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Polymer-immobilised nanoscale and cluster metal particles

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Abstract. The essential data on the immobilisation of nanoscale and cluster metal particles in polymeric matrices are considered and systematised for both macroligands and the matrices formed *in situ*. Special attention is paid to the controlled chemical **passivation (stabilisation) of extremely active particles of colloidal size using high-molecular-weight compounds. The routes of formation of polymer-immobilised nanoparticles directly in the polymer medium are analysed. This allows the preparation of compositions characterised not only by the most regular distribution of these particles over the bulk of polymer but also by a strong chemical interaction between the components. Studies in the field of polymer-analogous transformations, which offer a promising approach to the binding of mono- and heterometallic clusters as a new direction in the physicochemistry of nanoparticles, are discussed in detail. The peculiarities of the immobilisation of clusters, polynuclear structures, and nanoparticles by synthetic polymers, on the one hand, and by biopolymers, on the other hand, are considered. The basic fields of the application of the products obtained and the prospects of the development of this direction are outlined. The bibliography includes 394 references.**

I. Introduction

The possibility of combining the physicochemical properties of metals and polymers in a single material and of regulating these properties through concentrational changes has long been under discussion.[1,2] The progress in this direction is stimulated by the ever-growing interest in this problem shown in many fields of chemistry, physics, and materials science. Numerous materials have been already produced, that are unique with regard to their mechanical, electrophysical, magnetic, optical, catalytic, and often biological properties. Two major stages may be differentiated in the development of this direction. At the beginning, major attention has been given to the development of convenient and reproducible techniques for the synthesis of ultrasmall metal particles of nanometre size (with parameters not exceeding 100 nm in at least one dimension), their improvement, and bringing into practical usage. The second stage of studies in this field focused on the development of effective methods for the stabilisation of metal nanoparticles with the help of polymers.

These studies were largely advanced by the development of metal – polymer (metal-filled) composite materials (nearly single-phase, sufficiently homogeneous, and relatively stable systems) possessing specific physicochemical and mechanical properties: increased heat and electric conductivity, high magnetic susceptibility, and the ability to shield from ionising radiation. Specifically, these materials meet the major requirement for protective screens by providing the predetermined degree of decrease in radiation at minimum weight. Metal-polymer composite materials are most widely used in the electronics and radio engineering for producing electroconductive pastes and glues (in particular, printed circuit boards), special coatings (paint and varnish), photo- and X-ray-resistors, X-ray-contrast polymers, rheomagnetic fluids, as well as in instrument building, aviation, and space technology. The spectrum of practical uses of these materials has been much expanded by the discovery of their specific catalytic properties,[3] which display close similarity to those of polymer-immobilised catalysts,[4–5] by their application in chemisorptional and photographic processes (including the production of magnetic developers for xerography and photorecording media) and in the synthesis of antifrictional polymeric coatings, *etc*. Investigation of the interactions in the macroligand – nanoparticle systems may provide additional information on both the principal structural elements of the latter and the peculiarities of the surface of polymers. Finally, it is well known that the nanoparticles of certain metals are endowed with biological activity: they are used as effective drugs in medicine and plant protectors in agriculture.[6] Many polynuclear enzymes are known to contain clusters of metals (*i.e*., essentially ultrafinely dispersed particles) bound to biopolymers.[7,8] Thus, there are certain common characters in the behaviour of metal nanoparticles in synthetic polymers, polymer-immobilised clusters, and metal clusters (polynuclear structures) in biopolymers.

To date, especially over the last 10 – 15 years, a large body of diverse information has been accumulated on basic techniques for the preparation and investigation of the structure and properties of polymer-immobilised nanoparticles; nonetheless, all these data stand in need of adequate systematisation. Some of the relevant

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problems have been considered recently in the example of nanoparticles and clusters of the platinum group metals in polymers.[9]

II. General characterisation, methods of preparation and some properties of the metal nanoparticles

Small *n*-nuclear particles, which are structural elements of ultrafinely dispersed powders, occupy the intermediate position between clusters and massive metals. On transition from a single atom in the zero valence state (M) to a metal particle endowed with all of the compact metal properties, the system passes through a number of intermediate stages,

$$M \xrightarrow[k_1]{M} M_2 \xrightarrow[k_2]{M} M_3 \xrightarrow[k_3]{M} \ldots \xrightarrow[k_{n-1}]{M} M_n, \qquad (1)$$

among which the principal is the formation of clusters and nanoparticles characterised by small sizes of their morphological elements. This is followed by the formation of large stable particles of a new phase. The process of collectivisation of electrons in the core that is formed occurs spontaneously and is in essence similar to the formation of molecules from individual atoms. The attribute 'metallic' reflects solely the composition rather than the nature of these particles, which are regarded as transient species between the bulk metal and its individual atoms. Clusters are figuratively called metal embryos.[10] The extent of dispersion has a crucial influence on their chemical activity, and as a metal particle grows larger its properties change substantially. With regard to their size, such particles may be divided into three following types:[11] nanometric (ultradispersed) (from 1 to 30–50 nm),[12] highly dispersed (from 30–50 to 100–500 nm), and micrometric (from 100–500 to 1000 nm). The latter are as a rule composed of individual particles and their aggregates, being mono- and polycrystals of the fractal type. The particles of the first two types are called colloidal, while those of the third type are known as coarse-dispersion particles. When prepared under normal conditions, the aerosol metal particles with a mean size of $\sim$50 nm have the spherical or a close to spherical shape owing to their high surface energy.[13]

The terms 'ultrasmall particles', 'nanocrystals' (for designating the metal nanoparticles whose size ranges from 2–5 to 50 nm),[14, 15] and 'colloidal crystallites'[6] are also frequently used. The requirements for the size of nanocrystals of semiconductors in polymeric matrices boil down to the following:[17] the upper limit of their size should allow the optical homogeneity of a composite material (light is not scattered by the media composed of particles with the size below 1/4 of the light wavelength), whereas the lower limit is determined by the very fact of the existence of crystalline particles (the boundary of transition from the crystalline to the quasi-molecular phase). The notions of 'molecular aggregation' and 'crystalline clusters' are used less frequently.[18]

Naturally, a process occurring according to the Eqn (1) is not reduced to a trivial mechanical build-up of metal atoms involved in the formation of *n*-nuclear constructions. It is common practice to differentiate two types of nanoparticles: clusters, *i.e.*, the particles with ordered structures (their size ranging from 1 to 10 nm) composed as a rule of 38–40 (sometimes more) metal atoms, and the nanoparticles proper (disordered structures), having a size of 10–50 nm and including in most cases 10^5–10^6 atoms.

It is known that the cluster formations are characterised by a non-monotonic dependence of their properties (*e.g.*, ionisation potential and bond energy per metal atom, interatomic distances, optical and magnetic properties, electron conductivity, electron–substrate interactions, *etc.*) on the cluster size, *i.e.*, on the number of metal atoms incorporated. It is these criteria that determine the existence of the so-called 'magic numbers': a discrete set of numbers of atoms (N) corresponding to the formation of the energetically most favourable clusters.[19] These numbers equal to 13, 55, 147, 309, 561, 923 ... are calculated by the formula[20]

$$N = \tfrac{1}{3}(10n^3 + 15n^2 + 11n + 3).$$

The structure of small and medium-size homometallic clusters (3, 4, 5, 6, 10, 20, and 38 atoms) has been established by X-ray diffraction analysis.[21] Their metallic framework consists mainly of cycles, carcasses, and polyhedra. On going from clusters to nanoparticles, the non-monotonic character of structures becomes less pronounced. Still, the symmetry in the distribution of acting forces is violated because of the non-compensated character of bonds at atoms localised in the subsurface layers, *i.e.*, having neighbours mostly on one side (they amount a substantial proportion of the total number of atoms in a particle). As regards their properties, these 'ligand-deficient' atoms are to a certain extent similar to the superficial atoms of crystals. The disposition of atoms at the interface, their interaction with neighbours and motions near the crystal facets predetermine disturbance in the translational symmetry, strong anisotropy, a pronounced anharmonic character of oscillations, *etc.*[10, 13, 22–25] This results in the enhanced adsorption potential of such atoms, larger possibilities of ion and atom exchange, contact interactions of structural elements, *etc.* However, there appear difficulties in the interpretation of their behaviour due to the impossibility of distinguishing between the bulk and surface properties of these particles. Furthermore, if the parameters of their structural elements are commensurate at least in one direction with the correlation radius of a definite chemical or physical phenomenon (*e.g.*, with the length of free path of electrons, phonons, the coherence length in a superconductor, the size of a magnetic domain or a nucleus of a new phase, *etc.*) or are less than this radius, such systems or the reactions involving them manifest the so-called dimensional effects.

Thus, the nanoparticles with highly developed interfacial surfaces possess excess energy in comparison with homogeneous materials, and they are often called energy-saturated systems. Their investigation is the subject of a new rapidly expanding branch of science, physicochemistry of nanoparticles (also known as nanochemistry and physics of clusters). Since the progress in this field is closely associated with the development of methods for the synthesis of nanoparticles, we shall briefly dwell on the main of them.

The spectrum of techniques used for the preparation of nanoparticles is rather broad and is based on two major approaches: physical and chemical. The former is largely based on condensation techniques consisting in the 'assembly' of nanoparticles from individual atoms of metals. By way of their gradual assotiation and on reaching a definite size with the appearance of a clear-cut physical interface, these atomic aggregates become nuclei (embryos) of a new phase. The condensation methods include direct evaporation of metals, in particular with the use of Knudsen cells, induction heating, low-temperature condensation technology, spray and electron bombardment, condensation in electric arc discharges and by plasma techniques, explosion of conductors, *etc.* In most cases, these techniques prove to be mutually complementary rather than competitive. Less widespread are the techniques for preparing nanoparticles by dispersion of coarse particles (colloidal mills, shakers, sonication, high-frequency, and electric arc fragmentation, *etc.*).

Of the chemical methods, the most popular is the reduction of metals in solutions in the presence of different stabilisers dating back to the 19th century. Metal aluminium hydrides, borohydrides, amino boranes, hydrazine and its derivatives, hypophosphites, formalin, salts of oxalic and tartaric acids, hydroquinone, dextrin, a number of other compounds (H_2O_2, H_2S, CO, CS_2, NO, $SnCl_2$), and most often hydrogen serve as the reducing agents. The chemical methods also include diverse pyrolysis techniques of moderately stable metal compounds (carbonyls, formates, oxalates, organometallic compounds), various modifications of cryochemical synthesis, and plasmochemical techniques. As a rule,

the common disadvantage of chemical methods is the formation of polydisperse colloids with a wide particle size distribution.

A new direction in the physicochemistry of nanoparticles known as chemistry of 'giant' clusters deserves special mention. The most recent years witnessed the development of techniques for the synthesis of compounds with metal–metal bonds whose nuclearity may be as high as a few hundred units,† *e.g.*, $Pd_{561}Phen_{60}(OAc)_{180}$ or $Pd_{561}Phen_{60}(PF_6)_{60}O_{60}$,[26,27] and even the compounds containing up to 1415 Pd atoms.[10] In fact, these huge clusters are nanoparticles coated with a ligand envelope protecting them from environmental impacts.

The extremal conditions of the synthesis and a large specific surface of the nanoparticles characterised by a small size of morphological elements may induce changes in their physicochemical properties and even lead to the distortion of their atomic structure.[22] Very high (or very low) temperatures, high rates of processes, various external impacts (*e.g.*, rapid condensation, annealing) favour the formation of non-equilibrium 'frozen' states in the growing *n*-nuclear particles.

A highly developed interface surface, excessive energy of superfacial atoms, and decreased activation energies of different reactions determine the extremely high reactivity of nanoparticles. Therefore, the energy-saturated nanoparticles produced under strongly non-equilibrium conditions are highly reactive towards the components of the medium they are formed in.‡ When placed into an inert atmosphere, they usually undergo spontaneous aggregation leading to the eventual formation of powders with normal dispersity. In some instances, the exceptionally high chemical reactivity of nanoparticles is useful, though more frequently it poses a number of problems related to the necessity of their stabilisation for transportation and storage purposes. In this context, the search for effective ways of the controlled chemical passivation of nanoparticles is a topical problem. The solution of this problem is largely facilitated by a high adsorption capacity of these particles towards high-molecular-weight compounds.

III. Basic principles and mechanisms of the stabilisation of nanoscale metal particles by polymers

The interaction between nanoparticles and adsorbed macromolecules is the most important field in the modern science of polymeric colloids studying the regularities of the formation of the dispersion systems with highly developed interfacial surface, their kinetic and aggregative stability, diverse surface phenomena at the interface, and the adsorption of macromolecules on solid surfaces from liquid media.[28] The adhesion between polymers and metals is determined by a number of factors, among which the most essential are the nature of the molecular forces, surface defects, internal strain, and electrical charges. These factors influence the mechanism underlying the polymer–metal interaction.[28–30] They are best described within the framework of the theory of 'molecular solder' (the term used for strong adhesive interactions between components),[31] based on the concept of structural–mechanical factors of the stability of dispersion systems and spatial networks of the coagulation structure type.

A colloidal system is formally composed of a continuous phase, dispersive medium (polymer), containing distributed nanoparticles representing the dispersed phase. A colloidal system is regarded as stable, when the dispersed phase exists in the form of individual isolated particles for a sufficiently long period of time (a few months or even years).§ Sometimes, the sedimentation resistance is estimated from the quantity of pellet formed by centrifugation (*e.g.*, after a 20-min centrifugation of a Pt–polyvinyl acetate (PVA) system at 6000 *g*). The size of colloidal particles in the system Pt–PVA may be controlled by varying *g* and the centrifugation time.[37]

There are two types of polymer-stabilised colloids: lyophobic and lyophilic. In the former, the interaction between the dispersive medium and the dispersed phase is so weak that such colloids prove to be unstable (in the thermodynamic sense) and the attractive forces lead to the aggregation of particles. Nonetheless, the existence of a noticeable repulsive barrier and the remoteness of particles from each other can slow down this process so that the system remains virtually unlimitedly stable (the kinetic stability). Sometimes, these colloids are called thermodynamically metastable. A typical way of achieving the kinetic stability of lyophobic particles is electrostatic stabilisation. On the contrary, the lyophilic systems are thermodynamically stable, *i.e.*, their total free energy of mixing is negative, and the dispersed state may be characterised as a low-energy state. The prime cause of the aggregational resistance of such particles is their solvation.

The aggregation of such systems is called coagulation, when densely packed aggregates are formed, or flocculation, when the particles remain separated from each other by a polymer. The coagulation of nanoparticles on polymeric surfaces is sometimes called heteroadagulation. The non-charged particles coagulate rapidly owing to the dispersional attraction (the London forces). This process is described by the rate constants of fast coagulation according to Smoluchowski: $k_c = 4kT/\eta$, where k is the Boltzmann constant, T is temperature, and η is the dispersive medium viscosity. The constant k_c characterises the long-range attraction between colloidal particles. The van der Waals attraction between individual atoms or molecules extends only over the distance of a few decimal fractions of a nanometre. However, in the systems under discussion, a polynulcear (multicentre) interaction takes place: each atom or molecule of an individual nanoparticle attracts each atom of another particle containing 10^6–10^{10} atoms. The interaction force of the particles in the dispersed phase in coagulation structures is estimated, on the average, as 10^{-10} N per one contact. Summation of a huge number of all possible interatomic interactions between nanoparticles results in a considerable attraction.

The potential attraction energy U_r between two spherical particles with radius r at the minimal distance between their surfaces l_0 may be described by the following simplified equation:

$$U_r \approx \frac{Ar}{12l_o} \text{ at } r \gg l_o,$$

where A is the effective Hamaker constant having the energy dimensions. In its order of magnitude, the constant A is close to kT for latex particles, though in the case of metal dispersions it may also have higher values. For example, for poly(methyl methacrylate) (PMMA), polystyrene (PS), Ag, and Al_2O_3, the values of $10^{20}A$ are 6.3, 6.15, 40.0, and 15.5 J, respectively.[38] Note for comparison that the attraction energy of two latex particles, each being 120 nm in size, is $\sim 10\ kT$ at the distance of 1 nm and $2\ kT$ at 5 nm. In the absence of repulsion between particles, this would be quite sufficient for coagulation, since by its absolute value, the energy of attraction is greater than the thermal energy of particles, equal to $\sim\frac{3}{2}\ kT$ for the three translational degrees of freedom.

† Strictly speaking, such huge clusters are not individual compounds but rather include particles of different size and composition within a narrow distribution range (similar to the molecular mass distribution of polymers). The idealised formulae used to describe them are averaged over a statistical ensemble.

‡ The free energy variation during the dispersion of a homogeneous metal of volume V to particles with radius r is equal to

$$\Delta F(r) = \frac{\sigma V}{r},$$

where σ is the increment of free energy of a system during formation of a unit of new interfacial surface.

§ The theory of stabilisation of colloidal particles by polymers is considered in sufficient detail in Refs 32–36. We discuss here only the problems that are directly relevant to polymer-immobilised nanoparticles.

Hence, it may be assumed that in the systems under consideration the region of van der Waals attraction extends to the distance of 5 nm. The magnitude of London attraction and its action radius are the crucial factors in the choice of ways for the stabilisation of such particles.[32] A long action radius of attractive forces restricts considerably the possibilities of stabilisation. It follows that the stability condition of nanoparticles requires the occurrence of repulsion between particles at the distances at least commensurate with the action radius of attraction. Coagulation takes place at isoelectric points (when the particle charge becomes zero).

In order to stabilise the 'ligand-free' clusters, use is made of matrices of inert gases, low temperatures, and surfactants. The hydrophobic nanoparticles are homogeneously dispersed inside the core of micelles at surfactant concentrations above the critical micelle concentration (CMC). At lower concentrations, the stabilisation is achieved by adsorption of surfactants on the surface of nanoparticles.

The most important are the electrostatic and polymeric methods of stabilisation (also known as charge and steric stabilisation). The latter is brought about by the adsorptional coating of the nanoparticle surface with macromolecules.

It is known that the size of gold nanoparticles is increased in the presence of poly-4-vinylpyridine (P4-VPy) that is indicative of the chemisorption of macrocations on them and the formation of a 'soluble complex'.[39] The mean hydrodynamic radius of such stabilised particles (21±0.5 nm) is larger than that of nanoparticles in water (13±0.5 nm) (Fig. 1). According to Kiwi and Gratzel,[37] the mean hydrodynamic radius of Pt particles stabilised with PVA with a molecular mass of 60 kDa is 10.5 nm, the size of metal particles being small compared with the thickness of the protective environment.

The possibility of polymeric stabilisation is determined by the condition that the spatial dimensions of even relatively low-molecular-weight compounds are comparable with, or larger than, the action range of the forces of London attraction of particles. Assuming the 'diameter' of a linear polymeric macromolecule to coincide with the root mean-square distance between its ends, the ratio of the particle radius to the molecular weight of a polymer (M_r) may be calculated by the expression [32]

$$< r^2 >^{0.5} \approx 0.06\ M_r^{0.5}.$$

For the polymers with $M_r = 10^4$, $< r^2 >^{0.5} = 6$ nm, whereas for $M_r = 10^5$, $< r^2 >^{0.5} = 20$ nm.

Thus, the polymeric molecules with $M_r > 10^4$ have precisely the size range required for the stabilisation of colloidal particles (clearly, it is also necessary that the macromolecules induce repulsion of particles). Another necessary condition of the stabilisation is the ability of polymer to wet the nanoparticle surface,

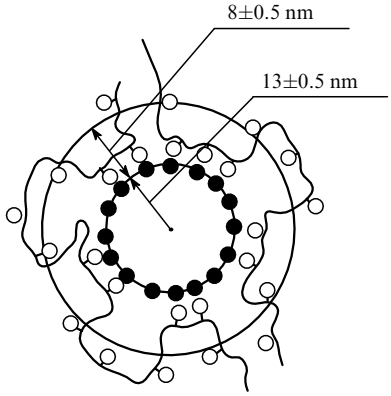


Figure 1. Structure of the 'soluble polyelectrolyte complex' formed by a gold particle and a polycation macromolecule.[39]

and this in turn is dependent on the character of the interaction of the polymeric medium with the active centres of the surface.

The steric stabilisation of particles can follow two different mechanisms. The first mechanism assumes the attachment of macromolecules to the surface of particles, for example, by grafting or physical adsorption. In this situation, irrespective of the form of the molecules (unfolded or globular) localised on the surface of nanoparticles, their interaction is determined by the number of polar groups in the adsorbed polymer per unit surface. According to the second mechanism, stabilisation is performed by macromolecules from solution. A combined method of electrosteric stabilisation based on the use of the superficial charges on the particle or on the polymer, *e.g.*, on a polyelectrolyte, is frequently used (especially in biopolymeric systems, see Section VI).

The mechanisms of the stabilisation have not been totally clarified yet because of their complexity. Simultaneous occurrence and mutual influence of processes of particle enlargement and adsorption of macromolecules on the surface of both initial and formed particles is to be noted. Here, the aggregative stability depends on the ratio of coagulation and adsorption rate constants. By analogy with the sorption processes, the quantity of sol coagulated per unit surface within a definite time interval is calculated by the equation [40]

$$q = \frac{(c_0 - c_e)V_1 S_1}{m_2 S_2},$$

where c_0 and c_e are the initial and equilibrium weight concentrations of a metal sol, respectively; V_1 is its volume; m_2 is the weight of the polymer; S_1 and S_2 are the specific surfaces of metal sol and polymer, respectively. In most cases, the 'sorption equilibrium' is reached within a few hours, while the calculated sorption isotherms have an S-like shape and are approximated by the Langmuir equation in its linearised form in the region of low concentrations of nanoparticles. This implies that the superficial layers of metal particles are formed on polymers following the pattern of molecular sorption.

Simulation of the adsorption–coagulation processes is a rather difficult task. Let us confine ourselves to a mere listing of the most significant effects.[32] The case with attached macromolecules involves elastic homosteric and enhanced steric stabilisation, flocculation (phase partitions, substitutive coagulation, crystallisational coagulation), and heterosteric stabilisation (selective flocculation, heteroflocculation, phase separation). In the case of free macromolecules, there occur substitutive stabilisation, flocculation, and phase separation. The efficiency of the sorption processes, to which the coagulation of nanoparticles is also referred, is determined by the overall balance of surface forces in the course of interaction of phases of different nature.[41] Thus, the stabilising effect of polymers, often called shielding with a protective colloid,[42] is the consequence of the adsorption of macromolecules on the surface of nanoparticles. By enveloping the nanoparticles, the macromolecules make them less sensitive to the action of electrolytes.

The attempts aimed at the quantitative estimation of the stabilising capacity of polymers date back to the times of Faraday (1857) who studied the effect of gelatin on the variation of the gold sol colour from red to blue upon addition of NaCl.

This phenomenon called subsequently protective action is associated with the ability of soluble polymers to prevent the coagulation of sol by electrolytes. To characterise various biopolymeric stabilisers, the notion of 'golden number' was introduced as the quantity of polymer (mg) capable of averting the flocculation of 10 ml of gold sol upon addition of 1 ml of 10% NaCl solution. The lower is the 'golden number' the more effective is the polymer in preventing the coagulation of the dispersed phase. Despite a sceptical attitude of some investigators [1] to such empirically established 'numbers', we believe that they are definitively useful for comparative analysis. For example, the 'golden numbers' for gelatin, albumin, gum arabic, and dextrin are 0.005–0.01, 0.1–0.2, 0.15–0.25, and 6–20, respectively.

The protective capacity of a polymer, *i.e.* its ability to stabilise colloids, is sometimes estimated as the weight of gold (g), which is stabilised by 1 g of polymer added to 1% aqueous solution of NaCl.[43] The protective capacities of gelatin, polyvinylpyrrolidone (PVPr) with the mean degree of polymerisation $P = 3250$, polyvinyl alcohol (PVAl, $P = 500$), polyacrylic acid (PAA), and polyethylenimide (PEI) are 90, 50, 0.07, and 0.04, respectively. The ability of polymers to stabilise dispersions increases as their protective capacity increases. The critical concentration of KCl ($10^3 c_{KCl}$) required for the change of the colour of gold sol from red to blue in the presence of a definite concentration of polymer (1.0 g litre^{-1}) is also used for the evaluation of the stabilising capacity of polymers. It is significant that c_{KCl} is also sensitive to the molecular mass of polymers. For example, the value of $10^3 c_{KCl}$ varies from 12.5 (in the absence of polymers) to 18, 22, 47, and 480 in the presence of polyethylene oxides with molecular the masses of 600, 4000, 6000, and 9000 Da, respectively.

A number of classical studies have established the physicochemical base of the existence of gold sols, their morphology, and structure.¶

The strength and rigidity of protective layers, their spatial extent, as well as the mode of polymer adhesion to the particles are the most important characteristics of the stabilising effect. Polyelectrolytes or relatively rigid non-ionic macromolecules may be attached by adsorption either by their one end ('tails') or both ends ('loops'). The adsorption in the form of loops is most characteristic of homopolymers. As a rule, homopolymers are rarely used as steric stabilisers because they are driven out of the interaction zone in the process of Brownian collisions of particles. However, their efficiency is substantially enhanced when there are centres of specific interaction in the homopolymers themselves or on the surface of the particles to be stabilised. Most often this concerns the protective action of polynucleotides possessing in their native state a complex architecture (secondary, tertiary, and even quaternary). Therefore, they bring about simultaneously both electrostatic and polymeric stabilisation.[45]

Here, the polymeric chain itself may undergo various conformational transformations. In this connection, it seems appropriate to mention the problem of 'blue silver': the radiation-chemical reduction of Ag^+ ions in slightly alkaline aqueous solutions is accompanied by the appearance of bright-blue colouration in the presence of PAA.[46,47] The reduced 'blue silver' possesses high stability even when exposed to air and may be isolated in the pure form by evaporation of water. This phenomenon is due to the stabilisation of silver by PAA. In alkaline solution, the PAA molecules become unfolded owing to the repulsion of groups COO^-, providing Ag^+ ions with the possibility to interact with groups COO^-. Further Ag^+ reduction leads to cluster formation.

Another example is the stabilisation of $Fe(OH)_3$ particles containing up to 120 iron atoms† in the presence of PVAl or polyvinyl esters with different degrees of polymerisation (Fig. 2).

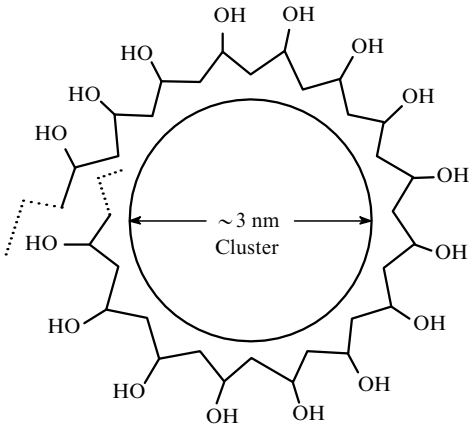


Figure 2. The 'inclusion' complexes consisting of PVAl and $Fe(OH)_3$-like clusters with hydrophobic bonding.

The optimum synthetic stabilisers are amphiphilic polymers, block- or graft-copolymers, which have one fragment ('anchor') in the form of a polymer insoluble in the dispersive medium, whereas the second part of the macromolecule is, on the contrary, soluble in this medium. A characteristic example may be polystyrene-block-polybutadiene subjected to epoxidation with subsequent modification by different nucleophiles.[48] The micelles of these copolymers in toluene dissolve salts of noble metals, as well as Zn and Cu, which are insoluble in pure toluene. The polymer-stabilised particles formed have the size of ~10 nm and are characterised by low polydispersity. Statistical copolymers are less effective.

As a rule, the anchor fragments are attached to the particles as a result of either physical adsorption (which is interpreted in a simplified approach as including processes determined by the van der Waals forces, dipolar interaction, or weak hydrogen bonding which is easy to break), or chemisorption (caused by strong specific bonding of the electrostatic or covalent nature, or by the acid – base interaction). The stabilising fragments ensure the steric protection owing to their mutual repulsion. This occurs in the following manner. When particles come close to each other in the course of the Brownian motion, the fragments are subjected to a stress generated by the compression of adsorption polymeric layers (in the collision of particles, the mutual penetration of polymeric chains is either weak or absent). The release of macromolecules from the region of strong compression requires either their desorption or displacement over the surface out of the stress zone, which demand a significant energy expenditure.

Naturally, in real systems the extreme adsorption of polymeric chains is often not achieved and there are superficial sites unsaturated with macromolecules. In addition, when the compression stress is sufficient for the desorption of macromolecules, the displacement of chains leads to their concentration at particular sites of the overall surface, and this process is accompanied by a decrease in the surface entropy. Furthermore, it is necessary to take into account the presence of defects in any metal surface, in particular, an almost unavoidable existence of an oxide film whose properties strongly depend on the nature of the metal. This leads to an enhanced adhesion due both to formation of hydrogen bonds between certain units of the macrochain and the oxide film and to 'infiltration' of polymers into surface defects or into a relatively porous oxide layer. Moreover, if a polymer contains hydroxyl, carbonyl, and other functional groups, there appears a possibility of heterogeneous chemical interactions. Preliminary treatment (lyophilisation) of the surface of nanoparticles or polymers with specific reagents may lead to the appearance of sites with increased electron densities. They play the role of preferential centres for the formation of nanoparticle primers

¶ There are two basic approaches to the preparation of stable monodisperse sols of colloidal gold:[42] (*a*) disintegration of metallic Au by an electrical arc in a liquid medium and (*b*) reduction of gold halides (most often, $HAuCl_4$) by sodium citrate at 100 °C or by sonication under conditions of pulse or laser radiolysis. In a standard citrate sol, the gold particles are charged negatively, which is due to strong adsorption of citrate ions the charge of which is equilibrated by weakly bound sodium ions. The charge of gold particles may be positive, if the citrate is removed by filtration through an ion-exchange column with subsequent treatment of solution with *N*-hexylpyridinium polyethylene bromide. The positively charged polymer is strongly adsorbed on gold (the size of sol particles is 10 – 20 nm), while the bromide acts as the counterion.

† Hydrolysis of Fe^{3+} in aqueous solutions leads to the precipitation of particles $Fe_x(OH)_{3-x} \cdot nH_2O$ in which the values of x and n depend on the reaction conditions; in some cases α-FeO(OH) with a mean particle size of 2 nm is formed instead of $Fe(OH)_3$.[35]

(embryos). For example, treatment of gelatin with bromine facilitates its subsequent decoration with gold.[49]

One should also take into account that ionomers manifest a clear-cut trend toward the association of ionic groups, which form ionic regions as a separate microphase in hydrophobic polymers. For instance, perfluoroalkylsulfonic acid (trade name 'Nafion') revealed morphological formations with ionic regions 3–4 nm in diameter generated by the sulfonate groups. These domains are connected by hydrophilic channels about 1 nm in diameter surrounded by fluorocarbon matrix (Fig. 3). These areas become the sites of concentration of ionic centres for the preferential formation of metalloclusters.[51] In matrices of this type, a restricted diffusion of nanoparticles is observed. In pores of solvated polymeric networks, the coefficient of restricted diffusion of iron hydroxide particles (3–9 nm) exceeds 2×10^{-8} cm^2 s^{-1}.[52]

In conclusion of the brief discussion of the modes of stabilisation of nanoparticles, let us dwell on the following points.

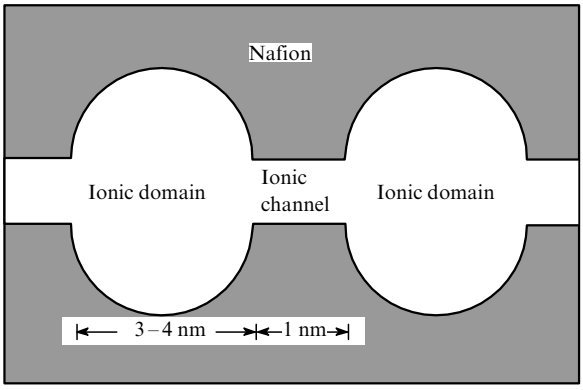


Figure 3. Schematic diagram of ionic domains in the Nafion ion-exchange resin.

Although the basic theoretical concepts of the formation and stabilisation of colloidal dispersions refer primarily to polymeric emulsions (latex polymerisation of vinylic and diene monomers, the directed choice of emulsion paints and surface coatings, *etc*.), they also seem to be well applicable to the problem of nanoparticle stabilisation. The differences would most likely be of a quantitative rather than qualitative character. Specifically, as noted above, the attractive forces between particles of dispersed organic polymers are considerably weaker than between particles of metals, their oxides, and salts (cf. the above-mentioned values of Hamaker constants).

The quantitative theory of stabilisation of colloidal particles is based on the analysis of dilute colloids, one of their principal properties being the kinetic (sedimentation) stability. In the case of concentrated, and particularly highly concentrated (containing up to 80% of metal powder) systems, the involvement of the dispersed phase particles in the Brownian motion does not play any critical role. According to the expert view of P A Rebinder, their distinctive features such as strongly developed interfacial surface and high concentration of the dispersed phase in a liquid dispersive medium result in a major consequence: within the concentrated systems, thermodynamically stable spatial structures appear spontaneously as a result of mutual cohesion of particles inside the dispersed phase.[31] The participation in the Brownian motion of nanoparticles, which are fixed in a spatial network owing to the atomic or coagulative contacts between the particles, is limited to oscillations around the equilibrium position. Indeed, the energy of thermal motion ($3/2\,kT$) is much lower than the total energy of the interaction of neighbouring particles, which is determined by the nature of the elementary contacts, their number, and the distribution pattern in structures. Therefore, the protective high-molecular-weight compounds and dry compositions of dispersed phases of sols are used in the preparation of concentrated hydrosols.

The protected sols acquire the properties of reversible colloids: the dry dispersed phase remaining after the evaporation of the dispersive medium can reform a stable sol upon repeated contact with this medium. In these systems, the lyophobic nanoparticles appear to be in a cobweb of the protective polymer. Such materials find diverse applications, because the practically valuable changes in their properties (higher thermal and electrical conductivity, heat capacity, ability to screen radiation, *etc*.) are realised only at large concentrations of nanoparticles (most frequently, above 50 vol.%, or 90 mass %). However, high viscosity of the molten polymeric matrix does not allow one to achieve regular distribution of nanoparticles, and this degrades the dielectric and mechanical parameters of the materials produced. Thus, the distribution character of nanoparticles in polymers is also significant from the practical viewpoint. For numerous purposes, it is important to achieve the formation of fractal clusters (fractal aggregates) *via* definite physical processes of growth in polymeric media.‡ The fractal cluster is close to the percolational one[54] that makes it possible to realise transfer processes (in particular, the system conductance).

The above-discussed concepts refer to the bulk stabilisation (in solutions, gels, swollen polymers). Though, stabilisation often takes place on the surface (*e.g*., in thin films or a thin subsuperficial layer of a polymer powder). Furthermore, natural 'cavities' are nearly always present in real polymers with a high degree of crystallinity, *e.g*. in polyethylene (PE) or polytetrafluoroethylene (PTFE) in which this index is 60%–85% and 75%–80%, respectively. Their existence is due to the peculiarities of polymeric chain packing upon transition from the amorphous to the crystalline phase. The amorphous regions are looser and include considerably more cavities, since here the cross-linking of macrochains is weaker than in the crystalline blocks. In these cavities, nanoparticles may be localised and stabilised. For example, the 'ligand-free' iron clusters (up to 35 mass %) are stabilised in the PE or PTFE matrices with a fairly narrow range of their sizes (the distribution maxima were observed for the particles measuring 1.48 and 1.81 nm, respectively).

A crucial role is also played by the pore size, which is one of the basic factors determining the stabilising capacity of matrices. The pores act as transport arteries for the penetration of nanoparticles or their precursors into the bulk of polymers. The incorporation of nanoparticles can also distort considerably the polymeric structure itself. The porosity is estimated from the specific surface (S_s), total volume (V_0), and radius (r) of pores and depends on many parameters, the most essential being the cross-linking density. With regard to their size, all pores are arbitrarily divided into three groups: micropores ($r < 1.5$ nm, $V_0 < 0.5$ cm^3 g^{-1}, the magnitude of S_s is meaningless in this case), mesopores or transient pores ($r = 1.5$–30 nm, $V_t \approx 0.8$ cm^3 g^{-1}, $S_s = 700$–900 m^2 g^{-1}), and macropores ($r > 30$–6500 nm).

There are two basically different modes of the matrix isolation of nanoparticles. The first one is the most usual and consists in mere addition of a suspended or solubilised polymeric stabiliser to a prepared dispersion of particles (a modification of microencapsulation). There are other versions of this technique including mixing of metal powders with latexes. Latex is mixed with the metal phase particles having a size smaller than that of latex particles (100 and 700 nm, respectively) and, after the stabilisation of the resultant mixture (which is often accompanied by coagulation), the dispersive medium is removed. Then the coagulates are heated and moulded to produce samples of metal polymers.

‡ It is assumed that in most of the colloidal dispersions, the aggregation of particles leads to the formation of fractal clusters regarded as geometric objects possessing a self-similar structure in different spatial scales.[53]

The second approach is based on the preparation of dispersions in the presence of a stabiliser or in the production of a stabiliser from its precursor in the presence of a prepared dispersion of nanoparticles. A widespread version of this method is the formation of nanoparticles in a polymeric medium. This makes it possible to prepare compositions in which the mixing occurs prior to the resin solidification.§ The materials produced are remarkable not only for the most uniform distribution of metal particles over the polymer bulk but also for strong chemical interaction of the metal with the polymer. On rare occasions, both components, *viz*. polymeric stabiliser and nanoparticles, are prepared *in situ*.

The complete stabilisation of nanoparticles by polymers is achieved when the adsorption–solvation layers are structured and form a structural–mechanical barrier for coagulation. The strength of these structures and their ability to recover rapidly after damage determine basically the aggregative stability of nanoparticles.

Now let us consider the most interesting techniques for the preparation of polymer-immobilised nanoparticles.

IV. Typical formation processes and the structure of nanometric metal particles in polymers

The difficulties of preparation and practical uses of polymer-immobilised nanoparticles are due, on the one hand, to a rather poor reproducibility of many synthetic procedures and, on the other hand, to rapid oxidation of particles of non-noble metals by potential oxidants at the stage of colloid formation. Virtually all of the known methods for producing polymer-immobilised nanoparticles are at least two-stage processes: they include molecular dispersion (atomisation or reduction) and subsequent condensation of atomic metal into nanoparticles. These stages occur in a rapid succession and virtually form an integral complex process of the appearance of nuclei and growth of a solid metallic phase. The very notion of 'solid phase nucleus' is somewhat equivocal. A cluster containing 25 Pt atoms corresponds in its adsorptional properties to a bulk metal.[56] On the other hand, in the course of gold chloride reduction, the collectivised ionic groups start to display properties characteristic of the metal nucleus (embryo) only after the accumulation of 300 and more Au atoms.[46]

The heteroadagulation of polymer-immobilised nanoparticles on polymeric powders, films, or fibres could be the simplest method for their preparation. These studies have been carried out mostly on mineral supports, though there are also reports on heteroadagulation of non-stabilised hydrosols (8–12 nm) and organosols (4–11 nm) of Fe, Zn, and Cu on the surface of Dacron (lavsan) and polycaprolactam (capron) fibres.[40] On the lavsan fibres, the heteroadagulation rate is higher, which is explained by the specific interaction and the formation of the surface M–O bonds. The lowest adagulation rate is characteristic of the iron sol. However, the materials thus obtained are heterogeneous: the nanoparticles are localised only on the surface of polymers.

1. Technique of the atomic metal evaporation

The most attractive, from the technological viewpoint, are the methods of cryochemical deposition (most frequently, vacuum deposition at pressures of 10^{-1}–10^{-4} Pa) of atomic (gaseous) metal on thin (~1000 nm) polymeric supports. The latter are usually high-molecular-weight paraffins, polyesters, oligo- and polyolefins, polydienes, vinyl- and phenyl-siloxane polymers. The metal atoms are first deposited at temperatures of 77 K and above (the so-called technique of 'bare' atoms).[57–64] Then, the stabilisation of small clusters stable at low temperatures is carried out. In these systems, both homo- and heterocluster particles are formed and stabilised at an evaporation rate of 10^{-8} mol min^{-1}. As shown in Scheme 1, first a single metal atom forms bonds with two functional groups (arene rings, or oxygen atoms) (stage *I*). This is followed by the stage of metal–polymer chain 'growth' (*II*), and finally the stabilisation of clusters by ligands takes place (*III*). The stabilisation may also result from the inclusion of clusters into a trap of highly viscous metal–polymer network (*IV*) and the enlargement of cluster particles (*V*).

Scheme 1

As a rule, the deposition results in the formation of miniclusters, the size of which depends on the conditions of process and the nature of the metal (in most cases, transition metals are used). Cr clusters contain 2–3 metal atoms, those of Mo contain 2–5 metal atoms, and clusters of other metals include not more than 10 atoms.¶

In principle, the kinetics of metal vapour condensation is analogous to the coagulation kinetics of an ideal suspension, which is in an absolutely unstable state, and which can be described by the Smoluchowski equation of fast coagulation.

Some spectral techniques have been elaborated for the identification of polymer-immobilised clusters. For example, mono-, di-, and tri-mers of molybdenum immobilised on poly(methylphenylsiloxane) absorb at λ_{max} = 318, 418, and 502 nm, respectively, whereas the four- and five-nuclear formations absorb at λ_{max} = 598 and 640 nm, respectively. This makes it possible to follow the growth of cluster particles. According to Scheme 1, this process comprises a number of consecutive irreversible bimolecular reactions:

$$M + L \xrightarrow{k_1} ML,$$

$$ML + L \xrightarrow{k_2} ML_2,$$

§ An interesting variant consists in the vulcanisation of rubber mixtures containing ferrite dust.[55]

¶ These formations are thermally stable only below 290 K and disintegrate rapidly under the action of oxygen (even under a pressure of 1 mm Hg). Note for comparison that the energy of Cr–Cr and Mo–Mo bonds are 150 and 400 kJ mol^{-1}, respectively.

$$ML_2 + M \xrightarrow{k_3} M_2L_2,$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$M_{n-1}L_2 + M \xrightarrow{k_n} M_nL_2,$$

where M is a metal and L is a ligand.

The formation of clusters may be regarded as a continuous deposition of metal atoms on a polymeric film over the time t at the rate W; then the corresponding rate equations are

$$\frac{d[M]}{dt} = W - \sum_{j=0}^{p} k_m[M][M_jL_2],$$

$$\frac{d[M_nL_2]}{dt} = k_m[M]\left\{[M_{n-1}L_2] - [M_nL_2]\right\}.$$

The concentration of cluster nuclei M_nL_2 of various nuclearity on the polymer may be expressed in general form as

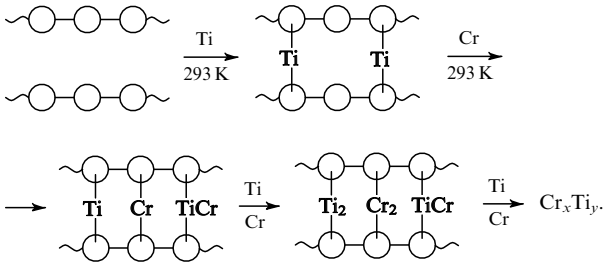
$$\frac{[M_nL_2]}{[ML_2]} = [M_0]^{n-1}\frac{2^{n-1}}{n[L_0]^{n-1}} = k[M_0]^{n-1},$$

where M_0 is the total mass of metal atoms deposited on the polymeric film over the time t.

Generally speaking, the cryochemical condensation of metals on cooled matrices leads to the formation of a variety of 'cluster series', which are interpreted [65] as a set of clusters with the monotonically increasing nuclearity with the same composition of ligands (M_nL_m, where $n = qx$, x is the nuclearity of the simplest member of this series, q is an integer). In these series, the basic structural elements (the simplest building blocks) are individual metal atoms, whereas the series *per se* are models of the atom-by-atom growth of metal particles. One can follow the course of their formation *via* the addition of individual 'bricks', which are elements of the nucleus formation.

It is significant that the cryochemical method allows the preparation of both homo- and hetero-metallic polymer-immobilised cluster particles. Thus the consecutive or simultaneous deposition of vapour of different metals, *e.g.*, Mo and Ti or Ti and Cr, especially at high concentrations, yields the non-solvated bimetallic clusters $M^1_xM^2_y$, which are close in size to the colloidal particles (Cr_xTi_y) (Scheme 2) or to small clusters (the cluster Mo_xTi_y includes 13 atoms).

Scheme 2



The particles formed are chemically bound with the polymer and possibly bring about the cross-linking of its chains.

Control of the conditions of metal evaporation also allows the preparation of polymer-immobilised nanoparticles. For example, colloidal silver was obtained with the particle size of 1.0–20 nm (the colloidal Ag particles less than 40 nm in diameter absorb light at ~400 nm).[66] The dispersion of gold nanoparticles (mean particle size ~2 nm) in poly(diphenylbutadiyne) has been obtained by cocondensation of vapour of Au and diacetylene monomer on a support at 77 K.[67]

Different versions of cryochemical synthesis have been developed using the protective properties of polymers. To this end, for example, an oscillatory contour is applied for the electrical condensational dispersion of metals. [69] In non-polar media, dispersions of Ag, Al, Bi, Cd, Cu, Co, Mo, Fe, Ni, Zr, Pt, Sn, and W with the particle size of 1–10 nm are stable only in the presence of stabilisers (the synthetic rubbers SKD, SKB-35) that can form three-dimensional structures in solution. In their absence, immediate coagulation takes place.

The evaporation of solid polymeric particles (accompanied by considerable pyrolysis) and the co-deposition of volatile products (mostly radicals) with the metal vapour are used less often. This technique is employed, *e.g.*, for the formation of copper islets of ~10 nm in diameter in a polyethylene matrix.[70] The explosive evaporation of a metal wire coated with a polymer, when a short-circuit causes an instantaneous evaporation of metal and the fragmentation of polymer,[71] processes of pulsed mechanochemical interaction (of the Bridgeman anvil type),[72] *etc.* are the modifications of this method. Over the recent years, a keen interest has been shown in the ionic spray of metals on polymeric surfaces. In this context, it seems appropriate to mention the studies into the vacuum deposition of Au and Zn on PE and PTFE.[73]

The low-temperature condensation of Cr vapour with macromoleular matrices containing aromatic rings (oligobenzyl, oligoarylene, benzene–*m*-xylene copolymer) was used for the preparation of macromolecular sandwich-type Cr complexes.[74] The direct interaction of atomic metal with the matrix is prevented by the joint condensation of the metal vapour and the solvent (*e.g.*, chromium and diglyme).[75] This interesting technique makes it possible to replace the direct metal–matrix interaction by the process of exchange of one stabilising ligand for another high-molecular-weight ligand (this procedure is called resolvation). Non-ionogenic surfactants are sometimes used for the replacement of dispersive medium. Thus the organosols of silver with particles 3–12 nm in diameter obtained by the cryochemical method in acetone are subsequently stabilised with 0.2% Triton X-100 solution in water and incorporated into a cross-linked polyacrylamide gel.[76] The nature of the solvent [64] and the polymer used for the cryochemical synthesis substantially affects both the reaction direction and the stability of products.

Resolvation may precede the preparation of polymer-immobilised nanoparticles. For example, the cryochemical synthesis of colloidal Ag particles is performed in acetone, which is then replaced by formamide. Such a dispersion remains stable for a few days. The system Ag (2–5 nm)–formamide is used as a solvent in the preparation of cross-linked polyacrylamide gel.[77] Three different resolvation variants for the synthetic purpose are documented.[78] In the first version, a Co–nonadecane system obtained by the cryochemical method was mixed with a solution of a polymer in nonadecane with subsequent sonication. In the second version, the nanoparticles of Co or Ni in toluene were added to a solution of low-pressure polyethylene (LPPE) in toluene at 363 K. Finally, according to the third variant, a toluene solution of a polymer was cooled from 383 to 185 K, and the gel-like system was mixed with nanoparticles obtained cryochemically and subjected to sonication. The above techniques make it possible to virtually preclude the aggregation of particles at all intermediate stages. However, along with the peptisation and resolvation, more complex physicochemical interactions of nanoparticles with the solvent may also take place.

In the preparation of polymer-immobilised nanoparticles, the matrix, as a rule, does not remain indifferent to the fixation of metal atoms. This is often accompanied by a sharp decrease in the molecular weight of polymers (in particular, in the case of oligoarylenes)[75] or by the matrix structuring leading to the loss of solubility. In some instances, the ester and other bonds are cleaved, while the interaction of the functional groups of the polymer with metal atoms yields new products (*e.g.*, the splitting of the terminal chlorine atoms in the oligobenzyl matrix synthesised from benzyl cloride in the presence of Cr results in the formation of $CrCl_3$). The interaction of atomic zinc with the polymer surface is accompanied by a profound destruction of the polymeric subsuperficial layers and the interaction of zinc with the degradation products.[73]

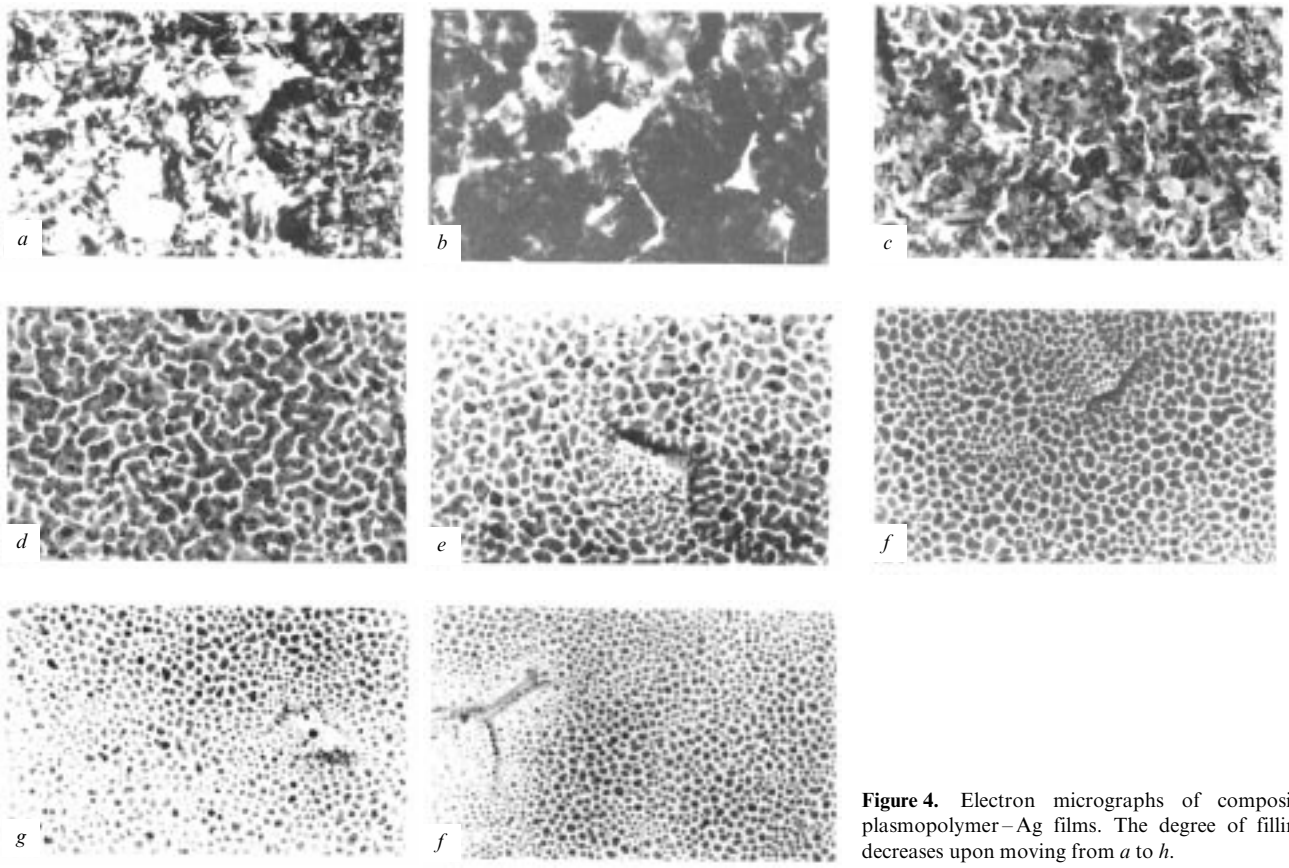


Figure 4. Electron micrographs of composite plasmopolymer – Ag films. The degree of filling decreases upon moving from *a* to *h*.

2. Preparation of polymer-immobilised nanoparticles by polymerisation in plasma

Polymerisation in a plasma (in a glow discharge) is initiated by ions, excited molecules, and photons with sufficiently high energy. The vapour pressure of a monomer (its concentration) during polymerisation in plasma is too low (10^{-3} – 10 mm Hg) to allow the production of polymers by the conventional technique. The role of polymer-forming substances is played by relatively simple compounds (CH_4, CF_4, benzene, chlorobenzene, perfluoropropane); less often, by more complex compounds. For example, homogeneous coatings enriched in beryllium are prepared by the thermal evaporation of Be with the concomitant deposition of a plasmopolymer of *trans*-but-2-ene.[79] In this method, mixtures of gaseous monomers with argon are often used. The chain mechanism of the polymer growth does not play a substantial role in the deposition of polymers from the gas phase. The chain propagation occurs basically according to a rapid stepwise mechanism with the predominance of reactions between active particles, which are often called reactions of polyrecombination. Although the products formed are regarded as polymers, they have however little in common with the usual materials of this type because of their structural peculiarities. As a rule, they are three-dimensional products with a high degree of cross-linking, especially when produced by extended (5 – 10 min) treatments with plasma. In the course of plasma-induced polymerisation, two competitive processes take place: the formation of a polymer by deposition from the gas phase and the etching (destruction) leading to its removal. The relationship between these processes at each specific site is determined by the energy of excited particles, their concentration, and the surface temperature, as well as by the nature of the monomer (*e.g.*, polymerisation predominates in the case of C_3F_8).[80]

A substantial distinction of the plasma polymerisation from the traditional ways of polymer formation consists in the possibility of forming thin (50 – 100 nm), virtually defect-free films on most varied supports. It is also significant that the polymerisation in plasma, is not restricted by the choice of material and the support shape. Therefore, this technique is well-suited for the preparation of microencapsulated nanoparticles (the so-called metal-doped polymeric films).[81]

Thin composite films are formed under the conditions of simultaneous polymerisation of corresponding compounds and vacuum evaporation of metals. Various modifications of this method † have been reported that differ basically in the mode of preparation and introduction of nanoparticles. One version of this method includes simultaneous evaporation of a monomer and metal from different sources,[85] while another relies on the combination of plasma polymerisation and metal evaporation.[81,86] There is an original variant, according to which the plasma-induced graft polymerisation of monomers of traditional type (*e.g.*, vinylimidazole on a capron film)[87] occurs concomitantly with the metal evaporation. Of special interest is the plasma polymerisation of organometallic compounds.[88] The plasma-induced polymerisation of diethylberyllium is remarkable for the simplicity of the equipment required.

The preparation of polymer-immobilised nanoparticles most often involves combined targets including a metal and a polymer.[89] The target material is sprayed by plasma, and the sprayed product is deposited, as a rule, outside the plasma zone. It is very convenient to use the cathode material (Mo, Cu, Au) as the source of the metal. In trifluoropropane – metal systems thus obtained the content of the metal in the thin-film material amounts to 18 mass % – 26 mass %. Metallopolymers with the formal composition $(C_3F_4O_{0.6}Mo_{0.3})_n$ and $(C_3F_{3.9}O_{0.3}Cu_{0.3})_m$ have been prepared and characterised.[82] An aluminium-containing material with enhanced adhesion properties is produced by the spray and polymerisation of CH_4 in plasma using aluminium as the electrode

† The conditions of low-temperature plasma generation and the technology of plasmochemical processes are described.[82–84]

material. Even at a relatively low frequency (10 kHz), the electrode surface is bombarded so strongly that the physical spraying of Al takes place with its inclusion into the growing macromolecule, the metal atoms being uniformly distributed over the bulk of the deposited material.

The volume portion (or the filling factor) of the metal embedded into the metallopolymeric material is calculated by the equation [90]

$$r = \frac{S_r - C_f}{S_m - C_f},$$

where S_r is the density of the metal-containing film, C_f and S_m are the densities of the 'metal-free film' and the metal, respectively. Depending on the conditions, the parameter r may vary from 0.1 to 1.0 reflecting the structure of the polymer-immobilised nanoparticles. Thus at low r values and short plasma treatments, the plasma polymerisation of benzene with silver yields quasi-two-dimensional particles.[91] Their distribution pattern in the polymer depends on both the conditions of plasma polymerisation and the filling factor. For example, the transmission electron microscopy has shown [92] that the composite plasmopolymer–silver films include three different structural regions with different r values (Fig. 4): the metallic region (*a*, *b*) composed basically of the metal particles with polymer inclusions, the percolational region (*c*) in which there are no aggregated metal particles and the formation of interacting cluster particles is initiated, and finally the region of the cluster particles completely isolated by the polymer (*d*–*h*), *i.e.*, microencapsulated polycrystalline silver particles. Similar structure is characteristic of the Cu, Au, and Ag particles of colloidal size encapsulated with thin shells.[93,94] This group also includes the particles of Au,[80,81,95–97] Co, Al, and Mo [98] in fluoropolymers, Cu in polyethylene,[85] Ag in a polymer obtained from chlorobenzene [86] and benzene,[91] *etc*. The distribution of gold nanoparticles in a polymer resulting from the plasma treatment of the C_3F_8–Au mixture has been studied in detail.[80,90] The mean size of gold particles is 5.5 nm (r = 0.15). The size of silver crystallites in thin composite films formed upon polymerisation of chlorobenzene and vacuum evaporation of Ag ranges from 5 to 10 nm [86] and from 100 to 200 nm at high Ag levels. Special studies have shown that neither AgCl nor silver carbide are formed.

Thus, the polymerisation in a glow discharge makes it possible to produce thin polymeric films of controlled size on the surface of nanoparticles prepared *in situ*. The complexity of this technique resides in the fact that it is difficult to control the rate of metal spray and its incorporation into the polymer formed.

3. Preparation of metal sols in polymers by the thermal decomposition of precursor compounds

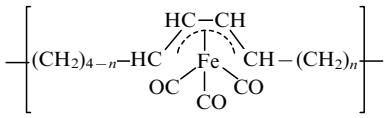
Heating of volatile metal compounds (primarily, carbonyls, π-allylic complexes, formates, acetates, and organometallic compounds) in organic media or in the gas phase leads to their degradation with the liberation of metals or their oxides in the form of dispersed phase. An example is the decomposition of iron pentacarbonyl:

$$Fe(CO)_5 \longrightarrow Fe_2(CO)_9 \longrightarrow Fe_3(CO)_{12} \longrightarrow Fe^0_n.$$

If these reactions are carried out in the presence of polymers, it is the simplest and apparently the most widespread method for the introduction of large (sometimes up to 90 mass %) quantities of colloidal particles of pure metals into polymeric compositions. This method underlies numerous processes intended for the preparation of polymer-immobilised ferromagnetic nanoparticles *via* the chemisorption of macromolecules on metal particles formed *in situ*. In the first place, this is pertinent to the thermolysis of metal carbonyls.

The stable homogeneous polymer-immobilised dispersions of colloidal particles of Fe, Co, Cr, Mo, W, Mn, Re, Ni, Pd, Pt, Ru, Rh, Os, and Ir can be produced using two modifications of the thermal decomposition of their precursor compounds.[99,100] The first version is based on the use of solution of 'active' polymer (containing amino, amide, imine, nitrile, hydroxyl, and other functional groups) in an inert solvent to which labile metal compound is added gradually. In this case, favourable conditions are created for the chemisorptional polymer–metal interaction. After this, the thermal decomposition is performed (mostly, at 100–170 °C). Sometimes the solution or suspension is subjected to different types of irradiation. The second modification relies on a 'passive' polymer that can react with the initial metal complex after the loss by the latter of at least one ligand (the CO group in the variant under discussion). The gradual addition to the solution of such polymers (*e.g.*, polystyrene, polybutadiene, co-polymers of styrene and butadiene, *etc*.) in an inert solvent of the initial complex at a definite temperature is accompanied by the dissociation of a ligand and the binding of the anionic complex with the passive polymer. Then the thermal degradation is performed.

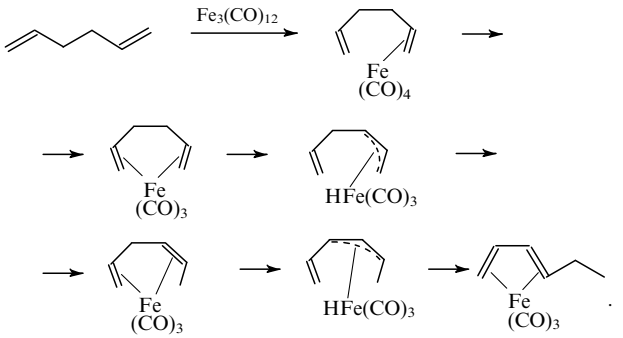
Certain stages of this multistage process (especially the particle growth) have much in common with the above-discussed transformations taking place during the condensation of metal vapour on polymeric matrices. One of the best studied processes is the thermolysis of cobalt carbonyl [101,102] and iron carbonyl [99,102–104] in the presence of polymers. For instance, the thermolysis of $Fe(CO)_5$ in a xylene solution of *cis*-polybutadiene or a block-copolymer of styrene and butadiene (408 K, 24 h, under argon) involving a number of consecutive stages leads to the formation of $[C_8H_{12}Fe(CO)_3]$ units:



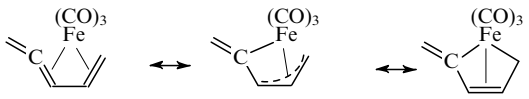
n = 1, 2, 3.

The initial stage involves the formation of a highly reactive anion $Fe(CO)_4^-$, which interacts with isolated double bonds, and then the isomerisation of double bonds occurs accompanied by the formation of π-complexes with the iron tricarbonyl residues. The final product is composed of the η^4-(butadienyl)irontricarbonyl units with the *trans-trans*- and *cis-trans*-tetramethylene groups. Since the iron tricarbonyl complexes with two non-conjugated double bonds are unstable, no intermolecular products are formed. The reaction of iron carbonyls with low-molecular-weight non-conjugated dienes is accompanied by the double bond migration (Scheme 3).[105]

Scheme 3



Three resonance structure are formed on the reaction of iron carbonyl with vinylallenes:[106]



A characteristic feature is that the carbonyl complexes of the same type bound with the allyl fragments of the polymeric chain were also detected upon immobilisation of $Co_2(CO)_8$ or $Fe_3(CO)_{12}$ by the polystyrene–polydiene block-copolymers.[107,108] The thermal decomposition of these polymer-immobilised π-allyl complexes

results in nanoparticles. In the case of polystyrene, the $Cr(CO)_3$ fragments are bound to π-complexes with the benzene ring.[109]

The size of nanoparticles depends on numerous factors, of which the major are the nature of the polymer-disperser, its molecular weight (M ≈ 100 000 is the optimum value), the nature of the functional groups (L), and the solvent. Thus under the conditions of annealing in vacuum at 493 K for 2 h, the cobalt-containing polystyrene–polybutadiene copolymer forms a non-magnetic phase of cobalt clusters ~1 nm in diameter, whereas the thermolysis at 473–573 K leads to the formation of particles with the size of 3–10 nm. Further increase in the thermolysis temperature up to 623 K leads to the enlargement of cobalt nanoparticles to the size of 50 nm and the appearance of the ferromagnetic properties in the materials formed.

The nature of the solvent plays a very important role. Metal carbonyls disproportionate in basic solvents (*e.g.*, in DMF) to form complexes of ionic type in which metal atoms have the formal charge 2+. The composition of products identified by IR spectroscopy was found to depend on the ratio of the components (the extent of the substitution of carbonyl groups) (Scheme 4).

Scheme 4

$$n\mathrm{Fe(CO)_5} + 6\mathrm{DMF} \longrightarrow \begin{cases} [\mathrm{Fe^{2+}(DMF)_6}][\mathrm{Fe_2(CO)_8}]^{2-} + 7\mathrm{CO} \\ [\mathrm{Fe^{2+}(DMF)_6}][\mathrm{Fe_3(CO)_{11}}]^{2-} + 9\mathrm{CO} \\ [\mathrm{Fe^{2+}(DMF)_6}][\mathrm{Fe_4(CO)_{13}}]^{2-} + 12\mathrm{CO} \end{cases}$$

In the general case:

$$\mathrm{Fe(CO)_5} + \mathrm{Nu} \longrightarrow [\mathrm{Fe^{2+}(Nu)_x}][\mathrm{Fe}_n\mathrm{(CO)}_m]^{2-},$$

where Nu is a nucleophile (Py, *N*-methylpyrrolidone, *etc.*), x = 2–6; n = 2, m = 8, or n = 3, m = 11, or n = 4, m = 13. Under these conditions, dicobalt octacarbonyl is transformed according to the scheme

$$2\mathrm{Co_2(CO)_8} + 12\mathrm{DMF} \longrightarrow$$
$$\longrightarrow 2[\mathrm{Co^{2+}(DMF)_6}][\mathrm{Co(CO)_4}]_2^- + 8\mathrm{CO}.$$

Basic solvents and high temperatures favour the binding of metal carbonyls by polymers. Stable colloidal dispersions are formed (*e.g.*, iron dispersion with 5–10-nm particles) upon the thermolysis of carbonyls in dilute polymeric solutions. The nanoparticles of this type are very reactive, the particles with the size less than 10 nm are superparamagnetic, while the magnetic hysteresis is observed for the particle size of 10–20 nm.[104]

The size of Co particles may be controlled within the range from 2 to 30 nm with a narrow interval of size distribution by varying the reaction temperature, the concentration of reagents, and the polymer composition (*e.g.*, ter-copolymer of methyl methacrylate–ethyl acrylate–vinylpyrrolidone)[102] in a solvent medium with low dielectric constant (*e.g.*, in toluene). It is also noteworthy that the polymers containing larger number of polar groups can form particles of a smaller size. The same result is achieved by the decrease in the metal carbonyl concentration in the polymer.

The nucleophilic fragments of macroligands (in particular, those in the copolymer of styrene with *N*-vinylpyrrolidone) catalyse the degradation of metal carbonyls according to the scheme[99]

$$\mathrm{(P)—L} + \mathrm{M}_x\mathrm{(CO)}_y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{(P)—LM}_x\mathrm{(CO)}_{y-1} + \mathrm{CO}$$

$$\mathrm{(P)—LM}_x\mathrm{(CO)}_{y-1} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{(P)—LM}_n$$

$$\mathrm{(P)—LM}_n + m\mathrm{M}_x\mathrm{(CO)}_y \xrightarrow{k_3} \mathrm{(P)—LM}_{n+m}$$

$$\mathrm{M}_x\mathrm{(CO)}_y \xrightarrow{k_4} x\mathrm{M} + y\mathrm{CO}.$$

The first stage involves the ligand functional groups to form a soluble macromolecular complex, which by releasing CO is transformed into a polymer-immobilised cluster particle M^0. The subsequent growth of this particle leads to the formation of a nanoparticle. As the matter of fact, there are stages of initiation, growth of particles, and the reaction termination, which may be regarded as a simple disproportionation of metal carbonyl on the particle surface.

The major requirement for the functionalised polymer consists in that the reaction rate on the polymer should be higher than the metal carbonyl decomposition rate in solution, *i.e.*

$$k_1 + k_2 - k_{-1} - k_{-2} > k_4,$$

$$k_3 > k_4.$$

Thus, in the thermolysis of metal carbonyls in polar media, as a rule, two major reaction routes are realised. First, the disproportionation products react with the polymeric chain and initiate the side reactions of cross-linking, destruction, and isomerisation of the chain, as well as the immobilisation of mononuclear carbonyl complexes. For example, the polybutadiene containing 92% of *cis*-1,4-; 4% of *trans*-1,4-; and 4% of 1,2- units (M_r = 246 kDa) if reacted with $Fe_3(CO)_{12}$ for 2 h at 350 K undergoes isomerisation resulting in an increase in the content of *trans*-1,4 units up to 76%.[103,110] Second, in parallel, there occurs major process of particle growth (enlargement) from the 'hot' metal atoms and the formation of nanoparticles with a size of 1–10 nm:

$$\mathrm{M}_n + \mathrm{M} \longrightarrow \mathrm{M}_{n+1},$$

$$\mathrm{M}_n + \mathrm{M}_m \longrightarrow \mathrm{M}_{n+m}.$$

The binding of small, insufficiently grown particles (M_n) by the polymer

$$\mathrm{M}_n + \mathrm{(P)} \longrightarrow \mathrm{(P)—M}_n$$

(in fact, the chain termination) leads, as a rule, to the formation of non-magnetic materials. Introduction of large (compared to the interchain distances and the size of crystalline blocks and cross-links) metal particles results in the perturbation of the polymer structure and deterioration of its physicomechanical properties. The reactions occur spontaneously along both routes, while the competition between them determines the ratio between the rates of thermolysis and diffusion towards the 'hot' metal centres in the solid polymeric matrix, depending on the nature of the reacting particles and the reaction conditions. In addition, these processes are considerably influenced by the character of the medium (oxidative or reductive).

The conditions of thermolysis of metal carbonyls in polymeric matrices and the size of nanoparticles thus formed are given in Table 1.

There is an original method for the formation of metallopolymers by localisation of particles resulting from the rapid unimolecular degradation of solutions of metal compounds in molten polymers, in natural cavities of polymeric matrices of polyethylene, polypropylene, polytetrafluoroethylene, *etc*. These materials were given a collective name of Claspol.[112–115] In this process, the melt temperature should considerably exceed the temperature inducing the degradation of carbonyls. Carbonyls are used as dilute solutions under conditions providing for the most rapid and complete removal of ligand from the reaction system. This technique offers a number of advantages. On the one hand, higher temperatures increase the extent of carbonyl decomposition and reduce the yield of by-products, on the other hand. In addition, in contrast to solutions, the melts preserve the close order of the initial polymer structure, while the cavities may host the particles formed. The polymer-immobilised particles thus obtained are characterised by a relatively high dispersity and homogeneous distribution over the polymer volume, while macromolecules are irreversibly sorbed on their surface. The metal particles are

Table 1. Thermal decomposition of metal carbonyls in polymeric matrices.

$M_a(CO)_b$	Polymeric matrix	Conditions of thermolysis	Content of nanoparticles (mass %)	Size of nanoparticles /nm	Ref.
$Co_2(CO)_8$	Without polymer	Toluene		> 100	101
	Copolymer MMA – vinylpyrrolidone (90:10)	Chlorobenzene	75	6 – 25	101
	Polychloroprene	Toluene	93	30 – 60	101
	Copolymer vinylchloride – vinylacetate – vinyl alcohol (91 : 6 : 3)	Chlorobenzene	75	7 – 47	101
	PS	Toluene	75	10 – 30	101
	Copolymer styrene – acrylonitrile (88 : 12)	"	75	6 – 13	101
	Atactic PP	"	75	> 100	101
	Polyesters	"	75	6 – 20	101
	Polyurethane	"	75	5 – 30	101
	Tercopolymer MMA – ethyl acrylate – vinyl-pyrrolidone (33 : 66 : 1)	"		20 – 30	102
$Fe(CO)_5$	Polystyrene – block-polybutadiene	Dichlorobenzene, 145 °C		7 – 8	99
	Polybutadiene	Decalin, 140 – 160 °C		5 – 15	99
	cis-Polybutadiene	Xylene, 135 °C			118
	Polybutadiene	Decalin, 150 °C		~6	104
	Copolymer styrene – butadiene (5.8 : 1)	Decalin, 150 °C		~6	104
	Copolymer styrene – 4-vinylpyridine (1 : 0.05)	*o*-Dichlorobenzene	2	~6	104
	The same (1 : 0.1)	*o*-Dichlorobenzene	1.8	~16	104
	Polyvinylidene fluoride	DMF, 140 °C		5 – 15	104
	cis-Polybutadiene	1% solution of dioxane – xylene, 135 °C,	37		93
	Natural rubber	8% solution of dioxane – xylene, 125 °C	17		103
$Fe_3(CO)_{12}$	*trans*-Polybutadiene	Benzene, ethanol, 80 °C	23		103
	Copolymer styrene – butadiene (25 : 75)	Benzene, 80 °C	8		103
	Polybutadiene (81% repeat 1.2-chains)	Benzene – dimethoxyethane, 80 °C	16		103
$Fe(CO)_5$	PE melt	–	1 – 29	1.5 – 7	112 – 114
	PP (isotactic, melt)	–	5		112 – 114
	PP (atactic, melt)	–	5 – 30		112 – 114
$Cr(CO)_6$	PTFE (fluoroplast-40), melt		0.5 – 4	1 – 5	112 – 114

primarily localised in the amorphous, less compact matrix regions. This renders difficult the segmental displacement of the amorphous phase resulting from both the reduced free volume and its possible cross-linking. The polymeric materials formed display enhanced thermal resistance (*e.g.*, in the case of atactic polypropylene modified with metal clusters, T_m is increased by 50 – 80 °C) and the product acquires a monolithic pseudocrystalline structure. The recurrent spacing of the distribution of metal clusters in it is concentration-dependent and in the case of iron, for example, is 9 – 12 nm at high concentration (20 mass % – 30 mass %) and 20 – 22 nm at low concentration (2 mass % – 3 mass %) with a narrow size distribution of particles (half-width ~1 nm). It is significant that the presence of the metal phase does not affect either chemical or physicomechanical properties of such materials as the strong interaction of nanoparticles with the polymer leads to the formation of pseudocrystalline materials. In other words, at definite ratios of ingredients, these products are one-phase metallopolymers.

Of particular interest is the thermolysis of metal carbonyls in the halogen-containing matrices, which apparently should be regarded as 'passive' in terms of the above-discussed classification. The modification of PTFE by Fe^{3+} or Mn^{4+} oxides is brought about by the sorption of the corresponding carbonyls and their subsequent decomposition under the action of $KMnO_4$ or H_2O_2.[116–118] The oxides formed are incorporated into the amorphous regions of PTFE.

In most cases, nanoparticles are prepared in polar solvents that form intermediate complexes with the carbonyls (see Scheme 4), which react with the fluorinated polymers. The main factors influencing the selectivity of the $Fe(CO)_5$ or $Co_2(CO)_8$ reaction with polyvinylidene fluoride (PVF) in the course of their thermolysis have been discussed.[119–121] The results of IR spectroscopy indicate that the adsorption leads to the formation of complexes $[Fe^{2+}(DMF)_6][Fe_3(CO)_{11}]^{2-}$ – PVF and $[Co^{2+}(DMF)_6][Co(CO)_4]_2^-$ – PVF, and made it possible to carry out kinetic studies and to elucidate the mechanism of their degradation. The thermolysis of both intermediates follows the mechanism of first-order reactions; however, the rate constant and the activation energies of these processes are substantially different (Table 2). The thermolysis rate constant of polymer-

Table 2. Reaction rate constants and activation energy of decomposition of different products in systems $M_x(CO)_y$ – PVF (140 °C, DMF).[120]

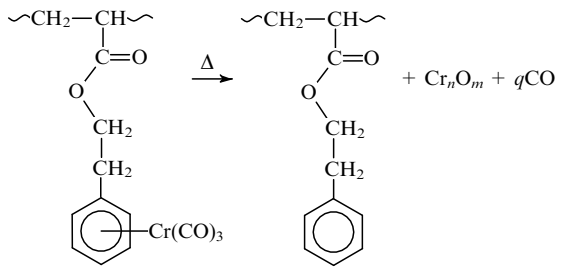
System	$10^{-5}\,k$ /s^{-1}	E_a /kJ mol^{-1}
PVF – $Fe(CO)_5$	8.41	142.59
PVF – $Fe_3(CO)_{11}^{2-}$	12.2	51.62
PVF – $Co(CO)_4^-$	104	45.80

immobilised cobalt carbonyl is one order of magnitude higher than that of iron carbonyl. This is consistent with the fact that the cobalt carbonyl anion is more reactive than the iron carbonyl anion. A very high activation energy of the decomposition of neutral $Fe(CO)_5$ in PVF compared with E_a for the immobilised carbonyl reflects differences in the mechanisms of these reactions. The thermolysis of Fe and Co carbonyls in PVF *in situ* leads to the formation of heterophase metallic domains in the polymeric matrix. When the same carbonyls are bound with the polymer, the homogeneously distributed ferromagnetic particles of 5 – 10 nm in diameter are produced. The mean surface area per particle varies from 80 to 700 nm^2. The electron diffraction analysis of these systems has revealed the formation of γ-Fe_2O_3 and FeF_2 particles from $Fe(CO)_5$, and of Co, Co_2O_3, and CoF_2 from $Co_2(CO)_8$.[120] The appearance of metal fluorides is associated with the involvement in this reaction of the polymeric chain with the cleavage of C – F bonds.

Hence, two parallel processes occur in these systems: the major process leading to the formation of nanoparticles upon the thermolysis and the side process, which consists in the attack of the polymer chain by metal ions and is accompanied by various transformations of the polymer itself (destruction, cross-linking, binding of metallocomplexes). Besides, the secondary carbenium ions formed from PVF (the formation of carbenium salts was also observed in the interaction of halides of transition metals with halogen-containing polymers)[122] are highly reactive and take part in various reactions. Recently, the formation of ZnF_2 was reported[73] as a result of the reaction of atomic zinc with the PTFE surface.

The character of bonding the clusters and nanoparticles with the polymeric matrix and their topography have not been totally clarified to date; nonetheless, it is obvious that the reactivity of the metal centres formed in the course of decomposition is a critical factor controlling the character of interaction between the polymer and the metal particle.

In the thermal degradation (especially, in the oxidative atmosphere), immobilised polynuclear complexes ‡ with volatile ligands may form nanoparticles of metals and their oxides, and sometimes also with admixtures of metal carbides. Thus heating of poly(η^6-phenyl methacrylate) – $Cr(CO)_3$ films at 423 K resulted in the formation of a mixture of chromium oxides enclosed in the matrix of a cross-linked polymer:[124]



In a similar way, the thermolysis of copolymers of acrylonitrile or styrene with (η^4-hexa-2,4-dieneyl acrylate)iron tricarbonyl in air at 473 K leads to the formation of nanoparticles of Fe_2O_3.[109]

‡ The fixation of mononuclear metal carbonyls on polymers[4] and the synthesis of organometallic polymers[123] are reviewed.

The distinctive feature of nearly all polymers of this type is that they decompose without melting, apparently owing to the formation of cross-linked structures. Since the metal oxides are the final products of the oxidative decomposition of any metal-containing polymer, the possibility of the replacement of toxic $Fe(CO)_5$ by polyvinylferrocene[125] has long been debated.

Less often, the carbonyls, which act as metal-forming substances in the preparation of polymer-immobilised nanoparticles by thermolysis, are replaced by other precursor compounds, usually by metal formates, acetates, and oxalates,[126–129] and by organometallic compounds. Recently, a metal – polymer composition of the 'Claspol' type was obtained by the thermolysis of a triethylenediamine complex of copper formate $[Cu(En)_3].(HCOO)_2$ in PS using dimethylformamide as the common solvent.[130] This complex disintegrates at 170 °C to form metallic copper in a highly dispersed state. It is noteworthy that this temperature is 20 °C lower than that of the thermolysis of the initial copper formate, which is explained by the catalytic effect of the polymer on the thermal degradation of this complex. The point is that the reactive centres of the polymer favour the formation of metal particle nuclei, which are precisely the centres of aggregation. This is followed by the thermolysis and redistribution of the copper complex. The maximum quantity of copper that can be incorporated into PS is 10%.

PTFE increases the decomposition temperature of cadmium oxalate trihydrate,[126] while the products of degradation of the latter, in turn, increase the temperature at which an intensive degradation of PTFE begins. The thermal decomposition of the highly dispersed copper formate leads to the formation of a metal – polymer composition (20% – 34% Cu); the maximum on the granulometric curve of nanoparticles corresponds to ~4 nm. No chemical interaction between the components was observed. The decomposition of a fine dispersion of palladium hydroxide in polyvinyl chloride (PVC) results in spatial structures with highly dispersed Pd particles (S_s = 26 m^2 g^{-1}) in the nodes.[131] It is significant that this process results in the increase in the temperature of complete dehydrochlorination of PVC. The thermolysis of cobalt acetate in the presence of PS, PAA, and poly(methyl vinyl ketone) proceeds at a much higher temperature and leads to the formation of metal clusters that catalyse the electroreduction of oxygen.[132]

The preparation of a highly dispersed Cd phase regularly distributed in the PS bulk by mixing PS with dibenzylcadmium in THF followed by removal of the solvent and decomposition of the organometallic compound at 130 °C has been reported.[133] Materials containing 1.4% – 4.3% of metal were obtained from the bisarene complexes $(C_6H_5CH_3)_2M$, where M = Ni, Co, synthesised by the cryochemical method, by their rapid degradation in LPPE at temperatures higher than the complex decomposition temperature.[78] Cobalt nanoparticles (with the mean particle size of ~1.6 nm and narrow particle distribution) were prepared[134] by hydrogenation of the organometallic compound Co(η^3-C_8H_{13})(η^4-C_8H_{12}) in the presence of PVPy at 273 – 333 K. An original method of impregnation of organometallic compounds into the amorphous regions of PS, high-pressure polyethylene (HPPE), PTFE, and polyacrylates followed by their structural modification and formation of clusters has been exemplified with cymanthrene (η^5-C_5H_5)Mn(CO)$_3$.[135] To this end, fluids are used in their supercritical state (CO_2 under a pressure of 8 – 25 MPa at 30 – 40 °C).§ According to another protocol,[139] a precursor, dimethyl(cyclooctadiene)platinum(II) is dissolved in CO_2, and the solution obtained is used to impregnate thin films of poly(4-methylpent-1-ene) or PTFE. The reduction of this system by thermolysis or hydrogenolysis yields polymer-immobilised nanocomposites with the Pt particle size of 15 – 100 nm.

§ The interest in the processes occurring in supercritical fluids has sharply increased over the recent years,[136, 137] especially in the reactions in supercritical CO_2.[138]

Despite the abundance of studies of this sort, the relevant literature does not carry any information on the thermolysis in polymer-immobilised carbonyl-hydrides, substituted (mixed) carbonyls, and mixed metal carbonyls (such as $Co_2Ir_2(CO)_{12}$, $H_3FeRu_3(CO)_{15}$, $Fe_2Ru(CO)_{12}$, or $MM'(CO)_n$, where M = Mn, Re; M′ = Cr, Mo, W), *etc*. The data on the thermolysis of metal carbonyls in reactoplasts are also very meagre. The only thing known is that the heating of the degradable metal carbonyls introduced into an epoxy resin leads to the deposition of nanoparticles on the surface of the polymer formed.[1] Possibly, in this process the highly reactive metal particles initiate the opening of the epoxy ring with the formation of three-dimensional structures.

4. Reductive methods in the synthesis of polymer-immobilised nanoparticles

The reductive methods appear to be the most common techniques for the preparation of polymer-immobilised nanoparticles. They may be divided into two types different in principle. The first type, or the 'impregnation' method consists in the chemical reduction of metals from solutions or suspensions of their salts (to this end, ammoniacal solutions of Cu, Cr, and Ag hydroxides are often used) or in the electrochemical or radiation-chemical reduction in the presence of macroligands. The second type resides on the reduction of mononuclear metal complexes chemically bound with polymers. The first method is more widely applied because it meets better the needs of catalysis. In particular, metal blacks, ultradispersed powders, *etc*. are prepared thereby. For example, Raney nickel is stabilised by incorporating it into the silicone rubber[140] with the subsequent polymer vulcanisation at room temperature.¶

Sols of Au, Fe, and Cr were prepared by the reduction of their hydroxides by hydrazine hydrate in a matrix of water-soluble polymers, and dispersions of particles of Pd (1–2 nm) and Au (1–13 nm) were obtained in synthetic rubber films.[143] The treatment of polymeric films prepared from aqueous solutions of PVAl and $AgNO_3$ with photographic reducing agents (hydroquinone, *p*-phenylenediamine, pyrogallol, *etc*.) yields the corresponding metallocomposite materials.[144] Monodispersed hyperfine powders of gold[145,146] and platinum[147–149] were prepared by the reduction of their salts in the presence of protective colloids.

Natural polymers (gelatin, gum arabic, agar, proteins and products of their hydrolysis, sodium protalbuminate, starch, cellulose and its derivatives) and polymeric compounds soluble in organic media (synthetic rubbers, naphthenic acids) are often used as protective high-molecular-weight compounds in the production of sols of silver, mercury, bismuth, copper, and platinum group metals by the reduction of corresponding ions. β-Cyclodextrin may also be employed as a stabilising agent for colloidal particles of Rh, Pt, and Pd (1–100 nm).[150] Ultrafine particles of Ni (5–20 nm) were prepared by reduction with hydrogen of $Ni(NO_3)_2$ following the diffusion into gel membranes of cellulose acetate.[151] It is significant that the adsorption of ions by protective polymers (see Section III) creates favourable conditions for the concomitant appearance of a large number of embryos (nuclei) of colloidal metal particles. The metal that is reduced is mostly consumed to form these embryos, while only small quantity remains for their growth. As a result, only small nanoparticles are formed, and this is also favoured by the high aggregative resistance of sols.

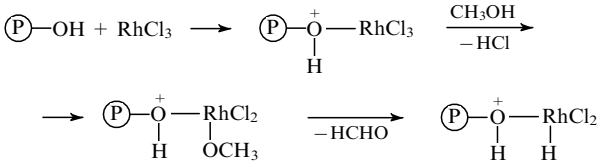
The radiation-chemical and photo-induced reduction is preferred to the reduction by hydrogen when it is necessary to prepare small particles with a narrow size distribution.[152] A characteristic example is the preparation of 'blue silver' in the process of γ-irradiation of slightly alkaline aqueous solutions of $AgClO_4$ containing 2-propanol and PAA.[45] The 'blue silver' is a linear Ag cluster stabilised on a polymer molecule. In the course of radiation-chemical reduction, the Ag clusters are transformed through a number of successive stages into a polymer-immobilised colloidal silver.

The interaction of H_2 with colloidal Pd obtained by the radiation-chemical reduction of Pd^{2+} in an aqueous solution of PAA does not increase the particle size and is accompanied solely by hydrogen sorption on the surface of nanoparticles.[153]

It is noteworthy that the 'impregnation' method does not rule out the chemical interaction between the compound to be reduced and the polymeric matrix. The absence of chemical interaction between the metal and the polymer is rather an exception than the rule. For example, in the systems based on polymers devoid of functional groups (polyacetylene and MX_n) the macromolecule plays the role of a specific ligand; this hampers the multicentre association of complexes and prevents their enlargement.[154] Most probably, the condensation of a metal in a liquid phase occurs at the moment when its ion undergoes reduction and not after the formation of a supersaturated solution of metal atoms. The formation of nanoparticle nuclei occurs spontaneously, basically at the sites of largest concentration of metal ions, whereas their growth results from the reduction of ions adsorbed on the surface. Apparently, this process has much in common with the growth of particles in the course of cryochemical synthesis.

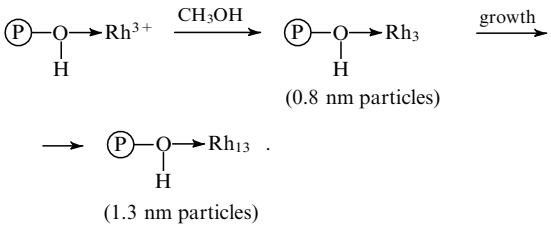
The mechanism underlying the reduction of metal ions chemically bound with polymers is rather complex. It has been elucidated in detail using the formation of clusters of zero-valent Pd, Ru, Rh, Ag, Os, Ir, Pt, Au, and Ni as the examples.[155–158] When solutions of salts of these metals in proton-donating solvents are boiled in the presence of polymers (*e.g*., a solution of $RhCl_3$ in aqueous methanol mixture in the presence of PVA), several chemical transformations take place (Scheme 5).

Scheme 5



At the first stage of this complex process, $RhCl_3$ coordinates with PVA, then an oxonium product is formed, which is further transformed *via* alkoxide into a polymer-bound hydride complex. These reactions lead to a homogeneous colloid resulting from the disproportionation of rhodium hydrides and subsequent growth of particles (Scheme 6).

Scheme 6



The 13-nuclear clusters formed have the structure of a face-centred cubic lattice with a rhodium atom coordination number equal to 12. The clusters are 4 nm in diameter. They interact with the protective polymer owing to electrostatic attraction or to physical adsorption, and possibly to the formation of coordination bonds.

By changing the reaction conditions, the nature of the medium, (ethanol, butanol, toluene–butanol), by introducing additional ligands (*e.g*., PPh_3), or using various polymers (*e.g*.,

¶ Synthetic rubbers may also be vulcanised by salts of unsaturated acids; this results in the formation of vulcanised metallopolymeric structures.[141] Metal–polymer compositions are prepared by introducing dispersed metal (Al, Fe, Cr, Ta, W) powders into oligomers, for example, into trioxyethylenedimethacrylate with subsequent solidification induced by a flux of accelerated electrons.[142]

PVPr, copolymer of MMA with *N*-vinyl-2-pyrrolidone, polyacrylamide gel, *etc*.), one can prepare metallopolymers with cluster particles of different size (0.9–4 nm for Rh^0 and 1.8 nm for Pd^0). These particles are stable in the protective colloid, they have a narrow size distribution and high stability (they remain in the gel upon variation of pH from 2 to 12). Thus, the water-soluble polymers act in these systems as protective colloids, while alcohols play the role of reducing agent.

The reduction of $NiCl_2$ by $NaBH_4$ in ethanol in the presence of PVPr may be used for the preparation of nickel boride sol, it is still more suitable for the preparation of organosols of noble metals. It proved to be very useful in the synthesis of colloidal dispersions of polymer-protected bimetallic Pd–Pt or Pd–Au clusters.[159–161] They were produced by the joint reduction of $PdCl_2$ and H_2PtCl_6 or $HAuCl_4$ in the presence of PVPr (by boiling in methanol or illumination with visible light). The products remained stable for a few months at room temperature. The size of Pd–Pt and Pd–Au clusters was ~1.5 and 3.4 nm, respectively. This method was also used to prepare the polymer-protected bimetallic Pt–Co colloids with Pt:Co ratios of 3:1 and 1:1.[162]

The obstacle to the synthesis of metal colloids based on insoluble polymers is the diffusion of ions to be reduced into the polymeric matrix. For example, reduction of Ni^{2+} with $NaBH_4$ in aqueous methanolic solution in porous isotropic isotactic polypropylene (PP) has been carried out using the method of countercurrent diffusion.[163] The process comprises the following consecutive stages: penetration of metal ions and the reducing agent into the polymeric matrix, in-depth diffusion of reagents described by the Fick's first law, and finally, the chemical reaction itself. The size of the nanoparticles formed depends on the reaction conditions and the parameters of the porous polymeric structure. This technique allows the microencapsulation, in the polymer pores, of metal crystallites (3–10 nm in diameter) assembled in polycrystalline aggregates with the controllable size of narrow distribution. Nickel particles prepared by the reduction in the polymeric matrix resisted oxidation in water for over two weeks, whereas when dried, it remained unoxidised for half a year.[164] At the same time, the nickel obtained in the absence of polymers rapidly oxidised in water and air. A mixture of reduced Ni with a polymer solution proved also to be unstable. Apparently, the shielding with polymers prevents not only further growth of particles but also provides their high resistance to oxidation. It is assumed that the macromolecules can trap and stabilise the nuclei of metallic phase owing to the cooperative interaction of chain segments according to the mechanism of matrix 'recognition' by the growing chain during the matrix polymerisation.[165]

Under the action of different reducing agents, the immobilised complexes (including the mononuclear ones) may undergo different transformations leading to the increased nuclearity. For example, compounds of Rh, Ru, and Pt fixed by ion exchange on the completely fluorinated resin Nafion (Fig. 3) undergo reduction in a flow of H_2 at 473 K with formation of metallic clusters with sizes of 2.8, 3.3, and 3.4 nm, respectively.[50, 51, 166] Cations of Ag, Cu, Rh, Ru, Pt, and Ir bound to perfluoroethylenesulfonic acid or to a partially sulfated PS oxidise CO, NO, NH_3, N_2H_2, and C_2H_2 at 373–473 K, and this process leads to the formation of metal particles 2.5–4.0 nm in diameter. [167]

Generally speaking, the formation of polymer-immobilised metalloclusters in the course of catalytic reactions is a rather common phenomenon, especially in complex organometallic catalysts deposited on polymers.[4, 168] This phenomenon may be the reason for both the activation of these catalysts (*e.g*., in hydrogenation reactions) and their inactivation (in particular, in reactions of ionic-coordinational polymerisation). Significant data on the transformations of immobilised Ni^{2+} in the course of ethylene dimerisation [169] were provided by measurements of magnetic susceptibility in strong magnetic fields (up to 70 kŒ) and low temperature (4.2 K).[170] Under these conditions, the susceptibility of different spin states depends non-linearly on the magnetic field strength (described by the Brillouin's function), which made it possible to establish the distribution of nickel states over the magnetic moment values. Evidence has been provided for the formation of one-nm microparticles containing 10–30 Ni atoms that display no ferromagnetic (supermagnetic) properties and are polymer-immobilised clusters with ferromagnetic exchange. In the polymer-immobilised cobalt systems (the catalysts of butadiene polymerisation) a considerable proportion of Co^{2+} ions are reduced to the metallic state in the absence of polymerised monomer. In any case, 90% of total ferromagnetic cobalt is localised in the relatively large particles 10 nm in diameter.[171]

There are other numerous methods for the chemical reduction of metal salts in the presence of polymers yielding polymer-immobilised nanoparticles.

5. Electrochemical methods for the preparation of polymer-immobilised nanoparticles

The electrochemical and electroflotation methods are widespread techniques for the preparation of chemisorbed macromolecules bound to colloidal metal particles generated *in situ*. Reactions of electrochemical polymerisation are heterogeneous: they are initiated on the electrode surface, while other stages (chain growth or termination) occur, as a rule, in the liquid phase.[172] The yield of a polymer depends on the chemical and physical nature of the electrodes and their surface, electrode overvoltage, potential under which the reaction occurs, and electrical current density. The nature of the electrode material (metals or alloys, thin metallic coats, *etc*.) determines the characteristics of electron transfer reactions (initiation) and polymerisation. Such types of electrode processes as direct electron transfer between the electrode and monomer, cathodic deposition and anodic solubilisation of metals are optimum for the electrochemical polymerisation. Metal salts, which are the precursors of nanoparticles, may act as specific electrochemical activators influencing the process through direct chemical binding to the monomer and by virtue of transfer, decomposition, or catalytic effect. Nonetheless, the method of electrochemical polymerisation has found only limited use in the preparation of polymer-immobilised nanoparticles.

A procedure for the preparation of metal organosols by electrolysis in a two-layer bath proved to be more suitable.[1, 2] The upper organic layer of the electrolytic bath is a dilute solution of a polymer in an organic solvent (sometimes, supplemented with a minor quantity of surfactant), which interacts near the interface with the nascent colloidal metal particles.

Less often, nanoparticles are formed on polymers by means of electrophoretic and electrochemical deposition of metals from solutions onto polymeric suspension that is used as an additive in the electrolysis.[173] The metallopolymer formation results from the polarisational interaction of polymer and metal particles during deposition on the electrode and the chemisorptional interaction of macromolecules with the surface of metal at the moment of its reduction. This process includes several stages, such as discharge of M^{n+} ions, crystallisation of deposited metal, a number of parallel electrochemical reactions, *etc*. The contributions from different stages depend on the concentration of the dispersed phase and electrolyte, and the particle charge. The ratio between these contributions determines the transition from polymer-immobilised nanoparticles to electrochemical plating with high metal content.

Owing to the shielding properties of polymeric particles, the surface of the electrode and metal particles is blocked, and a specific type of polarisation known as electrophoretic polarisation appears, which has an appreciable effect on the process of metal electrocrystallisation. The polymer is often deposited as a separate phase (liquid or solid) on the electrode surface. Therefore, the transfer of ions, electrons, or neutral particles through the layer of the new phase may face noticeable kinetic restrictions depending on the permeability of polymeric coating. Coating the anode with an insulating polymer layer reduces the electrode activity and the

current amplitude. This inconvenience can be partly eliminated by the use of liquid electrodes, *e.g.*, the dropping mercury electrode.

Let us consider some characteristic examples. Colloidal Pd particles are obtained by the electrolysis of aqueous solutions of palladium chloride at pH 1 in a two-layer bath in the presence of a hydrocarbon solvent and epoxy dianic resin or PVA.[174] Electrolysis results in the formation of organosols of colloidal palladium stabilised by the chemisorptional bonds of the polymer. The products remaining after the removal of solvent and residual electrolyte are metallopolymers containing up to 90% – 95% of Pd. They are formed under high cathode polarisation with abundant concomitant elimination of hydrogen adsorbed on the nanoparticles (5.5 – 7.8 nm in diameter).

The combined deposition of Ni nanoparticles and PTFE suspension from the sulfamic-acid electrolyte for nickel-coating at room temperature leads to polymer inclusion into the Ni deposit (up to 20 mass %). The process is controlled by varying the cathode current density and the concentration of suspension introduced.[175] The relationship between the homo- and heterocoagulational interactions of metal particles and polymer is determined by the rates of electrochemical deposition and isolation of metal in the Ni – PTFE systems.[176]

In turn, the electrode material may become the precursor of nanoparticles of noble metals; polypyrrole films containing functional groups such as 4,4′-dipyridyl, alkylammonium, and others may serve as protectors in this case.[177 – 180] Bimetallic Pd – Pt or Pd – Rh nanoparticles incorporated into such films are also used for the electrocatalytic hydrogenation.[181] Fine dispersions of iron powders ($\sim$200 nm) formed electrochemically may be used as modifying coats of various materials.[182]

Thus, the effect of polymeric dispersions on the reduction of metal ions depends on the concentration and composition of the electrolyte and the dispersed phase, charge and size of polymeric particles, and the mode of electrodeposition.

The thermal techniques have substantial advantages over the electrochemical ones because the latter occur with considerable degradation of the dispersive medium, noticeable oxidation of the colloidal particles formed, *etc.*

6. Preparation of polymer-immobilised nanoparticles at the polymerisation (polycondensation) stage

Of special interest are the methods including simultaneous formation of the matrix and nanoparticles. This large group of techniques is reported mostly in the patent literature. The early studies [183, 184] have already demonstrated the ample possibility of initiating the polymerisation of vinylic monomers by intensive mechanical dispersion of certain inorganic substances, including metals (Fe, Al, Mg, Cr, W). The degree of polymerisation of monomers (styrene, vinyl acetate, acrylonitrile, MMA) depends on the dispersion intensity. The role of catalyst and initiator is played by freshly formed metal surfaces: they are the sites of electron transfer from the superficial metal atoms to the monomers to form initiating particles of ion-radical type. Colloidal particles of Au, Tl, and Pt were found to influence substantially the bulk and solution polymerisation of styrene.[185]

Sometimes, organometallic compounds are used instead of compact metals in the preparation of polymer-immobilised nanoparticles. The addition of relatively small quantities of organocadmium compounds has virtually no effect on the initial rate of radical polymerisation of MMA.[186 – 189] In this case, nanoparticles may be obtained by two routes: from organometallic compounds (*e.g.*, from bis(triethylgermyl)cadmium) that decompose at a temperature close to that of polymerisation or by heating the composition formed including a component whose decomposition temperature is higher than that of MMA polymerisation (*e.g.*, alkyl derivatives of cadmium). Interestingly, the organocadmium compounds of this type diminish considerably the molecular weight (M_n) of the PMMA formed. For example, its M_n decreases from 800 to 60 kDa in the presence of 2.5 mass % of these compounds. Chain transfer on the organometallic compound may be probable reason. The formation of nanoparticles in the monomer – polymer mixture may be schematically represented as follows (Scheme 7).

Scheme 7

$$[(C_2H_5)_3Ge]_2Cd \xrightarrow[\Delta]{\dot{R} + MMA} Cd + 2\dot{G}e(C_2H_5)_3 .$$

(formation of nanoparticles immobilised in PMMA)

(initiation of MMA polymerisation; macroradical termination; recombination)

The size of Cd nanoparticles formed at the polymerisation stage increases as the content of the initial component in the monomeric mixture increases: from 6.3 nm at 8 mass % to 300 nm at 40 mass %. Compositions formed upon heating contain larger nanoparticles that have a regular hexagonal structure characteristic of Cd crystals.

In the processes under consideration, the critical parameters are the ratio of the rates of decomposition of the organometallic component and the polymerisation of the corresponding monomer, and the sedimentational resistance of metal dispersions formed in the monomer. Apparently, this also holds true for solidifying systems, for example, for the thermally generated epoxy-thiocol resin, into which colloidal Pb is incorporated at the moment of its formation by thermolysis.[190] In this case, however, one should also take into account the internal stresses existing in solidified systems.[53]

High stability is characteristic of nanoparticles prepared *in situ* by combining photopolymerisation (acrylamide and *N*,*N*′-methylene-bis-acrylamide, non-filtered light from a DRSh-250 mercury lamp), and photoreduction of highly stable Ag^+ ions.[76] In the presence of atmospheric oxygen, the nascent specimens remain stable for a few weeks, and films formed remain unaltered for a few months. The size of Ag particles ($\leqslant$20 nm) is comparable with that of nanoparticles prepared by the method of combined low-temperature condensation of vaporised metals. A modification of this method was reported recently.[191] It consists in the combined condensation, on a support refrigerated with liquid nitrogen, of the vapour of metals (Ag, Pb, Cd, or Mg) and monomers capable of low-temperature polymerisation (specifically, *n*-xylylene), which yields poly-*n*-xylylene films with regularly distributed nanoparticles more or less homogeneous in size. The formation of these films was induced by UV irradiation at 80 K or heating to 130 – 160 K.

Other modifications of this method for the preparation of nanoparticles in polymers have also been reported. Let us note here only one of them, in which the catalysts containing highly dispersed particles of transition metals immobilised in polymeric films were obtained by the electrolytic oxidative polymerisation of a monomer derived from mercaptohydroquinone containing metals of platinum group incorporated by electrochemical deposition.[192]

Not all of the approaches considered in this section are equally developed. The priority is given to the reduction techniques. The role of the dispersive phase is mostly played by carbon-chain polymers and less often, by condensation-type polymers. The immobilisation of nanoparticles is nearly always accompanied by interaction of the particles formed with the matrix, in contrast to mechanical mixtures of metals with polymers.

V. Polymer-analogous transformations in the immobilisation of metal clusters

Although the polymer-immobilised systems considered above are characterised, as a rule, by high dispersity, by homogeneous distribution of nanoparticles over the polymer bulk, and sometimes by the irreversible sorption of macromolecules on the surface of colloidal particles, which remain in the gel state over a

wide range of pH, the production of new materials on the basis of individual clusters or ensembles of several atoms (particles 1.5 – 5.0 nm in diameter with characteristic structures) is not an easy problem and requires the development of novel approaches. One of these, the assembly of polynuclear complexes from mononuclear ones on polymers, was analysed above (Section IV). It is often used for the immobilisation of nanoparticles on non-functionalised polymers. There are reports [193 – 195] on the dispersion of metal clusters in polymers. Several aggregates of organometallic compounds of low nuclearity of the type $[MR]_n$, where M = Cu and Ag, R is a ligand, and $n = 1-4$,[196] are regarded, sometimes without sufficient discussion, as polymeric clusters.

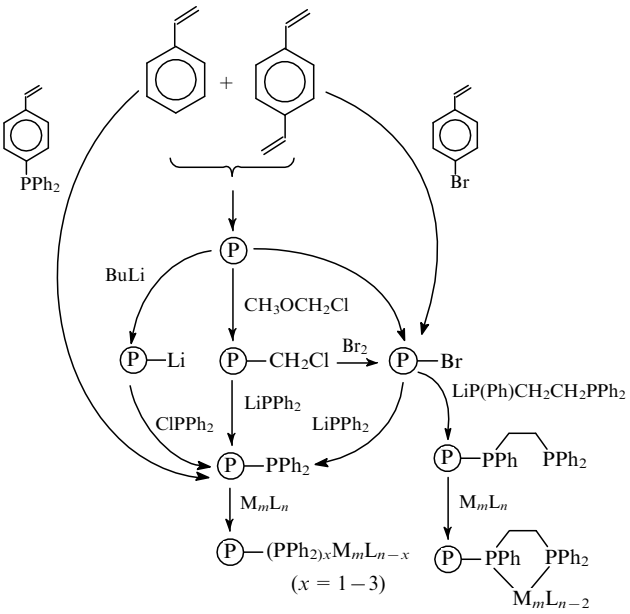
1. Immobilisation of clusters of monometallic type

Recently, the techniques devised for the immobilisation of clusters of known composition (M_mL_n) on polymers have found rather extensive use. The role of ligand is most often played by functionalised macroligands, *e.g.*, phosphorylated copolymers of styrene with divinylbenzene and also modifications of these systems, such as triple block-copolymers styrene – divinylbenzene – vinyl-(styryl)diphenylphosphine. Polymeric materials are sometimes used in the form of powders, often as particles 0.1 – 0.05 mm in size with high specific surface and porosity, and less often as thin films. The preparation of functionalised phosphorus-containing polymers and micron-sized (11 μm) films on their basis has been described in sufficient detail.[197] Metalloclusters are bound by means of ligand or ion exchange, oxidative addition, decarbonylation, *etc*. The synthesis of phosphorylated PS and copolymers styrene – divinylbenzene (CSDVB) and its binding with clusters may be schematically described by the Scheme 8.

The first attempts to prepare polymer-immobilised clusters date back to the 1970s.† There is a report [201] describing the immobilisation of $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$ on Ⓟ–PPh_2 (where Ⓟ is CSDVB). Clusters occasionally undergo decomposition to form mononuclear complexes as, for example, in the case of photogeneration of polymer-bound iron carbonyls.[202] The synthetic methods used to bind intact carbonyl clusters on the surface of polymers have been reviewed,[203] and there are reports on the immobilised triosmium clusters [204] and tetrairidium clusters.[205] Of interest is that the carbonyl cluster of tetrairidium fixed on a polymer is obtained *in situ* from a mononuclear complex.[203]

The basic polymer-immobilised clusters prepared by polymer-analogous transformations are presented in Scheme 9. The structure of these species can be established by comparing the IR and NMR spectra of the starting, model (clusters with the known structures), and final products, specifically carbonyl-containing ones (Table 3). This refers primarily to the trinuclear clusters of Ru and Os the spectra of which are highly informative owing to the presence of bridging ligands and high symmetry. These methods are also often employed in the studies of clusters of higher nuclearity, *e.g.*, Ir_4 (Fig. 5). It is the latter that are considered as the structurally characterised objects. Of all other currently employed methods, the EXAFS, UV, scattering of photoelectrons, and γ-resonance spectroscopy deserve mention.

Scheme 8



† The process develops in two parallel directions: binding of clusters by polymers and by metal oxide supports (SiO_2, Al_2O_3, MgO, TiO_2, ZnO, *etc*.). The most usual support is silica gel, including the phosphorylated one.[216 – 218] The pores of zeolites were found to be the sites of formation of grafted anionic molecular clusters $[Rh_6(CO)_{14}]^{2-}$, $[Os_{10}C(CO)_{24}]^{2-}$, and others stabilised on the surface of MgO.

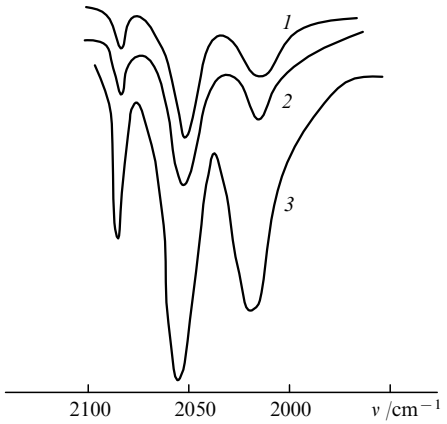


Figure 5. IR spectra of Ⓟ–$PPh_2Ir_4(CO)_{11}$ (*1*), Ⓟ–Diop $[Ir_4(CO)_{11}]_2$ (*2*), and $Ir_4(CO)_{11}PPh_3$ (*3*) in methylene chloride.

Scheme 9

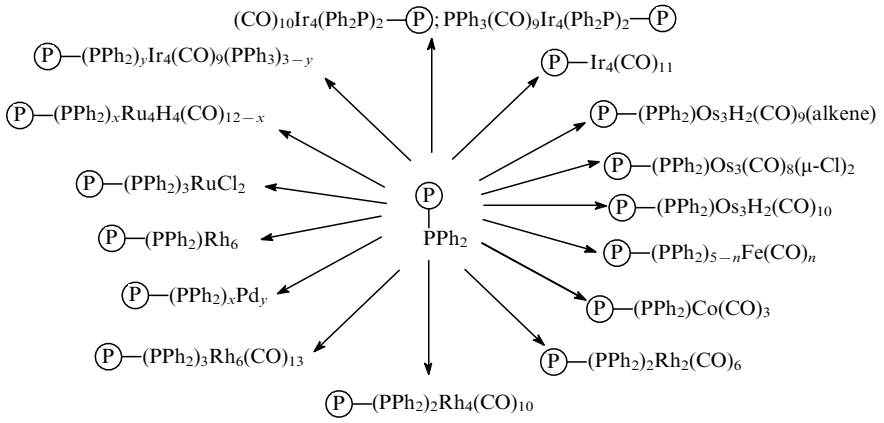


Table 3. IR and PMR spectra of molecular and polymer-immobilised carbonyl clusters.

Cluster	IR Spectra ($\nu_{C=O}$ /cm^{-1})	PMR Spectra (δ /ppm)	Ref.
$Ir_4(CO)_{11}PPh_3$ [a]	2088, 2056, 2020, 1887, 1847, 1825		206
(P)—$PPh_2Ir_4(CO)_{11}$ (membrane)	2087, 2055, 2017, 1848		206
$Ir_4(CO)_{10}$Diop [a]	2070, 2040, 2011, 1986, 1870, 1833, 1791		206
(P)—Diop$[Ir_4(CO)_{11}]_2$ (membrane)	2088, 2057, 2020, 1845		206
(P) Diop$[Ir_4(CO)_{10}]$ Diop$[Ir_4(CO)_{11}]_2$ (membrane)	2068, 2040, 2012, 1991, 2088, 2054, 2021		207
$Os_3(CO)_{10}Cl_2$ [b]	2116, 2081, 2069 2027, 2015, 1993, 1989		207
$Os_3(CO)_8Cl_2(PPh_3)_2$ [b]	2079, 2014, 2004, 1967, 1943		207
((P)—$PPh_2)_2Os_3(CO)_8Cl_2$ (block-copolymer)	2096, 2073, 2036, 2007, 1997, 1959, 1939		207
(P)—$PPh_2Os_3(CO)_{10}Cl_2$ (statistical copolymer)	2096, 2073, 2060, 2029, 2007, 1994, 1955, 1940		207
$(PPh_3Cu\text{-}\mu_3)FeCo_3(CO)_{12}$	2074, 2012, 1978, 1972, 1850		208
((P)—$PPh_2-Cu\text{-}\mu_3)FeCo_3(CO)_{12}$	2065, 2000, 1969, 1956, 1840		208
$(PPh_3Au\text{-}\mu_3)FeCo_3(CO)_{12}$	2075, 2003, 1969, 1930, 1823		208
((P)—$PPh_2-Au\text{-}\mu_3)FeCo_3(CO)_{12}$	2066, 1993, 1960, 1930, 1813		208
$(\mu\text{-}H)Os_3(\mu\text{-}4\text{-}VPy)(CO)_{10}$ [c]	2101, 2061, 2051, 2020, 2008, 2000, 1988, 1973	8.01, 7.25, 6.25, 5.72, −14.85 [$Os_2(\mu$-H)]	209
$(\mu\text{-}H)Os_3(\mu\text{-}4\text{-}VPy)(PPh_3)(CO)_9$ [d, e]	2087, 2047, 2012, 2004, 1997, 1984, 1975, 1945	7.32, 6.51, −5.71, −14.13 [$Os_2(\mu$-H)]	209
$Os_3H(CO)_9Py$ [c]	1940, 2040,	10.5, 12.0 13.75	210
$(\mu\text{-}H)Ru_3(\mu\text{-}SCH_2CH=CH_2)(CO)_{10}$ [c, d]	2108, 2069, 2059, 2022, 2020, 2000, 1988, 1955 (ν_{CO}), 1636 ($\nu_{C=C}$)	5.87, 5.28, 2.82, −15.38 ($Ru_2(\mu$-H)	209
$Rh_6(CO)_{15}(4\text{-}VPy)$ [c, f]	2104, 2068, 2038, 2010, 1788 (ν_{CO}), 1619 ($\nu_{C=C}$)	7.39, 8.88, 6.68, 6.10, 5.68	211
$Rh_6(CO)_{14}(4\text{-}VPy)_2$ [c, f]	2090, 2056, 2028, 1760 (ν_{CO}), 1619 ($\nu_{C=C}$)	7.35, 8.81, 6.65, 6.06, 5.63	211
(P)—$PPh_2Fe(CO)_4$	2060, 1975, 1940, 1897, 1875		212
$Fe(CO)_4PPh_3$	1875		

[a] Diop is 2,3-isopropylidenedioxy-1,4-bis(diphenylphosphino)butane moieties; IR spectrum in CH_2Cl_2; [b] IR spectrum in cyclohexanone; [c] ^{1}H NMR spectrum in $CDCl_3$; [d] IR spectrum in hexane; [e] ^{1}H NMR spectrum in CD_2Cl_2. [f] IR spectrum in chloroform.

The features of polymer-immobilised clusters formation may be reduced in the most general form to the following statements.[213–218] If the concentration of phosphine groups in the macroligand is low (*i.e.*, less than 2% of benzene rings are phosphorylated, see Scheme 8) or the PPh_2 groups are randomly distributed, then polymer-immobilised clusters are formed in which the metal cluster, particularly, of Ir, is bound with one PPh_2 group of the polymer. In the case of higher concentration of PPh_2 groups (with over 3% of functionalised benzene rings), a mixture of clusters is formed that are bound with one or two groups of the polymer. The product with two bonds is virtually the only one formed in the case of the styrene–divinylbenzene–vinyldiphenylphosphine block copolymer containing 8%–15% of PPh_2 groups.

The ligand exchange of the functional groups carrying equivalent numbers of electrons is a typical mode of immobilisation of clusters that undergo fast dissociation, which is especially characteristic of clusters of the $H_4Ru_4(CO)_{12}$ type. The exchange between the phosphine ligands of clusters and the phosphorus-containing groups in the polymer occurs under milder conditions than that involving the carbonyl ligands. Thus, an attempt to bind the carbonyl $Ir_4(CO)_{12}$ with a phosphorus-containing polymer has failed. Therefore, use is commonly made of mixed phosphine- and carbonyl-containing clusters as the precursors of polymer-immobilised nanoparticles (see Scheme 9).

In some cases, the immobilisation process leads to the appearance of small aggregates with indefinite structure. These polymer-bound particles can in principle be carbonylated or decarbonylated with the formation of clusters of definite structure. The

reaction conditions markedly affect the binding of clusters and the polymers. When $Rh_4(CO)_{12}$ reacts with Ⓟ−PPh_2 in hexane at 50 °C, binuclear clusters are formed.[216] When this reaction is carried out in benzene containing $Rh_6(CO)_{16}$, the reactor walls become covered with black spots of deposited atomic rhodium 2.5–4.0 nm in diameter (*i.e.*, about 100 Rh atoms in each spot).[217] The decrease in the reaction temperature and the use of CO lead to the immobilisation of $Rh_6(CO)_{13}(PPh_3)_3$ clusters. The increase in the temperature affects noticeably the behaviour of immobilised Ru clusters: they dissociate at 100–150 °C to form crystalline ruthenium. Interestingly, the cluster anion $Ru_5Cl_{12}^{2-}$ cannot penetrate inside the polymeric matrix for steric reasons, and an attempted binding to the PPh_2 group resulted in the dissociation of this anion with eventual formation of immobilised mono- and bi-nuclear complexes. Along with the immobilisation, decarbonylation may occur, which is particularly characteristic of the Fe and Co clusters, apparently because of similar energies of M−M and M−CO bonds (about 113 kJ mol^{-1}). The addition of $Fe_3(CO)_{12}$ to Ⓟ−PPh_2 leads to the fragmentation and formation of a monosubstituted complex Ⓟ−$PPh_2Fe(CO)_4$ and traces of Ⓟ−$(PPh_2)_2Fe(CO)_3$.[195] It is noteworthy that the homogeneous reaction of $Fe_3(CO)_{12}$ with the excess of PPh_3 yields nearly equal quantities of mono- and di-substituted products. Thus, the polymeric ligand brings about definite steric control. Subsequent thermal or photochemical impacts result in the decomposition of mononulcear carbonyl complexes with the formation of 'ligand-free' clusters dispersed in the polymer.

Of other phosphorus-containing polymers used for the immobilisation purposes, the most interesting seems to be the macroligand modified by optically active groups of 2,3-isopropylenedioxy-1,4-bis(diphenylphosphino)butane on which the cluster fragments of $Ir_4(CO)_{12}$ may be immobilised.[219]

The distribution of functional groups and clusters that are formed over the bulk of tha polymer is of principal significance, since the homogeneity of dispersion is a sign of the isotropy of the polymeric material. In this context, scanning electron microscopy was used to study the distribution of P and Pd along the diameter of the spherical granules of immobilised three-nuclear Pd clusters (Fig. 6).[220] The immobilisation may be performed in such a way so as to allow either uniform distribution of metal clusters along the diameter of the granule (2% of cross-links) or their preferential localisation in a thin subsuperficial layer (20% of cross-links) 0.2 mm thick, the diameter of the granule being 1 mm. The phosphorus-containing groups are distributed uniformly over the entire thickness of granules. The structure of the polymer-

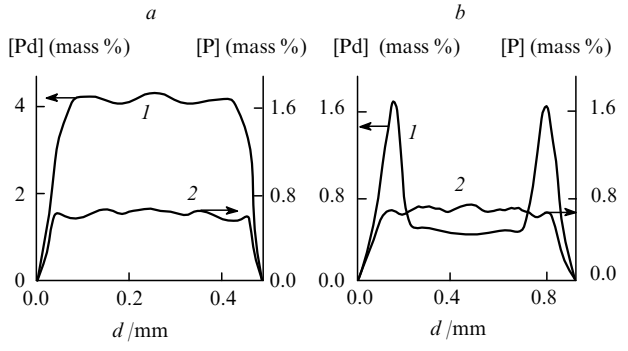
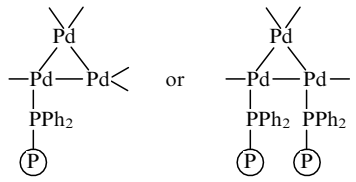
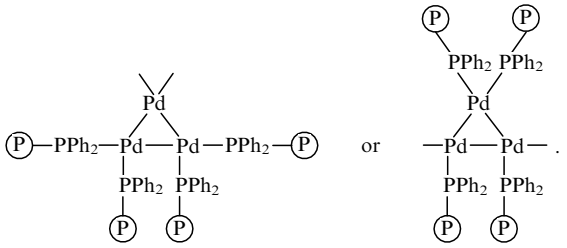


Figure 6. Distribution of palladium (*1*) and phosphorus (*2*) as a function of granule diameter in the palladium-immobilised phosphorylated polystyrene with the cross-linking degree of 2% (*a*) and 20% (*b*).

immobilised clusters depends on the [P]:[Pd] ratio. In the case of polymers with 2% of cross-links and [P]:[Pd] < 1, the structure may be schematically presented in the following form:



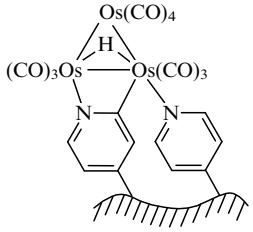
However, one can hardly imagine, at least for steric reasons, the structures that would be formed at [P]:[Pd] > 1:



Data on the immobilisation of clusters by polymers with other functional groups, *e.g.*, nitrogen-containing (aminated PS, P4-VPy, amino-containing ion-exchange resins of Amberlyst A-21 type, *etc.*) are more scarce. Carbonyls $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$, and $Rh_2(CO)_4Cl_2$ interact with aminated PS resulting in Ⓟ−$CH_2NMe_2HRh_x(CO)_y$ compounds.[221] The product of the Os_3 cluster binding by this ligand has the composition $HOs_3(CO)_{11}N^+Et_2CH_2CH_2$−Ⓟ.[222] Similarly $Ru_3(CO)_{12}$ is bound to macroporous chelating polymers functionalised with dipyridyl, 2-aminopropyl, 2-aminophenyl, and other groups. An anionic trinuclear iron cluster is immobilised through the NR_4^+ group on a 10 μm-thick ion-exchange membrane. $[Pt_{15}(CO)_{30}]^{2-}$ cluster is bound by the hydrophilic polymer QAE-Sephadex containing diethyl(2-hydroxypropyl)aminoethyl groups.[223]

The interaction of metal clusters with the amino-containing macroligands, contrary to that with the phosphorus-containing macroligands, yields a large number of by-products, especially when the polymer carries the primary and secondary amino groups. For example, the reactions involving carbonyl clusters of ruthenium and osmium lead to the activation of α- and β-C−H bonds, *trans*-alkylation (at 25–45 °C), and even the cleavage of C−N bonds (at 125–143 °C). The latter refers also to the interaction of tertiary amines with Os_3 clusters.

The mechanism underlying the binding of $Rh_4(CO)_{12}$ clusters by the 4-VPy macromolecules is not completely clear. The interaction of $Os_3(CO)_{12}$ with 4-VPy is carried out in DMF under CO for 3 h at 110 °C.[210] The structure of the product is difficult to interpret: the IR spectrum reveals two intense absorption bands with maxima at 2040 and 1940 cm^{-1}. These data in combination with those from ^1H NMR (Table 3) allowed an inference that the cluster fixation involves two pyridine rings of the polymer of which one is chelating. This mode of binding becomes possible owing to the flexibility of the polymeric chain.



Note also that the preservation of the polynuclear structure or its disintegration depend also on the nature of the proper ligand groups of the cluster. As a rule, the contribution to the cluster energetics from the ligand environment is rather large and diminishes as the nuclearity increases.[21] In the binding of the acetate complex $[Rh_2(OCOCH_3)_4]$ by polymers containing 3(5)-methylpyrazole or imidazole groups,[224] the binuclear structure is preserved and the rhodium retains its oxidation state 2+, whereas

in its binuclear complexes with acetonitrile, sulfate, and hexafluoroacetylacetonate the cleavage of the Rh—Rh bond occurs with the increase in Rh oxidation state. Thus, the cleavage of the Rh—Rh bond is favoured by the labile ligands which can be substituted by the amino groups, while in the case of binuclear Rh^{2+} complex the contracting action of bridging acetate groups favours the preservation of the initial structure.

The O- and S-containing matrices, including polymeric alcohols and ketones, are less often used for the immobilisation of clusters. The binding of an Os_3 cluster to polymeric alcohols follows, as in the case of inorganic oxides, the mechanism of oxidative addition:[225]

$$\text{Ⓟ}\!-\!CH_2\!-\!CH_2\!-\!OH + Os_3(CO)_{12} \longrightarrow$$
$$\longrightarrow \text{Ⓟ}\!-\!CH_2\!-\!CH_2\!-\!O\!-\!Os_3H(CO)_{10}.$$

High stability is characteristic of di- and tri-nuclear Ru complexes of the type $Ru^{3+}-O-Ru^{4+}-O-Ru^{3+}$, that are readily bound by the ion-exchange resin CR-10 containing iminodiacetate groups.[226]

Metal clusters can also be immobilised on natural cyclodextrins.[227] The cavity of γ-cyclodextrin, in contrast to that α- and β-cyclodextrins, is large enough to accommodate not only metal ions but also bi-, tri-, and even tetra-nuclear clusters (Fig. 7). It is significant that the incorporation of clusters into the γ-cyclodextrin cavities increases considerably their stability. For instance, the tetranuclear Co cluster dissociates at 393 K, whereas the product of its interaction with γ-cyclodextrin disintegrates only above 473 K.

Formally polynuclear formations, such as 12-heteropolyacid of Keggin type $H_n[XM_{12}O_{40}]$, where X stands for heteroatom and M = Mo or W, can also be immobilised on polymers. When they are stirred with 4-VPy at 30–35 °C, a product is formed in which, according to IR spectroscopy and chemical analysis data, one $H_4[SiMo_{12}O_{40}] \cdot 13H_2O$ molecule binds four protonated vinylpyridine units, and $H_3[PMo_{12}O_{40}]$ binds three such units.[228] The repeating units in the structures formed have the formulae $(H4\text{-}VPy)_4[SiMo_{12}O_{40}]$ and $(H4\text{-}VPy)_3[PMo_{12}O_{40}]$. The same type of binding is observed in the immobilisation of 12-heteropoly acids on water-soluble polyelectrolytes, *viz*., alkylated poly-(2-methylvinylpyridine), and poly(dimethyldiallylammonium) chloride:[220] the negative charge of the heteropolyanion is compensated by positive charges of the polymeric chain.

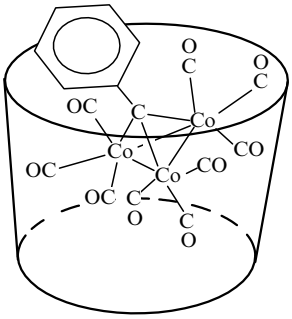


Figure 7. Supposed structure of an inclusion compound formed by a cluster complex of Co and γ-cyclodextrin.

2. Polymer-immobilised heteropolymetallic compounds

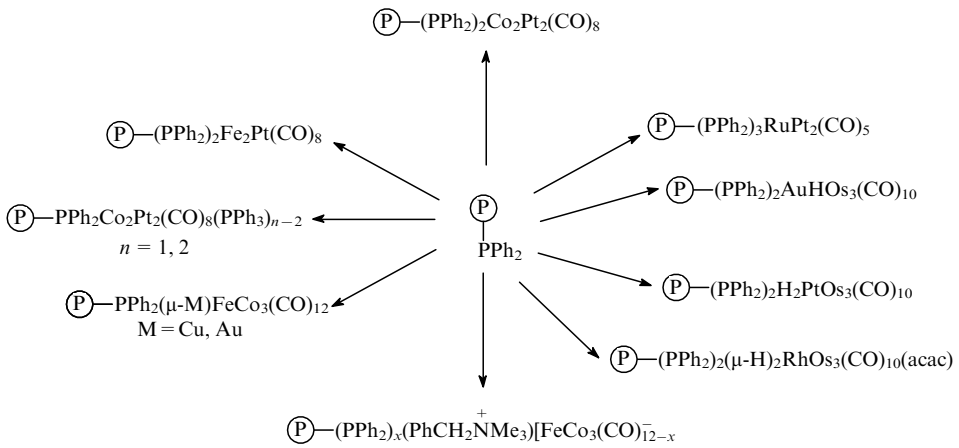
It is known that the heterometallic polynuclear centre is preferred to the monometallic one in the solution of numerous problems, in particular, in the field of catalysis. Immobilised particles of this type may be regarded as models of bimetallic catalysts that find industrial use for the reforming of petroleum fractions. However, in contrast to the industrial alloy-based catalysts, the bimetallic clusters are structurally homogeneous.

The binding of heterometallic clusters and the identification of the products may be based, as a rule, on much the same approaches as those used for the immobilisation of monometallic clusters. Usually, they are assembled from monometallic complexes or clusters (for example, through the joint decomposition of $H_2PtCl_6-Fe(NO_3)_2$ or $Rh_4(CO)_{12}-CoCl_2 \cdot 6H_2O$ mixtures in polymers). There are strong grounds for stating that bimetallic clusters are formed in colloidal dispersions of Pt and Pd stabilised by PVPr [159–161] at the initial molar ratio [Pd] : [Pt] = 4 : 1. In some instances, the preparation of required products is based not on the monomeric clusters but rather on the cluster compounds with different metals. Thus ion-exchange resins were brought into reaction with mixtures of $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$ in the molar ratio from 3 : 1 to 1 : 1.[219]

In the immobilisation, the preference is given to the heterometallic clusters with identified structures.‡ In most cases, the matrix is formed by Ⓟ—PPh_2, and the immobilisation is performed by means of ligand or ion exchange. A reliable technique for the identification of the structure of the polymer-bound products is comparison of the IR spectra of their carbonyl groups

‡ The number of known compounds in which one molecule contains several metal species exceeds 100. The common principle of their synthesis consists in the substitution of one metal by another in high-symmetry metallopolyhedrons with the preservation of the total number of cluster valent electrons and the type of ligands. The most common are the heterodi-, heterotri-, and heterotetra-metallic clusters obtained by addition, substitution, elimination, and restructuring. Their stability is enhanced by centring with μ_3-bridges consisting of elements of the main subgroups (specifically, C, S, P). The common aspects of the synthesis of these compounds, their structure, and classification based on the topology–geometry principle have been reviewed.[229]

Scheme 10

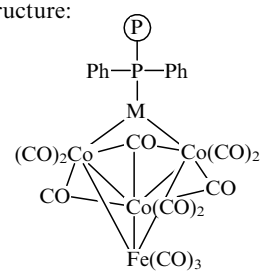


with the spectra of low-molecular-weight models. Typical examples of the immobilisation of intact heterometallic clusters on Ⓟ–PPh_2 are shown in Scheme 10.[3, 207, 214, 230, 231]

Also worthy of note is the binding of $H_2FeOs_3(CO)_{13}$ by cross-linked macroporous chelating polymers.[232] There are reports of the immobilisation of $Co_2Rh_2(CO)_{12}$ on Dowex-1 ion-exchange resin,[233] as well as of $H_2FeRu_3(CO)_{13}$, $[FeRh_4(CO)_{15}](NMe_4)_2$, and $Rh_{4-x}Co_x(CO)_{12}$ (x = 2, 3) on different macroligands. The mechanisms of these reactions remain obscure.

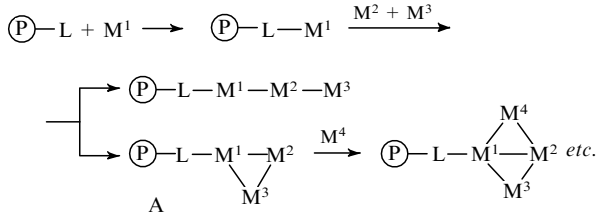
The binding of bimetallic Keggin heteropolyacids, *e.g.*, $H_6[CoW_{12}O_{40}]$,[228] to P4-VPy is analogous to that of monometallic ones. The repeating units have the composition $(H4\text{-}VPy)_4H_2[CoW_{12}O_{40}]$. In principle, similar processes can occur with polyoxoanions of niobium-containing polytungstates, such as $[(CO)_2Rh]_5[Nb_2W_4O_{19}]_2^{3-}$, $[(CO)_2Ir]_2H[Nb_2W_4O_{19}]_2^{5-}$ and others.[234]

The compounds mentioned above are formally of the trimetallic type. The trimetallic clusters bound with Ⓟ–PPh_2 are obtained by the assembly method, *i.e.*, through the interaction of a polymer with $MPPh_3Cl$ (M = Cu or Au) and subsequent treatment of the product with the tetranuclear bimetallic cluster $FeCo_3(CO)_{12}$.[208] The cluster thus obtained has the following structure:



The general strategy for the preparation of heterometallic clusters possessing high nuclearity may be described by Scheme 11.

Scheme 11



Most probably, the reaction involves the formation of heterometallic rings. The trimetallic units of type A serve as building blocks in the chemistry of clusters.[235]

The polymer-immobilised clusters of polymetallic type are more stable than the initial ones: the decomposition temperature of the cluster $(PPh_3)CuFeCo_3(CO)_{12}$ is 170–178 °C, while its polymeric analogue dissociates at 186–193 °C. The clusters based on gold are always less stable that the copper-containing ones (the dissotiation temperatures of the initial and fixed gold clusters are 163–165 and 171–176 °C, respectively). In general, the immobilisation increases the thermal stability of both the cluster and the binding polymer. Heterometallic clusters are also often immobilised on the surface of inorganic polymers. For istance, worthy of note is the fixation of $[Fe_6C(CO)_{16}](Et_4N)_2HFeCo_3(CO)_{12}$, $[Rh_5Fe(CO)_{16}](Et_4N)$, $[RhFe_5C(CO)_{16}](Et_4N)$ and other clusters on SiO_2.[236] According to the data from IR spectroscopy, the clusters do not undergo any changes in this case, except for the cluster based on $RhFe_5$ that reacts vigorously with SiO_2. The attempts to bind the clusters $H_2FeRu_3(CO)_3$ and $Fe_2Pt(CO)_8PPh_3$) with phosphorylated silica gel were unsuccessful.[231] A number of bimetallic clusters were encapsulated in channels of zeolites, while the clusters $Rh_{4-x}Co_x(CO)_{12}$ (x = 2, 3) were immobilised by deposition on carbon.[237–239]

The method of 'layering' was used for the binding of Prussian blue and its analogues with polyvinylamine hydrochloride: salts of the type MCl_2 (M = Fe, Co, and Cu) bound with ions $[Fe(CN)_6]^{n-}$ (n = 3 or 4) were fixed on a polymer in aqueous solutions.[240] The logarithms of the formation constants of binuclear complexes from mononuclear immobilised complexes of Fe, Co, and Cu are 9.8, 7.7, and 10.4 in litre mol^{-1} units, respectively. Although the degrees of freedom of the polymeric chain and the cluster decrease upon formation of polynuclear complexes, the ΔS value remains positive, which is indicative of the entropy increase, apparently due to the release of several molecules of water bound initially to M^{2+} and $[Fe(CN)_6]^{n-}$.

One can conclude that the studies on the immobilisation of heterometallic clusters are making rapid progress, although this research area has still numerous problems related mainly to the mechanism underlying the interaction of clusters and functional groups of polymers, transformations of immobilised reactants, and the structure of final products.

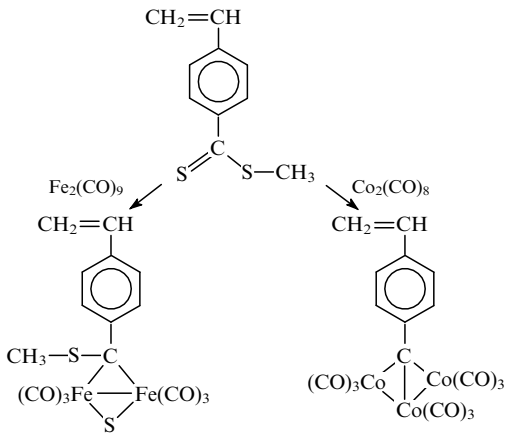
3. Polymerisation and copolymerisation of cluster-containing monomers as a route to the production of polymer-immobilised metalloclusters

By analogy with the formation of nanoparticles by means of polymerisation of appropriate monomeric mixtures (simultaneous formation of the matrix and nanoparticles, see Section IV), it could be expected that the polymerisation and copolymerisation of cluster-containing monomers are very simple one-step methods for the preparation of cluster-containing polymers. It was presumed that the major problem would be the synthesis of the appropriate monomers.

Recently, two promising approaches have been developed for the synthesis of cluster-containing monomers.[241, 242] According to the first approach, the groups capable of polymerisation are introduced as ligands into the known clusters. To this end, recourse is made to the replacement of the intrinsic ligands of clusters by their analogues carrying multiple bonds, oxidative binding, addition of new groups on multiple M–M bonds under mild conditions, *etc.* These reactions may lead to a higher or lower nuclearity of clusters. The reaction of $Ru_3(CO)_{12}$ with dimethyl fumarate in boiling heptane results in the formation of complexes with different nuclearity, their relative yields being dependent on the ratio of reagents and the duration of the reaction.[243]

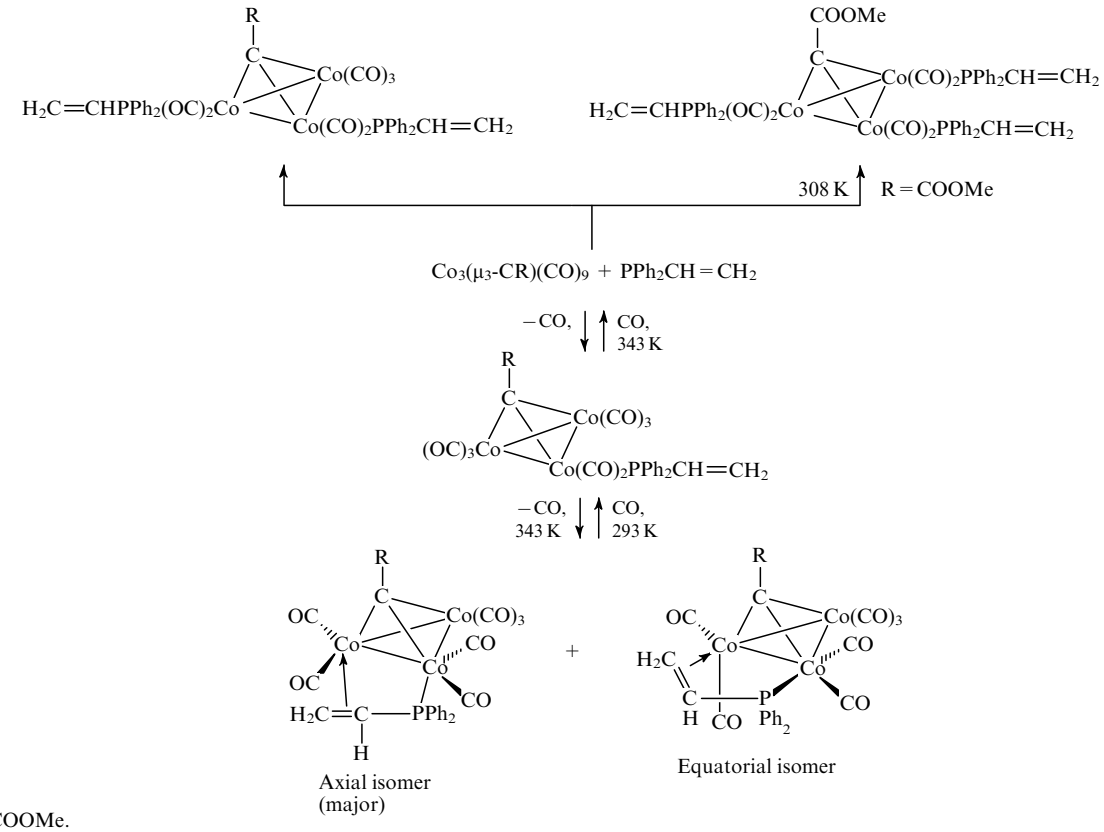
The second approach consisting in the build-up of conventional monomers with clusters is not as popular as the former. A characteristic example of this approach is the preparation of cluster monomers based on methyl *p*-vinyldithiobenzoate (Scheme 12).[244, 245]

Scheme 12



Although these reactions are complicated by a number of side processes (desulfurisation, formation of metal sulfides and products of ortho-metallation, *etc.*) not allowing the achievement of yields of target products above 40%, it is essential that the cluster skeletons are preserved, and the monomers formed can undergo polymerisation.

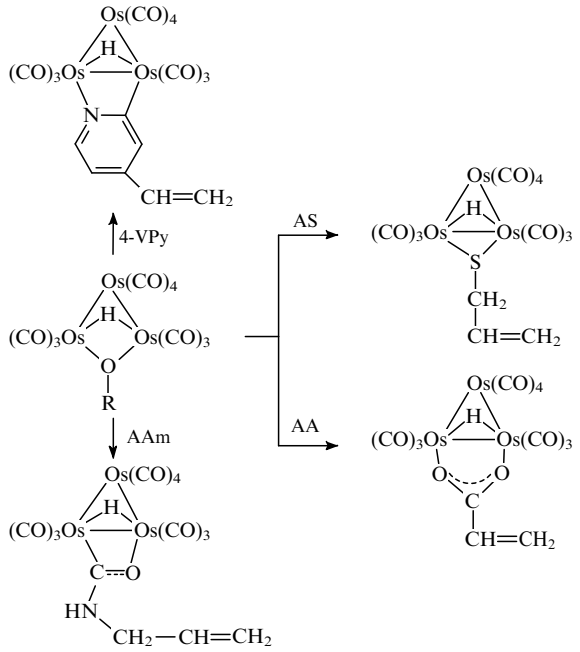
Scheme 13



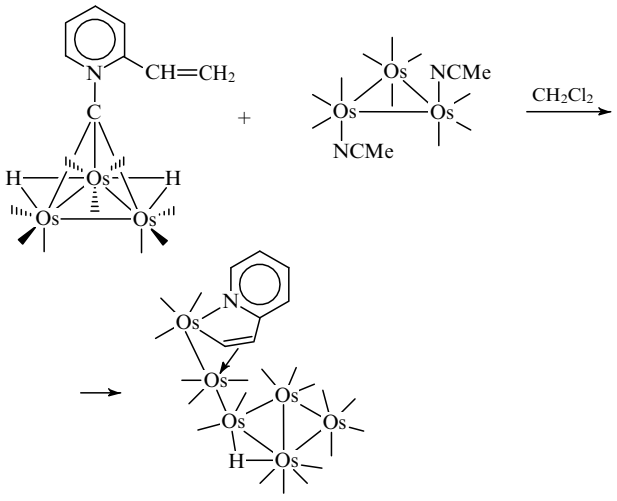
R = Me, COOMe.

An example of a more convenient route to the synthesis of this class of potential monomers is the reaction of tricobaltalkylidine complexes $Co_3(\mu_3\text{-}CR)(CO)_9$ with vinylphosphine ligands in heptane at 308 K. This allowed the isolation and characterisation of $Co_3(\mu_3\text{-}CR)(CO)_{9-x}(PPh_2CH=CH_2)_x$ (x = 1, 2, 3).[246] When the product with x = 1 is heated to 343 K, it eliminates CO groups (Scheme 13), and an additional coordination of vinyl groups with Co atom occurs.

High yields of cluster-containing monomers were obtained from trinuclear clusters $M_3(CO)_{12}$ (M = Os, Ru), $Os_3(CO)_{11}$(-MeCN), $Os_3(CO)_{10}(MeCN)_2$, and $(\mu\text{-}H)Os_3(CO)_{10}$. .$(\mu\text{-}OR)$ (R = H, Rh), and conventional monomers (4-VPy, acrylic acid (AA), allylamine (AAm), allyl sulfide (AS), *etc.*):[209]



Interestingly, like in the above-considered system obtained by the immobilisation of $Os_3(CO)_{12}$ on Ⓟ–4-VPy, the pyridine ring in the monomer based on 4-VPy was chelated. The complex $Os_3(CO)_{10}(MeCN)_2$ reacts rapidly with 2VPy to form a trinuclear cluster $HOs_3(CO)_9L$(2VPy) (L = CO or PMe_2Ph). The preparation of a triosmium alkylidine cluster $H_2Os_3(CO)_9[\mu_3\text{-}(2VPy)]$, which may be used as the starting material for the preparation of planar hexaosmium carbonyl cluster with an open structure, has been described.[247]



The reaction of 4-VPy with $Rh_6(CO)_{16}$ in the presence of acetonitrile or trimethylamine *N*-oxide occurs under mild conditions and yields a monosubstituted derivative $Rh_6(CO)_{15}$(4-VPy) as the major product and a small amount of $Rh_6(CO)_{14}$(4-VPy)$_2$, which can be easily isolated in a pure state by chromatography.[211] Contrary to the osmium derivative, the monomer $Rh_6(CO)_{15}$(4-VPy) is an octahedral cluster with 11 terminal and 4 μ_3-bridging carbonyl ligands, and the vinylpyridine moiety is linked with the rhodium atom only through the nitrogen atom and

occupies the coordination position of the twelfth terminal CO. The mean length of the Rh – Rh bond is 0.2762 nm, which is close to that in other Rh clusters. Apparently, this mechanism also operates in the reaction of Rh clusters with the allylic ligand $Ph_2PCHCH=CH_2$.[248]

The metallomonomers considered above incorporate only carbonyl clusters, though the solution of numerous problems requires monomers and polymers that contain other type of clusters, *e.g.*, halogenated ones.

Mo(II) halides, which readily form polynuclear complexes (of Mo_6Cl_{12} type) owing to a strong trend of divalent molybdenum to association, are highly promising.[249] Of special interest are the complexes with a stable group $[Mo_6Cl_8]^{4+}$, which is named a staphylonuclear group (Fig. 8). This group includes an octahedron with six molybdenum atoms surrounded by eight chlorine atoms localised in the apices of a slightly distorted cube. The octahedron is inscribed into the cube so that the Mo(II) atoms are localised at the centres of facets. It is this circumstance that provides for the existence of six equivalent directions (normals) along which the effect of shielding of molybdenum atoms by chlorine atoms is minimal. The diameter of this cluster may be estimated at $\sim$1 nm (as the sum of a cube diagonal Cl – Cl equal to 0.6 nm and the radii of two chlorine atoms, each being 0.18 nm). The stable staphylogroup plays the crucial role in the complexation reactions.[250, 251] It can bind up to six axial ligands, negative ions or polar molecules, including those containing multiple bonds thus making possible polymerisation of monomers. For the first time, vinylimidazole and vinylpyrrolidone were used as ligands.[252, 253] In principle, conventional vinylic monomers, *e.g.*, 4-VPy, acrylonitrile, acrylamide, *etc.*, can serve as these ligands.[254]

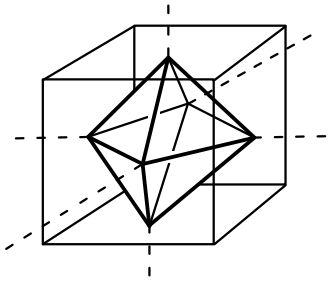
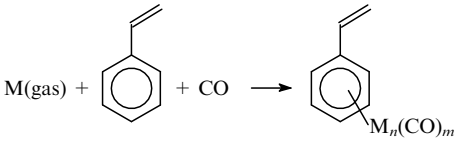


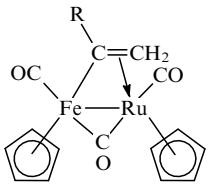
Figure 8. Structure of the staphylonuclear group $[Mo_6Cl_8]^{4+}$.

The methods of the synthesis and polymerisation of cluster-containing monomers are still in their infancy, though a breakthrough in this direction may be expected in the near future. For example, there are no essential restrictions on the application of the above-considered method of vaporisation of atomic metals to this end (see Section IV).



Recently, cryosynthesis involving atomic chromium and phenylacetylene as reagents has yielded Cr-containing polymeric products along with cyclotrimers of phenylacetylene.[255] The condensation of vapour of gold with large excess of a diacetylene monomer has been recently accomplished.[67]

These methods apply equally to the creation of monomers based on heteropolynuclear clusters. One possible way consists in the introduction of groups with multiple bonds into heterometallic complexes. For example, treatment of the iron – ruthenium complex $[FeRu(CO)_4(\eta^5\text{-}C_5H_5)_2]$ with olefins yields μ-vinylic complexes (R = H, Ph) with Fe – Ru bonds. [256]



In these complexes, the atoms of Fe and Ru are linked with alkenes through the σ- and π-bonds, respectively. The reactivity of bimetallic complexes as regards transformations of unsaturated hydrocarbons is close to that of homonuclear ones and decreases in the series FeRu > Fe_2 > Ru_2. The group of potential heterometallic monomers may be extended to include $FeCo(CO)_7$. .(μ-CH=CHR),[257] bimetallic η^2-complexes of Mo, V, or Fe with formaldehyde bridging,[258] and a number of other compounds (for example, $AuPt_2$-based clusters).[259] The acetylenide cluster of Pt_2Cu_4 (**2**) was prepared by treatment of 1,1′-[chloro(η^4-cyclooctadiene)platino]ferrocene (**1**) with an excess of phenylacetylene and CuI (Scheme 14). The same product is obtained from [phenylethynyl(η^4-cyclooctadiene)platino]ferro-cene (**5**). The bis-substituted ferrocene **3** gives the cluster **4** (Scheme 14, Fig. 9). The Pt – Cu bond length is 0.2845 – 0.2975 nm.

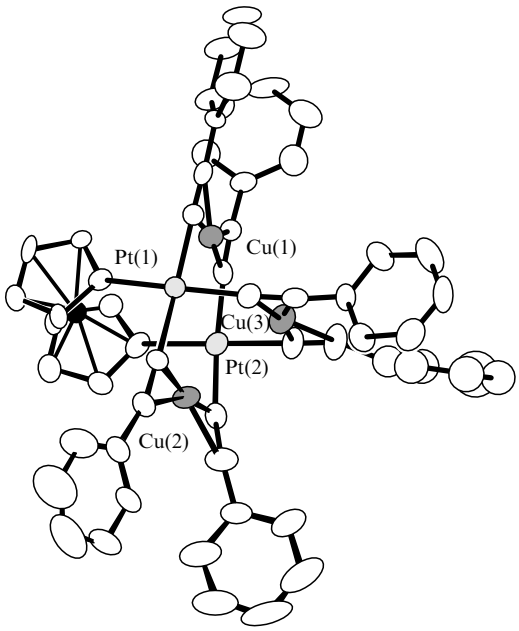
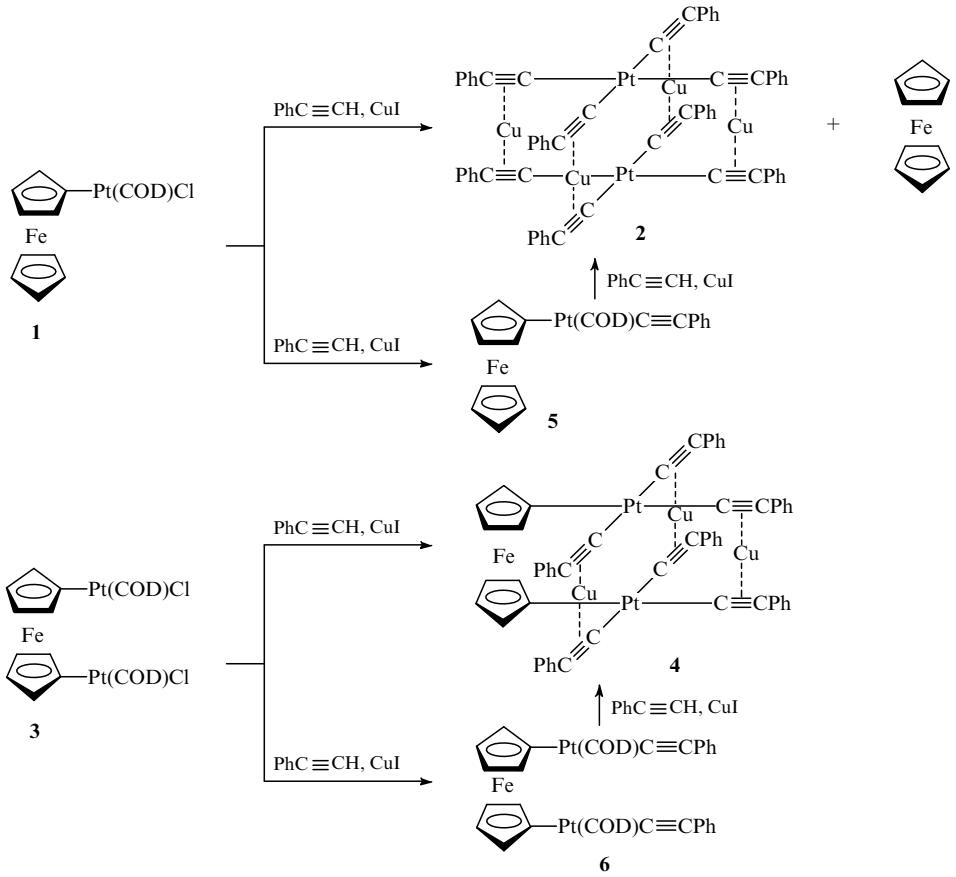


Figure 9. Molecular structure of the complex **4** (the hydrogen atoms are not shown).

One may also consider the monomers comprising atoms of the same metal in different valent states, *e.g.*, $FeCl_2$. .$(FeCl_3)_2(CH_2=CHCN)_6$, as heterometallic ones.[261]

Numerous attempts to polymerise cluster monomers [262] have always faced insurmountable problems associated with the presence of such bulky substituents as cluster fragments possessing specific electronic structures, with the reaction of the initiating radicals or ions with cluster-containing monomers leading to their degradation, *etc*. These complications rule virtually out the possibility of homopolymerisation of these exotic metallomonomers. The most successful proved to be the attempt to copolymerise monomers derived from dicobalt octacarbonyl or diiron nonacarbonyl and dithioesters (Scheme 12) or thioamides with styrene or *N*-[tris(hydroxymethyl)methyl]acrylamide. This copolymerisation has led to the products containing up to 1 mol.% – 2 mol.% of units with intact cluster framework (Table 4). The copolymers produced possessed large molecular weights.

Scheme 14



Special studies on styrene polymerisation in the presence of $Os_3(CO)_{12}$ and $(\mu\text{-H})Os_3(\mu\text{-4-VPy})(CO)_{10}$ have shown [263] that the starting cluster $Os_3(CO)_{12}$ has no influence on either the rates of the initiator degradation and styrene polymerisation or the molecular-weight parameters of the PS produced. The homopolymerisation of $(\mu\text{-H})Os_3(\mu\text{-4-VPy})(CO)_{10}$ proceeded with difficulty: an oligomer with 5–6 units in the chain was obtained with a yield of 1%–2% in benzene at 70 °C in the presence of 2,2′-azobis(isobutyronitrile) as an initiator. The copolymerisation of $(\mu\text{-H})Os_3(\mu\text{-4-VPy})(CO)_{10}$ with styrene or acrylonitrile under the same conditions resulted in the incorporation of up to 3% of cluster units into the polymeric chain without noticeable changes in the structure of these clusters. The IR spectra of the cluster carbonyls are virtually indistinguishable from the spectra of the corresponding initial monomers (Table 3), though some minor changes in the intensity and widening of individual absorption bands may still be revealed. Apparently, the conjugation of the double bond in $(\mu\text{-H})Os_3(\mu\text{-4-VPy})(CO)_{10}$ leads to the redistribution of the electron density in the Os–Os bonds and the decrease in their length. In the polymer, this conjugation disappears, and the photoelecton spectra of the framework become close to those of the unsubstituted cluster $Os_3(CO)_{12}$. Kinetic studies showed that each polymeric chain ($\overline{M}_n$ = 5–37 kDa) contained, on the average, one cluster unit and one terminal double bond.[263] This implies that the binding of the Os_3-containing monomer to the growing macroradical inhibits the chain growth (Scheme 15). This

Scheme 15

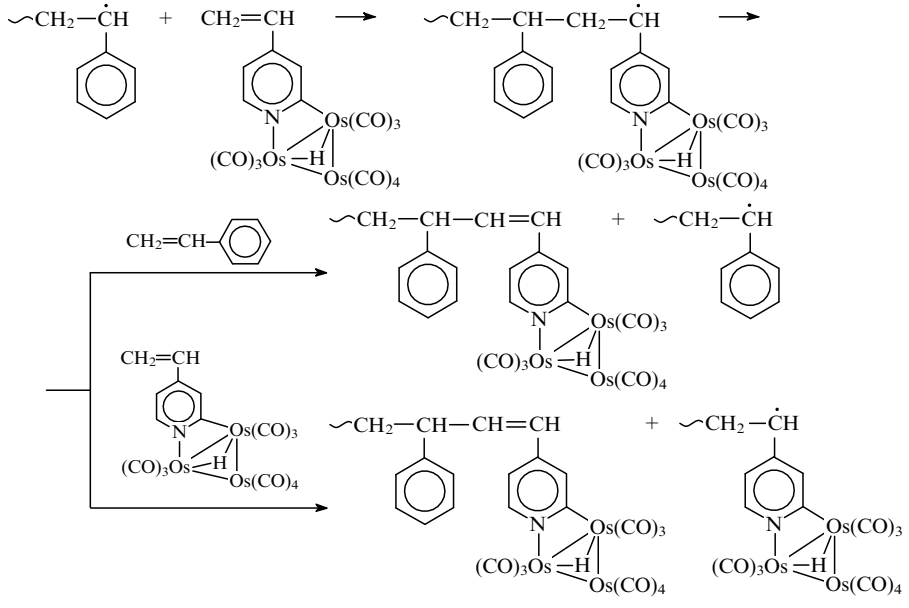
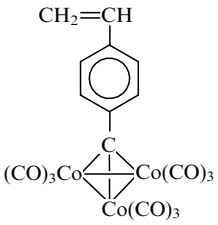
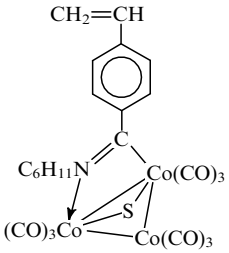
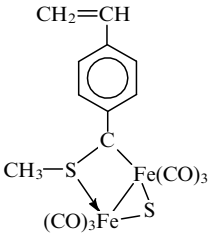
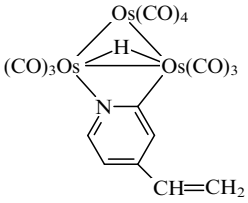
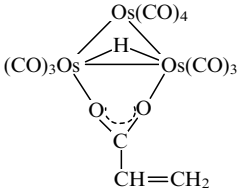
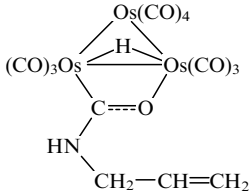


Table 4. Composition and characteristics of cluster-containing copolymers.

First component (M_1)	Second component (M_2)	Molar composition of monomeric mixture $M_2 : M_1$	Fraction of units with preserved cluster framework (mol.%)	$\overline{M}_w/\overline{M}_n$	Note
	Styrene MMA *N*-[tris(hydroxy-methyl)methyl-acrylamide]	99 : 1 99 : 1 99 : 1	3.7 1.0 1.6	14720/6400 44700/21300 –	
	Styrene MMA *N*-[tris(hydroxy-methyl)methyl-acrylamide]	99 : 1 99 : 1 99 : 1	1.3 1.8 1.6	16900/7200 41300/24600 –	
	Styrene MMA *N*-[tris(hydroxy-methyl)methyl-acrylamide]	98.8 : 1.2 99 : 1 98.5 : 1.5	1.4 1.1 1.5	3320/2250 18500/10060 7000/5500	
	Styrene AN	(99 – 99.5) : (0.5 – 1.0) (99 – 99.5) : (0.5 – 1.0)	0.2 – 1.0 0.1 – 0.2	– /5000 – 36500 – /1500	In mass In benzene
	Styrene AN	(99 – 99.5) : (0.5 – 1.0) (99 – 99.5) : (0.1 – 1.0)	0.1 – 1.0 0.1 – 1.0	– /12000 –25500 – /8000 – 26000	In mass In benzene
	Styrene AN	(99 – 99.5) : (0.5 – 1.0) (99 – 99.5) : (0.1 – 1.0)	0.1 – 1.0 0.1 – 1.0	– /21000 –26000 – /15000 – 17000	In mass In benzene
$[Mo_6Cl_6(N\text{-VI})](CF_3COO)_4$	*N*-Vinylimidazole (*N*-VI)	(99 – 99.5) : (0.5 – 1.0)	0.1 – 0.5	–	Comonomer as a solvent

does not however lead to the decrease in the concentration of active species owing to the fast transfer in the chain.

The role of chain transmitters may be played by both styrene and comonomer containing Os_3; however, as in the case of homopolymerisation, the steric hindrances impose certain restrictions on the chain transfer reaction onto the cluster monomer. Therefore, the role of this reaction is insignificant. It is most probably that the chain transfer is realised only *via* styrene. The analysis of the molecular mass characteristics allowed the estimation of the constant of the growing radical interaction with the double bond of the cluster monomer.[264] The lower limit of this parameter is within the range of 40 to 300 litre mol^{-1} s^{-1}. Similar features were revealed for the copolymerisation of Os_3-containing monomer with acrylonitrile.

The copolymerisation of $Rh_6(CO)_{15}$(4-VPy) with styrene in toluene occurs much easier,[265] and the content of the cluster monomer may be as high as 10%. This seems to be due to the fact that 4-VPy is linked to the cluster framework only by a donor-acceptor bond.

It may be assumed that the size of the metal-containing cluster particles is not much larger than that of the initial clusters, especially at their low levels in copolymers since the polymeric segment formed from the comonomer is a stabilising factor preventing associative processes. This view is supported by the direct evidence provided recently from a study[253] of the radical block copolymerisation of staphylonuclear monomers in solubilising monomeric media with $[Mo_6Cl_6(N\text{-VI})_6](CF_3COO)_4$, where *N*-VI is *N*-vinylamidazole. *N*-Vinylimidazole acts simultaneously as a solvent for the cluster monomer (at 0.1 and 0.5 M) and as a comonomer. At 70 °C, fast homogeneous copolymerisation took place with subsequent cross-linking and thickening of the reaction medium, which contained the chemically bound monodispersed clusters at a relatively high concentration. The sizes of the polymer-immobilised staphylonuclear and the initial clusters were close and amounted ~1 nm. Apparently, one should agree with the view of Golden *et al.*[252,253] who believe that the use of monomers as solvents may become a common practice in the preparation of polymer-immobilised monodispersed metalloclusters.

The incorporation even of small quantities of cluster monomers into a copolymeric chain improves the parameters characterising the resistance to destruction of both the metallocluster itself and the polymer. For example, the Os_3-copolymers manifest mutual stabilisation of PS and PS-bound clusters.[266] The decarbonylation of clusters begins at ~200 °C, while the decarbonylation temperature of copolymers is higher by ca. 150 °C. The thermal resistance of clusters is increased only when they are bound with a polymeric chain, while in mechanical mixtures this effect is absent. One of the major reasons for this phenomenon may be the transfer of energy at increased temperatures from the rotational-vibrational degrees of freedom of the cluster to the translational degree of freedom of the polymeric chain segments. The decomposition temperature of the polymers comprising metalloclusters is in turn increased by 50–60 °C, while the effective activation energy of thermal destruction is increased by 40–60 kJ mol^{-1}. The vitrification temperatures of polyvinylimidazole and of its copolymers with an imidazole staphylonuclear cluster at concentrations of 0.1 and 0.5 M are 164, 220, and 257 °C, respectively.[253]

Despite the sparse character of the data on the polymer-immobilised clusters prepared *in situ*, the recent progress in this direction promises the obtaining of new data and their systematisation.

The above statements referred to the preparation of polymer-immobilised clusters by polymerisation. There are no principal obstacles preventing the use of polycondensation reactions for this purpose. In all cases, the principal difficulty resides in the synthesis of appropriate metallomonomers with bi- or poly-functional ligands. The role of such ligands may be played by the groups capable of binding active hydrogen from diols, diamines, and other compounds.

The high diversity of reactions of substitution or exchange between the functional groups of reagents makes this approach rather promising. The synthesis of these polymer-immobilised clusters may also rely on the use of cluster-containing compounds with the ligands comprising epoxy or other (*e.g.*, ethyleneimine) cycles, isocyanate groups (*p*-phenylenediisocyanate, 2,4-toluylenediisocyanate), *etc.*§ This method allows the preparation of cluster-containing polyurethanes, polyamides, polyesters, and polyepoxy compounds.

Naturally, the controlled pyrolysis of polymer-immobilised clusters yields highly dispersed metal powders, while the pyrolysis of heteronuclear polymer-immobilised clusters may potentially be a suitable technique for producing nanometre-sized powder alloys (similarly to the pyrolysis of initial $HFeCo_3(CO)_{12}$, $[Co(MeCOMe)_6][FeCo_3(CO)_{12}]$,[268] *etc.*). One should not rule out that this approach may be beneficial in the development of the solid-phase method for reducing metal oxides (it is known[269] that if the contact between reagents is close, the reduction of Ag_2O in graphite is realised at temperatures as low as 100–200 °C). The incorporation of Pt clusters into a glass-carbon matrix was carried out by immobilisation of mononuclear complexes of (ethylene)-bis(triphenylphosphine)platinum(0) on the triple bonds on poly(-phenylenediacetylene) oligomer.[270] On heating to 600 °C, the toluene-soluble complex of composition 1:4 or 1:2 yields a Pt-enriched glass-carbon in the form of thin films with a narrow distribution of Pt clusters with a mean diameter of 1.6 nm. The structure of these clusters is shown in Fig. 10. Interestingly, the non-immobilised complexes form large Pt particles 600 nm in diameter. The ceramics of general formula $M_xSi_yC_z$ (M = Fe, Co) are produced by the pyrolysis of cluster-containing diacetylene oligomers at 1350 °C.[271]

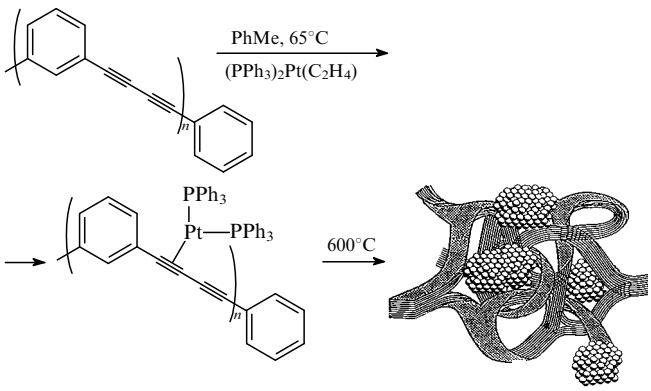


Figure 10. Structure of a Pt–poly(phenyldiacetylene) oligomer.

VI. Nanometre-sized particles, clusters, and polynuclear structures immobilised in biopolymers and their analogues

The interaction of metal ions and nanoparticles with biopolymers and cells plays a highly significant role in the enzymatic catalysis, geobiotechnology, and biohydrometallurgy. Of practical interest for the geomicrobiological transformation of heavy metals are natural and genetic-engineering microorganisms the vital activity of which occurs under extreme conditions (high temperature and pressure, highly acidic or basic media, strong salinity, the presence of metals at levels toxic for common microorganisms). By analogy with thermophiles, halophiles, acidophiles, *etc.*, a group of microorganisms is named metallophiles.[272–276]

§ Recently, platimun–gold phosphine clusters with isonitrile ligands of the type $[Pt(RNC)(AuPPh_3)_8]^{2+}$, $[Pt(CO)(AuRNC)(AuPPh_3)_7]^{2+}$ have been synthesised.[267]

It is believed [272] that the extent of selective metallophilicity of microorganisms is determined by a number of factors: the selective direction of motion of the colloidal particles relative to microorganisms, the nature of chemical fixation of particles on the surface and its strength, *etc*. Among the bonds formed, the covalent ones are predominant.

A consequence of selective metallophilicity is a genetically predetermined specialisation of microorganisms for the interaction with definite metals. This results in the appearance under natural conditions of a rigorously determined system including a cell of definite species and a metal (or a group of related metals).[272] Flocculation of cells by colloidal metal particles leads to the formation of rather large (up to 50 – 60 μm) bioskeletal aggregates undergoing sedimentation in aqueous media. Specific NADH oxidase, the protein capable of incorporation of gold into the active centre, has been isolated and characterised recently. Its molecular weight is 600 000, and it contains three metal atoms per mol of protein.

In addition to bacteria, the binding of metals is effected by yeasts, fungi, numerous algae, and some Protozoa, and this largely extends the potential of biochemical transformation and transfer of metals under natural conditions.

One of the manifestations of the colloidal-chemical binding is the coagulation of metal sols (in particular, the best studied is the gold sol that is characterised by the simplicity of its preparation and a relatively high stability, see above). The heterocoagulation of these sols results in the formation of biopolymer-immobilised nanoparticles or, in other words, mixed aggregates of living microorganisms and nanoparticles. Many of them possess specific properties that are apparently determined by the processes occurring in the diffusion layers of cells and are associated with the electrical heterogeneity of their surface.[277] These processes induce the binding of sol particles and simultaneously decrease the threshold of their coagulation due to the increased concentration of counterions. These highly dispersed biogenic aggregates are widely distributed in nature as economically important metal ores, the sole of sedimentogenesis facies,[278] *etc*. Furthermore, the very idea of immobilisation of metallocomplexes on polymers is largely borrowed from natural systems.

1. The pathways of formation of metallobiopolymeric systems

The peculiarities of the interaction of microorganisms with metal sols, as a rule, largely depend on the nature of the metal. In this respect, the best studied systems are the colloids of gold,[276] the colloids of other noble metals, as well as those of iron, copper, and manganese have been investigated to a lesser extent. Biosorption is the novel approach to the metal recovery from the dilute solutions. It was shown that microorganisms and algae allow the extraction of up to 100% of lead, mercury, zinc, nickel, cobalt, manganese, chromium, uranium, and some other elements, up to 96% – 98% of gold and silver, up to 84% of platinum, 93% of selenium from dilute solutions. It is shown also that bacterial polysaccharides are effective in the recovery of radioactive elements, as well as of copper and cadmium, from solution (Table 5).[279]

The bacterial concentration of metals is preceded by their adsorption on the cell surface with subsequent assimilation.[280] This can be accompanied by enlargement of sol particles (flocculation) and the adsorption and deposition of a coarse metal-bacterial mass (heterocoagulation). Like in the systems based on synthetic polymers, the sol with particle size of ~ 10 nm proves to be the most stable.

An important distinctive feature of the colloid-bacterial interaction is the diversity of the forces involved with mechanisms of electrostatic, molecular, and chemical origin. The preferential adhesion between colloidal particles and associations of bacterial cells is observed at sites of their contact. For example, the coccal bacteria *M. luteus* with the mean size of 2000 nm isolated from an auriferous placer form packages of 4 – 8 cells that sorb effectively the gold particles (up to 10 mg of Au per 1 g wet biomass),[276] but do not induce heterocoagulation; in this situation, one cell binds, on the average, 10^4 colloidal gold particles.

Table 5. Sorption of metals by microorganisms.[279]

Metal sorbed	Microorganisms	Metal content (mg) per 1 g dry cells mass
U, Th	Denitrifying bacteria	140
	Rhizopus arrhizus	180
U	*Pseudomonas aeruginosa*	$\leqslant 560$
	Saccharomyces cerevisiae, *Pseudomonas aeruginosa*	100 – 150
	Biosorbent M (*Penicillum chrysogenum*)	80 – 120 (purification of waters containing < 0.05 mg litre^{-1} of elements
Ag	Bacterial community of *Ps. maltophila*, *Staphylococcus aureus* and unidentified forms	$\leqslant 300$

At least in the initial stages, the interaction is reduced to the electrostatic binding, and it is this fact that explains the reversibility of heterocoagulation:[280] after the introduction of the protonophore into the incubation medium, the dispersed metal particles are released from the cell surface. In general, there are two routes for the realisation of this process. In cell associates, further concentration of particles occurs at the sites of their contact, which is accompanied by their enlargement. In single cells, the increase in the particle size is not preceded by aggregation: the particles formed in the process of concentration are gradually rejected by the cell surface.

Most probably, the electrostatic and chemisorptional attachment of colloidal particles of metals and their compounds to the cell surface occurs mainly due to the products of its metabolism including such functional groups as $-S-$, $-COO^-$, $PO(OH)O^-$, $-NH_3^+$. It is significant that, in contrast to positively charged proteins (trypsin, papain, lysozyme, RNAse),[281] the negatively charged proteins (human serum albumin, soybean trypsin inhibitor) do not cause flocculation of gold particles. Lysozyme manifests special properties: the flocculation of sol on it occurs in a narrow range of enzyme concentrations (1 – 10 μg mlitre^{-1}), while its higher levels stabilise the sol and enhance the aggregational stability of the system, on the whole. The occurrence of consecutive stages of flocculation and stabilisation of metal colloids with the increasing concentration is also characteristic of certain synthetic polymers, such as polyethyleneimine and nonionogenic polyethyleneoxide.

Let us note some differences in the behaviour of proteins and synthetic polymers. First, proteins differ in their selectivity towards different dispersed phases in the course of flocculation which is determined not only by electrostatic factors but also by specific binding of these phases by functional groups of amino acid residues, especially by the sulfhydryl and amino groups.[282] In particular, the addition of *p*-chloromercuriobenzoate, which specifically blocks the SH groups of proteins, was found to decrease their flocculating activity. Second, the native structure of the biopolymer is of prime importance for the sorptional processes to occur. For example, partial destruction of the polysaccharide skeleton of bacterial cell walls (by lysozyme) reduces considerably their sorptional ability.

The cells of monoculture tissues (*Pseudomonas sp*., *Bacillus cereus*, *Bacillus sp*., *Bacillus subtilis*) grown under similar conditions differ significantly in their ability to accumulate metal particles on their surface. The accumulative ability of cells was observed to correlate with the flocculating capacity of preparations isolated from them (Fig. 11).[283]

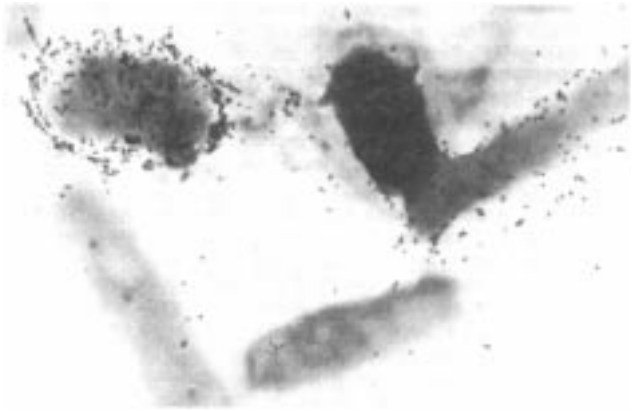


Figure 11. The cell of associate tissue culture in the presence of colloidal gold particles ($\times 35\,000$).[283]

There is experimental evidence for the binding of metal particles on the surface of cells by their carbohydrate or glycoprotein structures. A glycoprotein with a molecular weight of ~ 50 kDa providing for the binding of colloidal gold was isolated from different cells (including *B. subtilis*) by extraction with butanol. The specificity of binding of different compounds by this protein decreases in the series $Au \gg Pt > MnO_2 > Al_2O_3$.

The liposomes (which are the closest models of biomembranes having no effect on the aggregative stability of gold) modified by this glycoportein sorb actively particles of metals. Apparently, the glycoprotein is bound with lipids in the bacterial cell wall. As a matter of fact, it is the increased level of glycophospholipids in them and the extended branching of fatty acid residues that determine the ability of the above-mentioned *M. luteus* cells to survive under extreme conditions (at high Au concentration).[284]

Following the adsorption and heterocoagulation of colloids in biopolymers, the recrystallisation and enlargement of dispersed metal particles occurs on the surface of living cells. These processes result from the occurrence of intense oxidation–reduction of metals. In case of gold, at the first stage, the colloidal gold particles are oxidised possibly by hydrogen peroxide generated by cytochrome C, while the second stage involves the endogenous reduction of gold ions with the participation of the plasma membrane.[276] This may occur only at a sufficiently intense ion flux. The cationic $-NH_3^+$ groups are believed to be responsible for the solubilisation (oxidation) of gold by the *Bacillus subtilis* cells, whereas the anionic carboxyl and phosphoryl groups are responsible for the reduction of complexes of gold with metabolic products.[285]

Thus, in the system 'biopolymer–colloidal gold particles', the latter are redissolved to eventually form larger particles.

The mould fungi are known to reduce gold to its metallic state.[286] Sometimes, these transformations also involve humic and fulvic acids. As a result, a specific 'depot' of bioelements is formed.[287]

The surface of bacteria may contain several independent metal binding sites (M). This process is described by the equilibrium

$$M + L \rightleftharpoons ML.$$

The symbol L designates the binding site on the bacterial surface, while ML stands for the 'bacterium–sol particle' complex. The total number of binding sites (n), the quantity of bound metal particles (v), and the association constant $K = [ML]/[M][L]$ may be calculated by the Scatchard equation:[288]

$$\frac{v}{[L]} = nK - vK.$$

For example, the *M. luteus* cells have two types of independent gold-binding sites:[276] in the first type of sites (hydrophilic), the binding occurs as a result of electrostatic interaction ($K_1 = 3.85 \times 10^9$ litre mol^{-1}, $v_1 = 4.7 \times 10^3$), in the second type of binding sites it goes occurs *via* an oxidative process of the formation of gold complexes ($K_2 = 4.6 \times 10^8$ litre mol^{-1}, $v_2 = 4.3 \times 10^3$).

The model of bacterial concentration and crystallisation is rather complicated. The process may proceed *via* fusion (assimilation) of small (10–20 μm) needle-like crystalline polygons, which bind to each other to form visible gold grains extracted by the gravimetric method. In addition, the colloidal particles may play the role of crystallisation centres as nuclei of a new phase under conditions of continuous cooperative oxidation and reduction of the metal ions formed. Apparently, the transformation of endogenous gold under conditions of placers formation follows the same mechanism.¶

The processes of accumulation of heavy metals by cells occupy a special place. It is known that the most important cell components are the low-molecular-weight (5–10 kDa) metal-binding proteins thioneins, rich in SH groups, which accumulate both the metals essential for the cell (Cu, Mn, Fe, Co, Cr, Mo) and unessential ones.† The macromolecules of these proteins consist of two separate subunits. Each of them binds metal ions into a polynuclear metal-thiol cluster surrounded by cysteine residues. For example, Cd- and Zn-thioneins contain 7 metal atoms each, of which four are bound with 11 cysteine residues (M_4Cys_{11}) in a C-terminal A-cluster, while 3 metal atoms are bound with 9 cysteine residues (M_3Cys_9) in the N-terminal B-cluster.[291] At the same time, Ag and Cu form M_{12} metallothioneins containing 6 metal atoms in each domain.

The biological function of thioneins is, most likely, the storage and detoxification of heavy metals and possibly in the provision of the resistance of microorganisms to them.[292] Apparently, the accumulation of metals is associated with intense reduction, localisation, and adhesion on the outer membrane of metal particles formed. During the period of adaptation, the cells can acquire a plasmid of resistance to the metal, and this capacity is realised through the intensification of the reduction of metal ions. Thus, natural selection may result in the formation of metal-tolerant microbial strains.

The analysis of the immobilisation of nanoparticles on biopolymers allows one to note two aspects. First, most of the heavy metals bind simultaneously to several protein macroligands with a specific spatial environment and conformation. Triple complexes may also form, *e.g.*, protein–M–nucleic acid (M = Au, Pt, Pd).[293] Possibly, it is the presence of these formations that provides the anticarcinogenic effect achieved upon introduction of these metals into organisms. Second, heavy metals, *e.g.*, Au(I) react with mixed-metal thioneins (with native Zn-, Cd-, and Co-thioneins) by replacing selectively Zn and even Cd when added in excess. This process is characterised only by minimal changes in the protein conformation.

Metalloclusters play a very important role in the processes of bacterial mineralisation,[294–296] and their investigation is the subject of a new branch of science called bioinorganic solid-state chemistry. Its topic is the study of the formation and structure of nanoscale materials in biological environment. A characteristic example is the formation of nanoparticles on the base of ferritin (Fig. 12).[297] A nanoparticle of Fe_3S_4 is deposited in the inner part of the protein shell as a result of chemical transformations under mild conditions. The process is still more simplified when a 'metal-free' apoferritin is used for this purpose. For example, the biopolymer-immobilised Mn^{3+} oxides 8 nm in diameter are obtained upon oxidation Mn^{2+} to Mn^{3+}. This route is also effective for the preparation of nanoscale biomaterials based on Ag_2O and especially of calcium phosphates ($Ca_{10}(PO_4)_6(OH)_2$, $Ca_8H_2(PO_4)_6$, *etc.*) which are important components of osseous

¶ The solubilisation, deposition, and formation of new layers of gold on the surface of initial grains is characteristic of the entire history of hypergenic native gold.[289]

† Deposits of iron and manganese, which are highly important for functions of living organisms are mostly of biogenic origin.

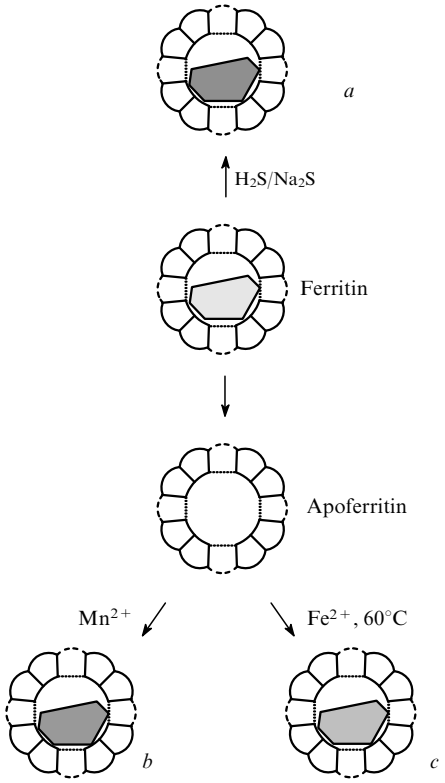


Figure 12. Synthesis of nanophase materials based on ferritin: (*a*) Fe_3S_4; (*b*) Mn_2O_3; (*c*) Fe_3O_4.

tissues. Special attention should be given to the intraferritin formation of *in situ* deposits of Fe_3O_4 with definite crystallochemical characteristics.[298] This leads to the formation of ferromagnetic proteins,‡ which are used to prepare magnetic images for clinical purposes. The complexity and precision of such bioinorganic reactions require strict ordering of the particles formed with regard to their size and morphology which are difficult to achieve under laboratory conditions.

Some heterometallic clusters of ferredoxin with the composition $[MFe_3S_4]$, where M = Zn, Co, Mn, are known. They are present, in particular, in the *Pyrococcus furiosus* cells. It is believed [295] that bacterial methods may be effective in the preparation of finely dispersed precursors of superconducting high-temperature ceramics and other materials.

Metalloprotein preparations are quite often used in medicine to regulate the enzyme activity and to devise new drugs of narrow targeted action.[300] Colloidal compounds of calcium and magnesium with plant proteins are employed for the regulation of gastric juice acidity, a finely dispersed Fe_3O_4 complex with serum albumin is administered intravenously as a contrasting compound for X-ray studies, *etc*. Colloidal gold and its biopreparations have been used since ancient times as medicaments, many of them are known to be effective antiarthritis drugs. Colloidal gold is widely used in immunochemical studies as an electron-dense cytochemical marker in electron microscopy. The hydrophobic character of gold particles and the existence of electrostatic charge on their surface have allowed the development of specific markers with numerous macromolecules, such as antibodies, lectins, enzymes, various proteins, glycoproteins, and polysaccharides.[301]

‡ This is clearly seen in electron micrographs of bacterial magnetite, [299] an intracellular product composed of Fe_3O_4 crystals arranged in a chain parallel to the longitudinal axis of *Coccus* and *Spirillum* bacteria (Fig. 13). Such magnetically ordered (magneto-tactical) bacteria may orient themselves (move) even in weak (0.25–0.5 G) magnetic terrestrial fields by performing the 'navigational' functions in living organisms.

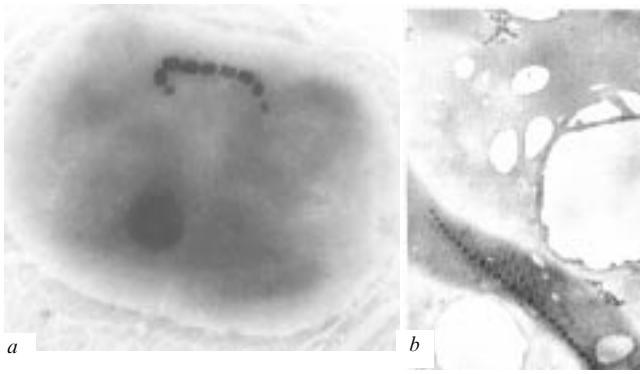


Figure 13. Electron micrographs of *Coccus* bacteria with a chain of nine intracellular magnetic crystals (*a*) and *Spirillum* cells with a chain of cubic-octahedral crystals (*b*). The cell length is 3 μm, the size of each crystal is $\sim 50 \times 50$ nm.

Special attention should be paid to the microbial geotechnology, *i.e*., to the extraction of metals from their ores, concentrates, embedding rocks, and solutions by means of microorganisms and their metabolites.[279] The bacterial leaching of copper and uranium has long been used in the industrial scale. This process includes fragmentation of ores and preparation of pulp, bacterial leaching of the target metal, filtration, neutralisation of solid residues, and cyanation. The colloidal-biochemical basis has been elaborated recently for the detoxification of cyanide-containing wastes.[302]

2. Polynuclear metalloenzymes

All metal-containing protein systems important for biocatalysis and metabolism are divided into four main groups:[303] enzymes (containing Mn, Fe, Co, Cu, Mo), redox proteins, transport, and storage systems (which regulate the concentration of metal(s) at specific sites of the organisms). Kidney proteins, which bind and withdraw heavy metals from living organisms, are also sometimes classified in these groups. The biological functions of these proteins and the types of interactions in them have been reviewed.[300]

The most typical representative of storage proteins is ferritin. This iron-storing protein contains 24 identical subunits with an inorganic core composed of 4500 iron atoms in the form of basic hydrophosphate $(FeOOH)_8(FeO-OPO_3H_2)$ and having a diameter of 7.3 nm (such a structure is similar to that of synthetic polymers considered above) (Fig. 2).[304]

The distinctive feature of this large group of redox biocatalysts is the presence of several interacting atoms of transition metals in one protein molecule. Nowadays, over 100 enzymes are known that include several atoms of iron, copper, molybdenum, or manganese, and in many of them the arrangement of atoms in polynuclear ensembles has been established. This refers especially to the metalloproteins containing non-hem iron complexes linked by oxy-, hydroxy-, and alkoxy-bridges.[7, 8, 305] Binuclear iron complexes (with the $Fe_2O(OCOR)_2$ core) were found in hemerythrin, ribonucleotide reductase, and acid phosphatase. Polynuclear $Fe^{2+}Fe^{3+}$ complexes are supposed to exist in numerous enzymes; the Fe_2S_2 groups, in ferredoxin; the high-nuclearity oxo-centres of iron, in the iron-storage proteins of ferritin and hemosiderin type, and in the magneto-tactic microorganisms mentioned above.

In the processes of biological nitrogen fixation, the active enzyme form is produced with the involvement of two components, iron- and iron-molybdenum-containing proteins (including 32–34 Fe and 2 Mo atoms), under the action of natural electron donors (ferredoxins, flavodoxins) in the presence of ATP. The molybdenum nitrogenase cofactor may possibly have the structure $MoFe_6(SR)_6L_3$; the MoFe- and VFe-proteins (nitrogenases) were isolated from *Azotobacter vinelandii* and *A. chroococcum*.[8]

Enzymic photosystems that are employed for the liberation of oxygen from water comprise polynuclear complexes containing a cubane-like manganese core Mn_4O_2 [306] immobilised on the protein complex by means of carboxyl groups. Of other bimetallic systems, the $Cu^{2+}-Zn^{2+}$-containing superoxide dismutases, Cu_2Co_2-superoxide dismutases, and some others deserve mention. The advantages of these structures with shared nuclear frameworks have been analysed in detail.[7,8] Biopolymers including clusters with nuclei of Rh_6,[307] Ru_3,[308] Fe_4,[309] and other are described.

Extensive studies of synthetic oligopeptide models of complexes may provide additional information on the mechanisms of action and routes of electron transport in native proteins.

VII. Major fields of the application of polymer-immobilised metal nanoparticles and metal clusters

As noted above, these species have found applications in diverse, sometimes unexpected fields of chemistry, physics, and biology, which largely stimulates their further studies.

The interaction of nanoparticles or clusters with traditional polymers improve their physicomechanical properties and performance. This is explained by the ability of these particles to form ionic and coordination cross-links, restricting the mobility of molecular chains or their segments, by cohesional and adhesional interactions, and by other reasons.

The incorporation of metal nanoparticles into a polymer (polymeric shell) may lead to changes in the properties primarily of the polymer matrix itself and also of immobilised nanoparticles or clusters (in particular, to their passivation). An in-depth analysis of these changes goes beyond the scope of this review, and we shall dwell here only on the most essential ones.

1. The modifying effect of nanoparticles on polymer matrices

Virtually all of the methods used to prepare polymer-immobilised nanoparticles are associated with the metal–matrix interaction, especially at the interface. The incorporation of even such a small species as a nanoparticle perturbs substantially the polymer structure.[310] The extent of structural changes depends on the concentration of nanoparticles, which are the knots of the emerging structural network. The presence of as little as 1% of highly dispersed Fe + FeO mixture resulting from the decomposition of iron oxalate in HPPE alters the sizes of the structural element of the polymer, increases the density of the fluctuational network of molecular anchoring and the proportion of oriented polymeric chains.[311] This results in a considerable increase in the impact elasticity of the material, its tensile strength, and resistance to cracking. The processes of structuring in the polymer phase in the presence of nanoparticles occur in different ways. The interaction of nanoparticles with each other (especially at their high concentrations) leads to the formation of coagulational structures. At low levels of nanoparticles, when the formation of coagulational structures is impossible, the polymer matrix itself undergoes structure changes. These processes are accompanied by changes in the temperatures of vitrification, fluidity, thermal destruction, and in the thermomechanical parameters (as a rule, towards their enhancement), which is connected, as noted above, with the restricted mobility of macromolecules due to their interaction with the surface of nanoparticles, and also with the formation of secondary structures.

Thus in the Claspols (see Section IV) obtained by the thermal decomposition of metal salts and carbonyls in polymers melts (PE, PTFE, *etc.*) particles appear that reduce the mobility of molecular chains and increase thereby the thermal resistance of polymeric compositions.[312] As noted above, the decomposition of a fine dispersion of palladium hydroxide in PVC leads to the formation of network structures containing in their knots the highly dispersed metal thereby raising the temperature of the complete dehydrochlorination of the polymer.[131] The nanoparticles produced by the thermal degradation of copper oxalate increase the size of the polyamide crystallites, the interaction energy between the structural elements, and strength, but they reduce the overall degree of the polymer crystallinity.[126] The water of crystallisation released during the decomposition of cadmium oxalate trihydrate accelerates the crystallisation of structural elements, decreases the cohesion energy, and leads to a looser polymer matrix. The π-complexes of iron tricarbonyl with polystyrene-butadiene block-copolymers influence, in the temperature range of their softening, the segmental mobility of the polybutadiene microphase and even when present at levels below 2 mass % Fe they manifest an ordering effect, which increases the macromolecule rigidity.[313] At higher metal concentrations, this effect is enhanced owing to the development of a physical network. The dispersed metals formed *in situ* appear to be promising modifiers of the polymer fluidity.[188] Of special interest is the method of 'non-chain' inhibition of the thermo-oxidative destruction of temperature-resistant polymers [314] based on the binding of oxygen by highly effective acceptors, metal nanoparticles formed directly in the polymer matrix.

There are numerous examples of the improvement of adhesive properties of the systems under discussion.[315] The tribological coatings (of Ni–PTFE type) are characterised by the homocoagulational interaction between the polymer and nanoparticles at the moment of their isolation on the electrode.[176]

2. Electrical and magnetic properties

Various atomic and electronic processes that occur at the interface in polymer–nanoparticle composites largely determine their unique properties. These materials become electrical conductors only at definite ratios of the components when conducting chain-type coagulational structures and not matrix systems are formed. In other words, the role of current-conducting channels is played by the fractal clusters [54] formed upon cohesion of nanoparticles. The highest conductivity is attained when the metallopolymeric material is permeated by interconnected chains of contacting conducting particles, *i.e.*, when it has a percolational structure. As a rule, this is achieved at a content of nanoparticles of ~ 50 vol.%.

These materials find extensive uses in microelectronics (in the production of connecting circuit boards, flexible cables, *etc.*), in the production of highly dispersed conducting coatings, and in the film and membrane technology. They are also applied as precursors in the preparation of superconducting ceramics. Materials with the superconductivity transition temperature of 90 K were obtained on the basis of Y-, Ba-, and Cu-chelates of polycondensation type.[316] This temperature is still higher (110 K) in the polymers with components of bismuth ceramics.[317]

To prepare ultradispersed metal particles in polymeric matrices, nearly all of the methods described in Section IV are used, including the vacuum metallisation of polymers. The properties of these magnetic materials, ferroplastics or ferroelastics, namely, their magnetisation curve, magnetic permeability, coercive force, magnetic hysteresis loop, magnetostriction, *etc.*, depend on their prehistory, the nature of the polymer and the nanoparticles, concentration and structural state of particles and can vary over very wide ranges. For instance, the magnetic behaviour of the systems Ni–HPPE and Co–HPPE depends on the conditions of cryosynthesis.[78] At temperatures above 370 K, the irreversible interaction of Ni clusters with the matrix takes place in the Ni–HPPE system. In the Co–HPPE system, at 470 K the form of the thermomagnetic curve is completely changed due to the enlargement of Co particles.

The peculiarities of the magnetic behaviour of systems obtained by the reduction of metal salts in the medium of a swollen interpolymeric complex of polyacrylic acid with an urea–formaldehyde oligomer [164] and by the thermolysis of cationic complexes of iron arenecyclopentadienyl and arylenecarborane oligomers [72,318] have been considered. Studies along the same lines were carried out with composites obtained by the thermal and oxidative decomposition of Co and Fe carbonyls in PVF

matrices,[120] and the hydrogen reduction of organocobalt percursors [134] and Ni carbonyl in epoxy resin films in different solidification conditions.[319] Interestingly, the conductivity and the percolation parameters of the latter system depend on the internal stresses arising during solidification.[53] Magnetic particles are rather often introduced in different gels: silicone,[320] polyacrylamide,[321] polyethyleneoxide,[322] and other gels.[72] The conducting Ag-containing films are produced by the reduction of $AgNO_3$ in PVAl.[144] Sometimes, ferroplastics are formed in magnetic fields (for example, neodymium ferrites, in 3–30 G fields), and then are subjected to mechanical (pressing,[321] processing on Bridgeman anvils [72]), thermal,[323, 324] and other [325] impacts. In recent years, these studies are being developed extensively.

Of interest is the preparation of thin (3–7 nm) modifying magnetic coatings (that can be obtained, *e.g.*, by electrochemical deposition) on the surface of self-assembling thin films of the Langmuir–Blodgett type. Thus, the coatings including α-Fe (70 at.% Fe), magnetite Fe_3O_4, and admixtures of Fe_2O_3, may be formed on organosilanes.[182] Polymer-immobilised particles are formed *in statu nascendi* in magnetic fields. These materials seem to be rather promising as drug carriers, for magnetic recording of information, magnetic separation, as materials possessing the magnetic-optical properties, and as magnetic fluids,[326] the latter being colloidal solutions with strong magnetic properties. The role of carriers operating under extreme conditions (wide temperature range, vacuum, aggressive and biologically active media) may also be played by polymers, *e.g.*, oligoorganosiloxanes.

3. Polymer-immobilised nanoparticles as optical materials and semiconductors

The composite materials that comprise polymeric optical media and nanoparticles possess a unique set of the optical (in the visible light range) and semiconductor properties. The ease of mechanical processing and the film-forming properties of these materials make possible their use for the preparation of dispersive optical elements, band light filters, *etc*. To this end, the products of joint condensation of Au with a large excess of a diacetylene monomer, diphenylbutadiyne, or its polymer are most often used.[67] The metallopolymers produced contain 7%–16% of metal with a mean particle size of ~2 nm. The composite material is characterised by a 200-fold increase in the third-order optical coefficient. Thin films of Au- and Ag-plasmopolyfluorocarbon possess good optical properties.[86, 90]

Homogeneous composite materials with high absorption and refraction indices suitable for the production of optical elements are prepared on the basis of polymeric glasses with sulfoselenides of transition metals, photochromic glasses with Ag and Cu halides, holographic emulsions of Ag halide nanoparticles in gelatin,[327] *etc*. As a rule, the semiconductor component concentration in a polymeric binder (4-VPy, PVAl, *etc*.) does not exceed 0.1%, *i.e*., 'dilute solutions' are used.

As in the synthesis of metal nanoparticles, the methods of the assembly of semiconductor components directly in polymeric matrices have found extensive applications. For example, nanocrystals of CdS and ZnS are obtained from their salts and H_2S in polymeric solutions. The content of cadmium sulfide (in the form of ~50-nm particles) in these materials may be as high as 50%.[17] It is known that the optical characteristics of gelatin films depend on the particle size of incorporated $PbCrO_4$.[328] In this connection, it is noteworthy that the effective control of the particle size may be realised by varying the composition of copolymers and thereby the size of domains (Fig. 3) in ionomers.[329, 330] Thus, the mean size of CdS particles in toluene solutions of the block-copolymer of styrene with acrylic acid increases from 1.8–2.3 nm to 3–5 nm as the number of acrylic units in the ionic block increases from 4 to 32. Note also good promises for the application of materials of this type in the systems for solar energy accumulation and transformation.[331, 332]

4. The specific nature of catalysis with polymer-immobilised nanoparticles and clusters

The Group VIII metals in the colloidal state were among the first known catalysts of hydrogenation of organic compounds. As early as in the 1940s, PVAl, PVA, and PMMA were used to protect these colloids.[333] Later, silk fibroin, nylon, PETF, *etc*. were used to this end.

Catalysts of this type are of prime theoretical interest since they allow modelling of the size effects on the catalytic activity. They may be used to exemplify many concepts of basic theories of the catalysis: A A Balandin multiplet theory, N K Kobozev theory of active ensembles, and D V Sokolskii theory of skeletal catalysis. Multiple attempts were undertaken to assess the influence of the catalyst particle size on its activity. For example, the size of nickel particles was varied from that of individual atom to the bulk metal.[334] Quantitative estimates were made for the effect of the size of Ni_n/SiO_2 and Ni_nCu_m/SiO_2 on the course of hydrogenation.[335] Similar studies were performed with regard to the behaviour of deposited polynuclear complexes in the processes of hydrogenation and isomerisation of alkenes.[217, 336]

The application of polymer-immobilised cluster and nanoscale particles provides an additional possibility to shed light on the relationship between homogeneous, heterogeneous, and enzymic catalysis.[4] According to some features, these particles are close to homogenous catalysts: they are obtained from ordinary, soluble metal compounds by increase in their nuclearity, the polymer often performs the functions of macroligand and stereochemical environment, they can function under mild conditions, *e.g*., at temperatures below 100 °C. At the same time, these contacts also inherit major properties of heterogeneous systems: reactions occur at the interface, the activation of the substrate results from adsorption on the surface, the catalyst is easily separated from the reaction products and may be regenerated. The peculiarities of enzymic catalysis (substrate enrichment, structural correspondence, favourable orientation of reacting molecules, additional activation of the substrate by the multicentre catalytic system, *etc*.) are also easily simulated using polymer-immobilised clusters and nanoparticles. For example, additional introduction of neodymium ions into ultradispersed Pd particles immobilised in water-soluble polymers exerts a promoting effect on these catalysts of acrylic acid hydrogenation.[337] The reason for this effect consists in the substrate concentration resulting from the additional coordinational interaction with neodymium ions.

The above-discussed cryochemical technique for combining different elements, *e.g*., Ag, Pd, or Pt with liquid oligo- and polyesters, and polydienes makes it possible to achieve the 'critical loading' of polymer (when the concentrations of metals exceed the coordination possibilities of polymers). Subsequent deposition of such polymer-immobilised nanoparticles on carbon powder may lead to the formation of Ag^0_n/C, Pd^0_n/C, and Pt^0_n/C systems, which are traditional catalysts of numerous processes. Nanoparticles of Pt incorporated in glass-carbon matrices (Fig. 10) may also be referred to this type of catalyst.

In many cases, the polymer-immobilised nanoparticles manifest high activity and selectivity. This may be exemplified by the processes of ionic-coordinational polymerisation, hydrogenation, and oxidative transformations.[5] The activity of these catalysts essentially depends on the nature of the polymer and the size of nanoparticles. After the removal of heavy Pt particles by centrifugation (20 000 rpm), the transparent supernatant containing about 20% of the initial Pt in a finely dispersed form manifests much higher activity in the catalytic reaction of hydrogen liberation from water.[37] The size of the remaining Pt particles is critical for their catalytic activity to be manifested irrespective of the nature of the protecting colloid.

Of special interest is the regioselectivity observed in the hydrogenation of undecenoic and oleic acids on clusters stabilised by surfactants or polymers.[148] The surfactant micelles surrounding a cluster not only stabilise it but also orient appropriately the

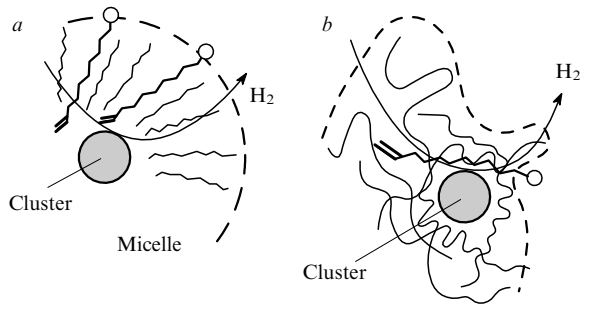


Figure 14. A supposed mechanism of the hydration of unsaturated fatty acids in micellar (*a*) and polymeric (*b*) systems.

unsaturated fatty acids (Fig. 14). In the case of a linear polymer, the double bond of substrate is more accessible to nanoparticles since the macromolecules are in a chaotic molecular motion.

The polymer-immobilised bimetallic Pt–Co colloids exhibit high selectivity (up to 99.8%) in the reaction of hydrogenation of cinnamaldehyde to the corresponding alcohol.[247] The application of polymer-protected nanoparticles is expected to lead to the discovery of new specific effects in catalysis. The cluster $[Pt_{15}(CO)_{30}]^{2-}$ fixed on Sephadex is used as the catalyst of the hydrogenation of selective redox-active cofactors.[223]

VIII. Conclusion

Among theoretical problems of the formation of clusters and nanoparticles in polymeric matrices, the most topical seem to be the questions of structural-morphological and spatial organisation of these systems at the local, molecular, and supramolecular levels, including thermodynamic peculiarities of their formation. Such an analysis has recently been performed using macrochelates as an example.[338] The most important problem seems to be the stabilisation of nanoparticles by monolayers of polymers and Langmuir–Blodgett films. The number of studies carried out in this direction is clearly insufficient. Thus, the nature of the adhesion at the interfaces formed still remains obscure.

The passivation of nanoparticles formed should be realised within reasonable limits allowing preservation of their energy-rich state. A highly significant theoretical and practical problem is to learn to control the processes that occur on the surface or in a thin subsuperficial layer of polymer granules, films, or fibres. In this context, of interest is the preparation of self-assembling colloidal layers of Au, Ag, and Ag–Au on the surface of compounds of different origin (including the plasma-purified PTFE) premodified by hydrolysed alkoxysilanes containing functional groups.[339] On such surfaces brought into contact with dilute solutions of monodisperse colloids, the assembly of nanoparticles takes place only as a monomolecular layer, which is 5–70 nm thick in the case of Ag and 5–20 nm thick in the case of Au and Au–Ag.

One may expect further progress in the development of novel methods for the preparation of polymer-immobilised clusters and nanoparticles. A promising direct synthesis of these products appears to be the dissolution of zero-valent metals in solutions of polymers that function as macroligands (like the solubilisation of metals in the presence of organic low-molecular-weight ligands)[340] with subsequent recrystallisation of particles, as it occurs in biological systems (Section VI). The technique of stabilisation of nanoparticles and clusters in the course of polymerisation of micelle-forming monomers is likely to become practically significant. These methods have been devised using Pt clusters as models resulting from the photodecomposition of H_2PtCl_6 in the presence of monomers of the type of $CH_2=CH(CH_2)_8COO(CH_2CH_2O)_nCH_3$.[341]

It is only recently that studies of the formation of nanoparticles with polymer–polymer compositions have began.[1] Hybrid PMMA–epoxy resin compositions and clusters of noble metals have been prepared,[342] which are currently used as functional light-sensitive solid solutions and non-linear optical materials.

Formation of an inorganic phase $Ti(OR)_4$ or $Zr(OR)_4$ in copolymers of styrene and 4-vinylphenol (with the particle size ranging from 20 to 250 nm),[343] preparation of nanoparticles by pyrolysis of metal carbonyls and mesogenic petroleum pitch,[344] production of drug carriers composed of nanoscale particles,[345] *etc*., have been described.

Undoubtedly, the progress of research into such small particles requires further development and the application of modern physicochemical methods, including the visualisation of the surface structure at the atomic level by means of scanning tunnel microscopy, transmission electron microscopy, ferromagnetic resonance, small-angle X-ray scattering, X-ray photoelectron spectroscopy, *etc*.

The polymer-immobilised nanoparticles are already used to solve specific technological problems associated with the surface modification: its metallisation, the imparting of antistatic and magnetic properties to it, design of new materials for photo- and cinematography, design of efficient fibrous filtering materials allowing isolation and concentration of precious metals, *etc*. Specifically, the surface metallisation is required to decorate plastics,[49, 310, 346] to modify polymeric films,[347] to make tribological coatings, and other purposes. The coatings made of polymer-immobilised nanoparticles on the basis of Be and plasmopolymers have found unexpected applications in the reactions of thermonuclear synthesis.[79]

It should be noted that clusters of metals can also be formed in such specific 'polymers' as fullerenes. In this case, both inclusion compounds of the type of endohedral complexes $M@C_{60}$, which are localised in the inner cavities of the spheroidal molecule C_{60}, and organometallic polymers of the type $C_{60}Pd_n$,[348, 349] or oligomers containing manganese carbonyls[350] are formed.

Nanocomposite materials are also formed upon evaporation of metals in carbon nanotubes. The clusters of metals (Cr, Ni, *etc*.) are localised both inside these tubes and on their ends and surface.[351, 352] On the other hand, the evaporation of metals in the oxidised nanotubes leads solely to the decoration of nanotube surface with nanoparticles (Fig. 15). An analogous pattern is also characteristic of lipid structures:[353] their electrochemical polymerisation and metallisation result in metal-coated polymers having the shape of hollow cylinders several tens of microns long, ~0.5 μm in inner diameter, and ~50 nm thick walls. Of interest is the similarity of such materials with the metallophilic microorganisms (Fig. 11).

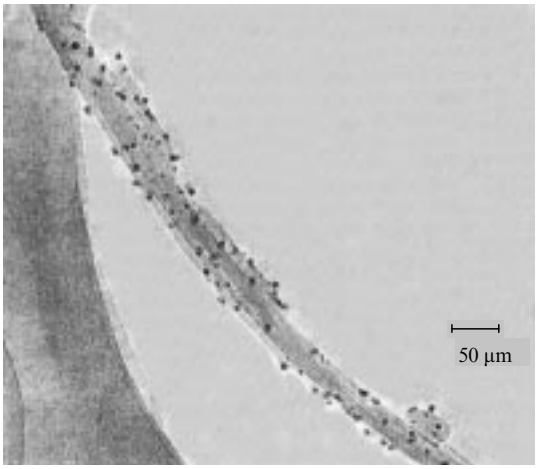


Figure 15. Electron micrograph of oxidised nanotubes decorated with silver.

Under mild conditions, biological systems bring about a controllable growth of iron oxide crystals (including magnetite) of definite size and morphology with strictly defined crystallochemical characteristics, which are so far difficult to achieve under laboratory conditions. Extensive studies of these processes (bioinorganic solid-phase chemistry) will allow one to establish the basic principles of targeted synthesis of the products classed as 'crystal engineered'. The discovery of the phenomenon of selective aggregation of microorganisms with dispersed metals and their compounds has already laid the foundation for the methods of biotechnological enrichment used in metallurgy and for the environment protection. Many of these principles are employed in the rapidly developing field known as nanotechnology [354] and are likely to form the basis of a new branch of science which may be defined as chemistry of highly organised compounds, including supramolecular chemistry and chemistry of hypermolecular compounds.[355]

* * *

Several publications related to the problems surveyed in this article have appeared since its submission. Of special note are an A.C.S. publication,[356] a special issue of 'Chemical Materials' Journal,[357] and a conference on electronic materials.[358] The theoretical problems of stabilisation of nanoparticles by polymers have been discussed.[359–366] Further development of the methods for preparation of polymer-immobilised nanoparticles [367–378] and clusters [379–382] has been documented. The research in traditional and novel fields of application of polymer-immobilised nanoparticles and clusters is in progress.[371, 375, 383–394]

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