently complex molecular planar structures possessing different properties. Metal particles in LBF can exist as a 'two-dimensional gas' (if their concentration on the surface is small and they do not interact with each other). Three-dimensional states, *viz.*, the 'gaseous' (the distance between the molecules is substantially larger that their sizes), 'liquid' (the distance between the molecules is comparable with their sizes), 'liquid-crystalline' (the lability of the molecule in the plane of the monolayer is retained) and 'solid' states, are formed as the two-dimensional gas is compressed.

Two procedures for the formation of nanosized particles in these films are distinguished. The first of them is based on a combination of the principles of colloid chemistry and self-organisation and growth of monolayers.[470–472] In this case, the formation of nanosized particles (for example, by chemical and photochemical reduction of aqueous solutions of metal salts) is performed in the presence of stabilisation agents and components forming LBF. The resulting layers act as specific templates.[472–474] This approach is also of interest as regards studies of biomimetic processes of mineralisation, including studies with the use of the sol-gel method considered above.

The second procedure consists in deposition of LBF on the surface of stabilised nanosized particles and insertion of these particles into polylayers (with the participation of functional groups), including layers of an inorganic nature. For example, LBF based on amphiphilic Ru^{2+} complexes was immobilised on a monolayer of hectorite.[475] In this case, lamellar films and polylayers were formed. Langmuir–Blodgett films with a specified organisation either were formed directly on the surface of colloidal particles or were formed on the water surface and then were transferred to a support of nanosized particles with the use of the Langmuir–Blodgett technique.[476–479] Thus a gold hydrosol stabilised with 4-carboxythiophene was immobilised on a monolayer of octadecylamine by the electrostatic method.[480] The charge on the film was controlled by changing pH. Multilayer films with different densities of the Au–octadecylamine clusters with dimensions 10 ± 3 nm can be prepared according to this procedure; the films contain from 2 to 20 monolayers (the surface pressure in the monolayer is 25 mN m^{-1} and the film area (A) is 0.37 nm^2 molecule^{-1}). Apparently, the method of immobilisation of nanosized particles on LBF has a number of advantages over the chemical insertion of metal ions into LBF followed by assembly of clusters, *viz.*, the deformation of films is excluded, ordering of the lamellar phase is not disrupted and various nanosized particles, including bi- and polymetallic particles, can be used by choosing appropriate hydrosol mixtures. When particles are immobilised on LBF, not only adsorption or chemical interactions occur, but also a higher recognition level is achieved. Examples are provided by self-organisation of monolayers of alkylsiloxanes, fatty acids, dialkyl sulfides or thiols on surfaces of Al, Au, SiO_2, *etc.*[481, 482] Thus two processes occur on the mosaic $Au-Al_2O_3$ surface, *viz.*, recognition of the 'own' support (selective adsorption) and self-organisation of diphilic thiol (on Au regions of the support) and acid (on Al_2O_3 of the support).

However, the majority of studies were devoted to self-organised hybrid nanocomposites based on mononuclear complexes (in particular, on CdS), procedures for the assembly of nanosized particles from these complexes, investigations of the quantum dimensional effects typical of semiconducting nanoparticles, and practical applications of these nanocomposites.[483, 484] It was demonstrated that a dispersion of CdS particles (2.65–3.4 nm) stabilised with dodecylbenzenesulfonic acid in $CHCl_3$ spreads over a water surface to form stable monolayers of nanosized particles.[485, 486] According to the $\pi-A$ compression isotherms, an increase in the π value leads to the transition from the 'gaseous' state to a close-packed monolayer of particles and, finally, to a polylayer. The resulting LBF are characterised by $A = 0.65$–1.1 nm^2 particle^{-1}, which is close to the corresponding values for the hexagonally packed rigid spheres (0.608–0.887 nm^2 particle^{-1}). The transfer of these monolayers to a solid support by the Langmuir–Blodgett method produces polylayers of dimensionally quantised CdS clusters. Their optical density increases linearly as the number of monolayers transferred increases.

The formation of nanosized semiconducting particles in LBF *in situ* by the reactions of metal ions with H_2S or Na_2S has been

described (see, for example, Refs 487–489). For example, sulfiding of layers of cadmium, zinc or lead behenates $(C_{21}H_{43}COO)_2M$ afforded films 100 nm thick (34 layers) containing sulfides of these metals.[490,491] The films are anisotropic and the resulting nonspherical nanosized particles (the diameter is 5–10 nm) form the so-called cluster layers possessing pores (the thickness of the layer composed of the clusters is 1.12 nm). The formation of CdSe nanoparticles upon treatment of films of cadmium arachidate $(C_{19}H_{31}COO)_2Cd$ with a H_2Se vapour occurs in the interlamellar space of films in the solid phase and is accompanied by their substantial deformation and even by disruption of the lamellar structure.[492]

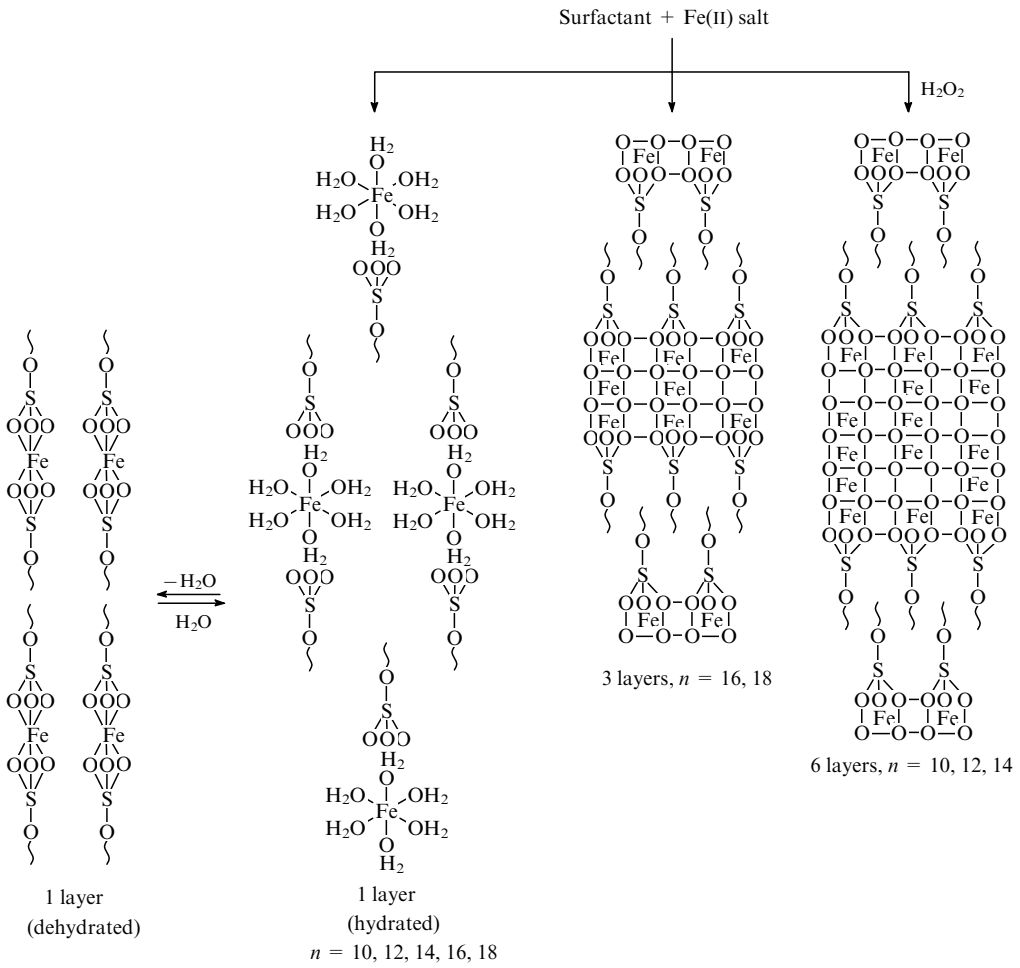
Multilayer LBF are rather often prepared from cadmium stearate,[493] magnesium stearate [494] and α-Fe_2O_3.[495] It was found that self-organised structures were formed in hydrophobic layers of stearic acid as films of silver stearate (8–14 layers). The film was transferred to electrodes (π = 25 mN m^{-1}) and was electrochemically reduced in a neutral or acidic solution to form two-dimensional Ag clusters (the diameter was 20–30 nm).[496] It was found that these films also contained Ag clusters of the sandwich type. Self-organised metal-containing LBF ensembles are rather often used for the modification of the electrochemical properties of electrode surfaces on the molecular level.[497,498] These ensembles are exemplified by self-assembling LBF based on the $C_8H_{17}C_6H_4N{=}NC_6H_4O{-}(CH_2)_3COOH$ and $X(CH_2)_2SH$ (X = OH, COOH) compounds linked though a hydrogen bond and deposited on Au. These systems are electrochemically stable and their behaviour is predictable and reproducible.

One of the promising approaches of electrochemical synthesis involves the formation of two-dimensional (Langmuir) monolayers of nanosized particles under monolayer matrices of surfactants, which are present on the surface of an electrolytic solution, in the course of kinetically controlled electroreduction with the use of an electrochemical circulating cell.[499,500] Two-dimensional aggregates of silver particles are formed only when a monolayer of a surfactant carries a negative charge. Of special note is the possibility of the use of the LBF technique, which involves controlled precipitation and hydrolysis of iron salts in surfactant layers,[501] for the preparation of nanomaterials of a new type. The thickness of the layer is determined by the concentrations of Fe^{2+} and Fe^{3+} salts as well as of their oxides in aqueous solutions and by the redox $Fe^{2+} \leftrightarrows Fe^{3+}$ equilibrium (oxidation by H_2O_2). The properties of self-assembling iron–surfactant nanocomposites (n is a number of carbon atoms in the surfactant molecule) containing 1, 2, 3 or 6 layers of iron oxide depend on their sizes. These composites exhibit the superferromagnetism and occupy the first step in the hierarchy of nanocomposite magnetic materials (Scheme 4).

Magnetic LBF can be prepared based on heterobimetallic oxo complexes, for example, $Cr^{3+}-Fe^{2+}-Cr^{3+}$,[502] or using sulfiding of bimetallic Pb–Cd or Zn–Cd stearates.[503]

Classical LBF can be prepared with the use of not only low-molecular-weight but also polymeric systems. In this case, with the aim of imparting the hydrophobicity to the chain, thus providing the formation of monolayers, the chain is functionalised either using polymer-analogous conversions or by grafting side chains, which can respond to the external factors. As in the case of the preparation of nanocomposites of other types, polymerisation of functional monomers and their copolymerisation with monomers, which serve as spacer units, are also used. In principle, diphilic LBF based on polymers have advantages over polymolecular films based on low-molecular-weight compounds, if for no other reason than their higher stability. These materials support the required density of a monolayer upon formation of a film (an

Scheme 4



n is a number of carbon atoms in a surfactant.

equilibrium pressure of spreading of monolayers is a more rigorous criterion for their thermodynamical stability). To solve some applied problems, it is necessary to introduce functional groups of different types into LBF monolayers. For example, components of a redox pair can serve as such functional groups. However, serious limitations emerge when employing low-molecular-weight reagents because diphilic compounds are not mixed at the molecular level and phase separation occurs. The use of polymers allows one to solve this problem rather readily. The effect of the composition and the structure of polymers and copolymers as well as of the external conditions on the formation and properties of organised polymeric monolayers and LBF on surfaces of liquids and solids were analysed in detail in a review. [503] The formation of LBF was performed with the use of polymeric metal complexes based on porphyrins and phthalocyanines.[504, 505] For example, the diphilic properties can be imparted to polymers by copolymerisation of long-chain α-alkenes with maleic acid, maleic anhydride and other compounds [506] because the carboxyl group is a convenient fragment for binding a metal complex. When reagents, such as 4-aminomethylpyridine, are used for the opening of the anhydride ring, groups capable of providing donor–acceptor bonding of metals possessing coordination vacancies are formed in the polymer. This procedure was used for binding tris(phenanthrolino)iron(II) sulfate or bis(salicylidenoaminopropyl)aminocobalt(II) to diphilic copolymers, *viz*., to copolymers of maleic acid–pyridinemonoamide with octadecene or maleic acid–picolinemonoamide with *N*,*N*-dioctadecylacrylamide. [507] The dependence of the surface tension π on the area of the monolayer per molecule (A) at the air–water interface is shown in Fig. 13. The type of isotherm for the film formation is determined by the concentration of a metal complex because its dimensions are substantially larger compared to the area of monomeric units (it is assumed that a cubic complex molecule is located nearly parallel to the water surface). At concentrations of the complex higher than 10^{-7} mol litre^{-1}, this fact is of considerable importance in the organisation of a monolayer. After compression (π = 25 mN m^{-1}), a stable homogeneous monolayer is formed. However, the stability is lost at concentrations of $\sim 10^{-4}$ mol litre^{-1}.

An important point is that one monolayer as a component of a multilayer system can contain metal complexes of two different types. Their bonding by two functional groups possessing opposite properties prevents phase separation.

Recently, the preparation of mono- and polylayer LBF based on a copolyimide the chain of which contains carbazole groups (as an electron donor) and copper phthalocyanine has been reported.[508] The stack molecular organisation of the layers and small intermolecular distances in these LBF ensure the high lability of the charge and impart the good photoconducting properties to LBF.[509]

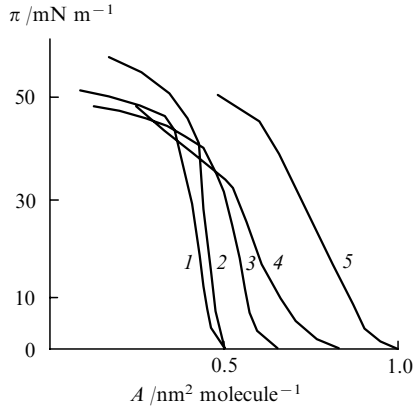


Figure 13. Isotherm of the film formation of maleic acid–pyridinemonoamide–octadecene copolymers on different subphases: (*1*) an aqueous solution of an alkali with pH 10, (*2*–*5*) solutions of [bis(salicylideneaminopropyl)amine]cobalt(II) with the concentration/mol litre^{-1}: (*2*) 10^{-7}, (*3*) 10^{-6}, (*4*) 10^{-5} and (*5*) 10^{-4}.

Regular ensembles of nanocomposites organised in LBF miltilayers are also constructed through electrostatic interactions between charged sol nanoparticles dispersed in a subphase and charged monolayers of the surface (for example, between anionic nanoparticles and a cationic polyelectrolyte).[408] This procedure was used for the synthesis of regular nanowire Tl_2O_3–PVC–arachidic acid composites (PVC is polyvinylcarbazole) based on cross-linked polycationic PVC, which was prepared by electrochemical polymerisation of *N*-vinylcarbazole in the presence of $NaClO_4$, and a sol of thallium oxide (*n*-type semiconductor).[510] The resulting polymeric layer (2.7 nm) serves as a peculiar template coated with regularly organised Tl_2O_3 particles (3.2 nm). The resulting 5.5 nm thick monolayers can be transferred layer-by-layer to the hydrophobic surface (π = 25 mN m^{-1}). Evidently, this method will gain wide acceptance because electrochemical polymerisation allows one to produce a large number of positively charged conducting polymers, for example, polyaniline, polypyrrole, polythiophene, *etc*.[511]

Apparently, this mechanism is also realised in the formation of self-organised layers of TiO_2 on SO_2-functionalised polymer surfaces [512] as well as in the preparation of ordered TiO_2 layers on poly(sodium 4-styrenesulfonate) (PSS). TiO_2 particles ($\sim$ 3 nm), which were prepared by acid hydrolysis of $TiCl_4$, formed organised layered structures on surfaces of polymers of the cationic type, *viz*., on superthin ($\sim$1 nm) PSS or PDAMAC.[513] Optically transparent LBF organised on the molecular level and containing up to 120 layers (60 bilayers) were formed on surfaces of various substrates, *viz*., metal, silicon or a polymer cleaned with a 5% *N*-2-(2-aminoethyl)-3-aminopropyltrimethoxysilane solution. The thickness of the bilayer was estimated at 3.6 nm. It is expected that this procedure will allow one to realise various combinations of materials with semiconducting metal–dielectric structures containing nanosized units of the *p-n-*, *p-n-p-*, *n-p-n-*, *etc*. types. Recently, polylayer (2–12 layers) films of hybrid nanocomposites with the N$\rightarrow$Cd coordination bond have been prepared by the reaction of poly(4-vinylpyridine) (P4VP) with nanosized particles of cadmium sulfide.[514]

Nanocomposites of yet another type, *viz*., clusters in a Langmuir monolayer, are of interest for the design of metal-film materials used in the electronics as well as for the modelling of structures of fixed catalysts. For example, the reaction of $Os_3(CO)_{11}(NCCH_3)$ with self-organised layers of (3-mercaptopropyl)trimethoxysilane on a gold surface resulted in the disruption of the well-organised thiol surface to form cluster aggregates (the diameter was 1.0–2.2 nm).[515] Layer-by-layer adsorption of one- and two-dimensional complexes of the $[Cd_4L_4]^{8+}$ type, which are characterised by the octahedral coordination, on monomolecular poly(ethyleneimine hydrocloride) and polystyrenesulfonate films on silicon can be considered to be an efficient method for the preparation of new metal-containing supramolecular thin films.[516]

Particular attention is given to metal clusters in LBF deposited on the surface of highly oriented pyrolytic graphite (HOPG). Their application allows one to solve many catalytic problems as well as to prepare stable reproducible tunnel nanostructures. The $Rh_4(CO)_{12}$ and $(NEt_4)_2[Pt_{12}(CO)_{24}]^{2+}$ clusters sorbed on HOPG from solutions of organic solvents were studied by scanning tunnel microscopy.[517] Under laser irradiation, these clusters underwent decarbonylation and transformation to highly dispersed Pt crystallites of dimensions 1.8×0.5 nm bound to the graphite surface.[518] The procedure for the deposition of isolated 'naked' silver clusters on the HOPG surface with the topography characterised by planar dimensions of 3–5 nm and the height of 2–3 nm and the technique for the 'assembly' of their ligand shell from PPh_3 were developed.[519] The voltammetric characteristics of individual clusters on the surface of freshly cleaved HOPG were measured. The insertion of the clusters into monolayers of stearic

acid and their transfer to the HOPG surface also afforded cluster-containing LBF.[520] In the resulting monolayer, the cluster molecules form an ordered two-dimensional lattice. By this means the problem of fixing of clusters on the surface was solved and the reproducible one-electron mode of tunneling was realised at room temperature. The regularities of the insertion of cluster molecules (Pd_3, Pt_5 and Pd_{10}) into LBF and their voltammetric characteristics were analysed in the study.[521] A multilayer LBF was transferred from magnesium stearate (from a monolayer of stearic acid to the surface of aqueous solutions of $MgCl_2$) to the HOPG surface in the disrupted state; the surface per molecule is 0.15 nm^2, $\pi = 36$ mN m^{-1} (see Ref. 494).

The above-considered examples demonstrate that metal-containing Langmuir–Blodgett films, including those based on nanosized particles and clusters, are of considerable interest for the preparation of hybrid organised nanocomposites.

VIII. Major fields of application of hybrid nanocomposites

When considering synthetic problems, we have already drawn attention to the properties of the resulting nanocomposites and to the possibilities of their practical application. Undoubtedly, these problems merit detailed consideration. In the present review, only the major problems are briefly analysed.

Hybrid nanocomposites are primarily used for the preparation of plastic materials possessing semiconducting and superconducting properties. Among them are nanowires on polymeric matrices, films with special properties,[309] and different-purpose ceramics, including membranes, luminophors, antireflection and reflecting coatings on optical units, carriers and catalysts, reinforcing agents for plastics and rubbers, binders, adsorbents for pharmaceutic and cosmetic industry, *etc*.[116, 522–527] The recent review [278] devoted to the use of materials prepared by the sol-gel method in electrochemistry includes more than 300 references. Optical waveguides were constructed based on hybrid polymer-inorganic nanomaterials, which were prepared by the same procedure and possess improved thermal and mechanical properties compared to the starting polymers.[164, 528, 529]

Nanoparticles, for example SiO_2, TiO_2, CdS, $CaCO_3$ and $BaSO_4$, including those formed by the sol-gel method, are used as specific fillers, because the properties of materials are noticeably improved at a substantially lower concentration in a matrix than those prepared with the use of standard fillers. Thus when fillers are inserted into composites by mechanical dispersion using mixing equipment (the size particles is ~ 1 μm), it is necessary that up to 40 mass % – 50 mass % of the filler should be taken for 100 mass % of polyisopropylene to attain the required reinforcing effect, whereas the same effect is achieved by the insertion of only 0.6 mass % – 0.8 mass % of a filler *in situ*.[530] Highly filled (up to 75%) composite materials based on nanosized particles of the high-T_c superconductor $Tl_2Ba_2Ca_2Cu_3O_y$ ($T_c = 125$ K) and polychlorotrifluoroethylene possess improved physicomechanical and thermal characteristics and stability to atmospheric moisture.[531] These materials can be used for the design of cryoelectronic instruments, levitation equipment and magnetic screens.

Recently, efforts have been made to describe the viscoelastic properties of a composite taking into account the specificity of interactions between segments of the macromolecules and the active centres of the nanoparticles. The Kerner equation, which relates the elastic modulus of a composite upon simple extension to the portion φ of the inorganic phase, was modified [532] when applied to systems with strong interactions between nanoparticles and a polymer. Based on scaling theory, the equilibrium mechanical properties of a complex of colloidal particles and macromolecules some segments of which are adsorbed on active centres on the surface of particles (which are 'polynodes' of a network of the nanocomposite) were described.[533] Under deformation and changes of the temperature, some segments leave the surface and the fragment of the macromolecular chain linking the surfaces of two particles is increased by the same number of the segments. If this fact is taken into account, two nontrivial conclusions can be made: (1) the elastic properties of the composite are not only determined by the volume fraction of filling but are also inversely proportional to the linear size of the particles; (2) the shift modulus of the nanocomposite, unlike the shift modulus of nonfilled polymeric networks, does not approach zero as the temperature is extrapolated to zero. These conclusions agree well with the results of studies of the relaxation mechanical properties of the composite as well as the dependence of its viscosity on the molecular and structural parameters, such as the energy of interaction between the segment of the macromolecule and the active centre of the nanoparticle, the number of segments of the macromolecule, their size, the φ value, the particle size (the diameter is $\leqslant 30$ nm) and the temperature.[533]

Let us briefly consider the conducting properties of hybrid nanocomposites. These properties are manifested only with particular inorganic component : polymer ratios when current-conducting channels of fractal metal-containing clusters are formed in a polymeric matrix for one reason or other. The highest conductivity is achieved when the composite is converted into a network of interrelated current-conducting chains, *i.e*., it has a percolation structure (see, for example, Ref. 534). To put it differently, critical concentrations of the filler φ_{cr} (the percolation threshold) exist above which ($\varphi > \varphi_{cr}$) the conductivity sharply increases.

With a knowledge of the percolation threshold, the minimum necessary filling of conducting composites can be predicted. For example, φ_{cr} for epoxysilicon resin filled with spherical particles of dispersed nickel is 0.25 and the critical parameter (X_{cr}) determined by the number of bonds at conducting nodes in the lattice of the solid is 0.30.[535]

The conductivity of metallopolymeric nanocomposites is substantially affected by the dispersity of an inorganic component. Different nanocomposites are characterised by different relationships between the conductivity and the metal content. The percolation threshold of composites based on layered poly-pyromellitimide films containing inserted silver particles is attained when the filler content is > 9 mass %. At the same time, when silver nanosized particles (10–15 nm), which are prepared in the course of thermolysis of a prepolymer [a solution of silver acetate in poly(pyromellitamide acid)], are uniformly distributed over a film, the composite does not take on the conducting properties at the same filler content. The dielectric characteristics of films ($\sigma = 10^{-15}$–10^{-12} S m^{-1}) are retained at a high level, which is in many respects associated with the presence of a substantial fraction of dielectric polymeric interlayers between conducting particles of the filler.

It is possible to enhance the conductivity of polymeric composites as a result of the formation of a filler as 'nucleus' (conductor or dielectric)–'shell' (conductor) constructions. This is of practical interest primarily in the technology of the production of glues and varnishes. For example, the conductivity of dielectric SnO_2 particles coated with a silver layer (8 vol. %) using thermal treatment of a precursor, *viz*., an Ag(I)-containing polymer, is substantially increased ($\sigma = 1 \times 10^{-3}$ S m^{-1}), whereas $\sigma = 2 \times 10^{-7}$ S m^{-1} for a mechanical mixture of SnO_2 and Ag powders (16 vol. %).[536]

Particular attention has been given to multicomponent metal-containing hybrid nanocomposites, which find use in the production of electrode materials for galvanic cells,[537] high-T_c superconducting ceramics, *etc*. Materials prepared by the sol-gel method are used as piezoelectric ceramic fillers in acoustic converters as well as in the medical diagnostics. Thus coatings with dense homogeneous microstructures possessing the enhanced mechanical strength and improved piezoelectric characteristics were formed by sheet rolling (413 K, 20–30 MPa) of polymer–ceramic mixtures of polyvinylidene fluoride with $PbTiO_3$ (up to 65 vol. %).[538]

The preparation of modifying thin (3–7 nm) magnetic coatings by electrochemical methods has considerable promise. In particular, organosilanes are coated with a film containing α-Fe (70 at. % of Fe), magnetite Fe_3O_4 and an admixture of Fe_2O_3.[539]

Sometimes magnetically active particles are introduced into different gels, *viz*., into silicon,[540] polyacrylamide,[541] poly(ethylene oxide)[542] *etc*. gels.[543]

To improve the electrophysical and magnetic characteristics of nanocomposites, ferroplastics are often formed in magnetic fields. In this case, magnetic orientation occurs. Thus neodymium ferrite is prepared in fields with the intensity of 3×10^{-4}–3×10^{-3} T and then it is subjected to the mechanochemical action (pressing,[541] treatment between Bridgman's anvils[543] or a combination of these procedures[544]). This makes it possible to produce magnetically filled matrices with oriented chain structures, which are used in the techniques for the production of varnishes and films and are of considerable interest as elements of systems for data recording. The formation of coatings under conditions of hardening in a variable magnetic field makes it possible to prevent precipitation of nanoparticles, which are either concentrated closer to the film surface or uniformly distributed throughout the body of the film. These materials are used as drug carriers as well as for the magnetic recording of data, magnetoseparation and the preparation of composites possessing the magneto-optical properties and magnetic liquids (for example, oligoorganosiloxanes). Organometallic ferromagnetics based on polymetalloorganosiloxanes possess peculiar magnetic properties.[545, 546]

Hybrid polymer-inorganic nanocomposites are characterised by a unique combination of the optical and semiconducting properties associated with the sensitivity of plasmon vibrations (the frequency, the intensity, the shape and the width of the band) not only to the nature of the matrix and the morphology of the nanocomposite but also to the particle size. The character of interactions between the electronic and atomic subsystems changes substantially as the linear sizes of semiconductor particles decrease to values comparable with the electron wavelengths, which is manifested in the quantum dimensional effects, *viz*., in nonlinear optical effects, doubling of the frequency of the incident radiation (generation of the second harmonic), the 'blue shift' of the exciton absorption band, *etc*. The ability of these nanocomposites to form films and the ease of their treatment make it possible to use them for the preparation of dispersing optical elements, band-pass light filters and other high-quality thin-filmed coatings (only ~ 5–20 nm thick), which are used in the optoelectronics. For example, the production of modern integrated circuits is based on the so-called planar technology combining processes of the nanolithography (the formation of nanosized surface figures as lines and dots) and the etching. With the aim of decreasing the sizes of elements of optoelectronic integrated circuits to < 100 nm, new techniques of the lithography (in particular, electron-ray, ion-beam and X-ray) as well as new procedures for the dry etching (plasma-chemical, reactive ionic, *etc*.) are used.

Almost all materials of this kind are characterised by a nonlinearity of the optical properties manifested in a substantial strengthening of the local field of the light wave. The latter is quantitatively characterised by the third-order susceptibility, the nonlinear indices of refraction and the nonlinear absorption coefficient. These effects are widely used in spectroscopic practice (local nonperturbing methods of diagnostics, electron-optical image converters, *etc*.). This is particularly true of sol-gel glasses based on CdS, nanohybrid composites based on polymers and SiO_2 (or V_2O_5), Langmuir–Blodgett films, *etc*.[547] If the sizes of semiconducting nanosized particles in matrices are much smaller than the wavelength of the exciting field ($\ll\lambda/20$), the nonlinear optical properties manifest themselves in the fact that 'quantum points' appear in nanocomposites (quantum-point polymers).[548–550] There is a definite relationship between the wavelength of the exciting radiation and the sizes of nanoparticles. Nanocomposites of this type can be used as active layers of light-emitting diodes.[551]

In the previous sections, procedures for the insertion of transition metal ions into polymers in the stage of the sol-gel synthesis or intercalation have already been mentioned. The materials thus obtained serve, for example, for the preparation of coloured light guides, which have a broad spectrum of applications, *viz*., from storage elements to highly sensitive detectors.

Let us consider the use of hybrid nanocomposites in catalytic, most often hydrogenation, processes. Under conditions of formation of catalysts and hydrogen adsorption, dislocations are fixed at interblock boundaries of polymer-stabilised nanoparticles. These particles have highly active surfaces and developed internal structures. A polymeric matrix hinders smoothing of numerous defects upon catalyst ageing. Of prime importance in the catalysis is a knowledge of the surface composition and S_{spec} and the possibility to control these parameters. The inherent size of nanosized particles is comparable with the molecular sizes of the compound subjected to catalytic conversion. This fact is responsible for the characteristic features of the kinetics and the mechanism of the reactions with the participation of nanosized particles. In particular, the high efficiency of colloid-metallic catalysts in multiple-electron processes results from the fact that these catalysts are 'reservoirs,' which can readily incorporate electrons.

Polymer-stabilised metal nanoparticles are primarily of theoretical interest as excellent models for studying the influence of the dimensional effects on the catalytic activity. Using these particles as examples, many concepts of the fundamental theories of catalysis can be verified. In addition, since nanocomposites are involved both in homogeneous and heterogeneous catalytic processes, they provide an additional possibility of revealing the relationships between homogeneous, heterogeneous and enzyme catalysis.[552] In a number of characteristics, these nanocomposites are similar to homogeneous catalysts although they also inherit the principal features of heterogeneous contacts. Thus huge Pd_{561} clusters can be considered as a bridge between homogeneous and heterogeneous catalysts.[553] Composites based on nanosized particles of platinum and other metals, which are incorporated into glassy carbon matrices, can be assigned to the same type of catalysts.[554] Of particular interest are catalysts based on organic–inorganic hybrid materials in which catalytically active metals incorporated into an oxide network are dispersed. For example, highly dispersed heterogeneous catalysts in a SiO_2 network prepared from substituted alkoxysilanes are known (see the review[555]).

$$MY_n + nAXSi(OR)_3 + xSi(OR)_4 \xrightarrow[-ROH]{NH_3,\ H_2O} Y_m(AXSi_{3/2})_n\cdot xSiO_2 \xrightarrow{O_2,\ \Delta} MO_y\cdot(x+n)SiO_2 \xrightarrow{H_2,\ \Delta} M\cdot(x+n)SiO_2$$

Protective polymeric coating prevents poisoning of a metallopolymeric catalyst by potential catalytic poisons of the dibenzothiophene type.

Nanocomposites exhibit the high catalytic activity in elimination of hydrogen under the action of visible light[556] [for example, the ethylenediaminetetraacetate (electron donor)–Ru^{2+}(bipy)$_3$ (photocatalyst)–methyl viologen (electron acceptor) system]. Substantial success has been achieved in charge separation as well as in the design of efficient photocatalysts with the use of semiconducting nanomaterials (primarily, based on TiO_2) prepared by the sol-gel method (see the reviews[557, 558]). The additional introduction of transition metal ions (for example, of copper[559, 560]) in the stage of formation of these materials substantially enhances the efficiency of the photocatalytic reaction. These systems exhibit high activity also in low-temperature oxidation of CO.[561, 562]

The use of polymer-protected nanoparticles can contribute new specific features to catalysis. A platinum sol as well as Pt on Al_2O_3 are the well-known enantioselective catalysts of hydrogenation processes.[563] The potential possibilities of the use of hybrid nanocomposites in catalysis are far from all realised.[564]

IX. Conclusion

To summarise, a great diversity of aspects of the chemistry of nanocomposites is progressing extensively. In the coming years, procedures for the synthesis of multicomponent materials based on ecologically pure solid-state reactions will be developed. Apparently, the use of alcoholates or oxoalcoholates of nontraditional metals, for example,[565] of Ta^{5+} or Nb^{5+}, in sol-gel procedures will have promise. This refers equally to new intercalation systems. Procedures for the preparation of hybrid materials of the 'network-in-network' type will be studied in more detail. The mechanism of their phase separation and the structures of the resulting nanocomposites will be elucidated. These materials will be formed with the use of monomers, which are traditionally used for the preparation of network polymers, including interpenetrating networks. A search for the optimum modes of formation of new types of lattices ('host' and 'guest' components in intercalated nanocomposites) is still in progress and studies of intracrystalline 'host – guest' interactions and their effect on the electronic properties of complex systems are being continued. For this purpose, it is necessary to reveal principal mechanisms of the orientation effect of pores and interlayer formations on the crystallinity and the stereoregularity of the polymer formed, which is one of the fundamental problems of physical chemistry of polymers and composite materials by itself. The approaches to the preparation of organic-inorganic nanocomposites surveyed in this review may be useful in the synthesis of different single-phase crystalline nanometal-ceramic products with complex compositions, for example, the $MgM_2O_4 - \alpha\text{-}Al_2O_3$ systems (M = Al or Cr) (< 10 nm). These products can also be synthesised with the use of Grignard reagents. Theoretical studies of the nature of bonds between metals (Fe, Ni, Cu and Ag) and the surface oxygen anion in cluster models started by Johnson and Pepper [566] will help in the understanding of the structures of these materials. The use of LBF, which incorporate isolated cluster molecules or nanosized particles, in molecular electronics may have considerable promise. Finally, the nanophase materials technology requires the appropriate scientific support, *i.e.*, the construction of new instruments as well as the development of techniques for working with nanosized materials.

The generality of many processes occurring both in the living and nonliving nature can give impetus to studies of nanobiocomposites. In this review, a reasonably fair, though incomplete, picture of applications of nanobiocomposites to studies of organised matter and the preparation of hybrid bioceramic nanomaterials is given.

The statements that the science and engineering will be developed on the nanosized level in the XXI century seem to be realistic because nanometer sizes of individual elements (for example, densities of the arrangement of microelectronic elements on crystal surfaces) are attained in many traditional technologies.

The structure – property relationship is the fundamental problem of modern chemistry and physics of hybrid nanocomposites. A great deal needs to be done before this problem is solved.

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