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Nanostructured polymeric systems as nanoreactors for nanoparticle formation

L M Bronstein, S N Sidorov, P M Valetsky

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Abstract. The review concerns the syntheses of polymeric nanocomposites containing encapsulated nanoparticles formed in nanostructured polymeric systems including block copolymers, dendrimers, nanoporous polymers, polyelectrolyte gel – surfactant complexes and multilayered films. Nanostructures in amphiphilic block copolymers can form spontaneously both in the bulk (block microsegregation) and in solution (block copolymer micelle). In polymeric systems, nanostructures play the role of nanoreactors for the growing nanoparticles. The nanoparticle size, shape and size distribution are controlled by the nanostructure characteristics and synthesis conditions. The catalytic, magnetic and optical properties of these nanostructured polymeric nanocomposites are discussed. The bibliography includes 131 references.

I. Introduction

At present, increasing interest in the synthesis of nanoparticles and nanosystems and in the studies on their properties has been expressed.[1–3] Various methods for the synthesis of nanoparticles and the properties of these systems have been thoroughly reviewed (see Refs 4, 5 and 6 – 8, respectively). However, no systematic review of nanoparticle formation in nanostructured polymeric systems has been reported so far.

Nanostructures in a polymeric composite are defined as regular nanosized heterogeneous domains (*i.e.*, certain regions of the polymeric material that are separated by some interface). Due to the presence of nanostructures one can control the growth of nanoparticles, the particle size distribution and interfacial interactions. These factors are to a great extent responsible for the unique catalytic, magnetic, semiconductor, nonlinear optical, *etc.* properties of nanocomposites and, finally, for the fields of their application. Nanostructured matrices are quite promising for being used for nanoparticle formation. This is indicated by the tremendous progress achieved during the decade that has passed since the first use of block copolymers (the first representatives of nanostructured polymeric systems) for the formation of metal nanoparticles. At present, it is possible to obtain nanoparticles of different shape and size (*e.g.*, nanotubes, nanowires and other nanoscale objects) in nanostructured polymeric environment using various polymeric systems and different approaches.

L M Bronstein, S N Sidorov, P M Valetsky A N Nesmeyanov Institute of Organoelement Comounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-085) 135 93 00. E-mail: lybronst@indiana.edu (L M Bronstein), dist@ineos.ac.ru (S N Sidorov). Tel. (7-095) 135 93 07. E-mail: val@ineos.ac.ru (P M Valetsky)

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II. Nanoparticle formation in amphiphilic block copolymers

A feature of amphiphilic block copolymers is the ability to undergo microsegregation in the bulk and to form micelles in dilute solutions in selective solvents.[9–11] To synthesise nanoparticles, one block of a diblock or triblock copolymer must contain functional groups that can be involved in reactions with metal compounds.

1. Nanoparticles in microsegregated blocks

Block copolymers containing incorporated complexes or encapsulated nanoparticles in a specified block can be prepared in several ways. These are, *e.g.*, copolymerisation of organometallic monomers followed by corresponding transformations of the system; reactions of metal complexes with functional groups of block copolymers in solutions followed by microsegregation of the organometallic block copolymers (either in the form of films or in the bulk); and sorption of organometallic compounds into microdomains of block copolymer films. The sorption of metal complexes into diblock and triblock copolymers causes significant changes in the properties of polymeric systems (first of all, in the Flory – Huggins interaction parameter χ_{AB}). One can expect the greatest changes in χ_{AB} for non-polar flexible blocks, *e.g.*, polyisoprene (PI) or polybutadiene (PB) due to the appearance of polar groups and to the change in the chain conformation.

A typical example is provided by the introduction of $Fe(CO)_3$ groups into the PB block of a polystyrene – PB – polystyrene triblock copolymer (Kraton) containing 30 mol.% of polystyrene (PS) *via* complexation.[12] Complexation leads to a considerable increase in the force of adhesive binding of the polymer film to polar surfaces (glass, metals) and in the rigidity of the PB block (the higher the iron concentration, the higher the glass transition temperature of the PB block) and causes reduction of the PB block mobility. At the same time, in spite of significant changes in the chemical structure, the material retains its morphology ('cylinders in matrix').

A similar mophological stability was also observed in highly assymetrical diblock ionomers in which the shorter polyacrylic

acid (PAA) block forms spherical microdomains encapsulated in the matrix of the major component (PS).[13] It was found that neither sorption of Cd^{2+} ions nor formation of CdS nanoparticles change the block copolymer morphology. Experiments with a diblock copolymer based on isoprene and 2-vinylpyridine (2VP) showed [14] that at low content of palladium nanoparticles the block copolymer retains its lamellar structure and that an increase in the palladium content causes distortion of the ordered (regular) structure. The growth of nanoparticles influences the block copolymer structure. The system is also characterised by feedback, namely, the interfaces between different domains and the free surfaces of the polymer films affect the formation of nanoparticles inside the block copolymer microphase. In particular, as was shown by transmission electron microscopy (TEM), the size of the growing silver,[15] palladium [14, 16] (Fig. 1) and other metal nanoparticles confined within microsegregated layers is limited to the corresponding layer thicknesses. Almost no penetration of the metal seeds and growing particles into adjacent non-polar layers was observed; *i.e.*, the block copolymer domain acts as a nanoreactor in the formation of metal nanoparticles. The synthesis of nanoparticles in thick homopolymer films led to uncontrolled growth of nanoparticles and resulted in large particles characterised by a broad size distribution.[15] As the thickness of the metal-containing homopolymer film decreased down to the characteristic lamella size in the block copolymer ($\sim$100 nm), the free surface of the thin film behaved as an interface.[15]

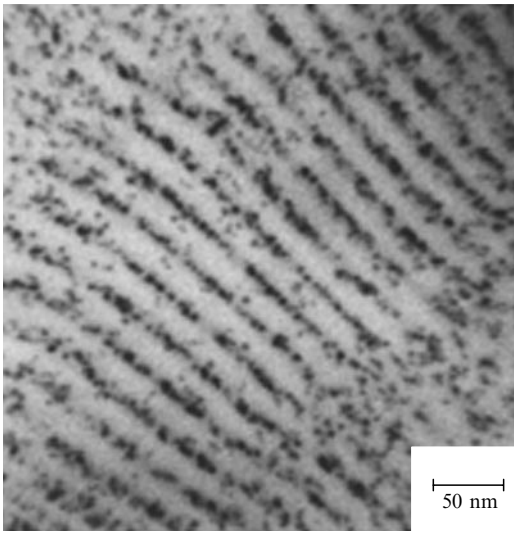


Figure 1. TEM image of a sample prepared by reduction of the system [polyisoprene-*block*-poly(2-vinylpyridine)] – $Pd(acac)_2$ – benzyl alcohol with a component ratio of 32.5 : 2.6 : 64.9 (mass %) after evaporation of the solvent.[16]

Metal nanoparticles encapsulated in multilayered thin films based on block copolymers were synthesised analogously.[17] The films were prepared by adsorption of symmetrical PS and poly(4-vinylpyridine) (P4VP), which form a lamellar structure, in the bulk, on a solid substrate. These films (they resemble multilayered films fabricated by adsorption of oppositely charged polyelectrolytes) were pre-loaded with a metal compound (*e.g.*, $HAuCl_4$) and then with the reducing agent. Nanoparticles were formed only within the P4VP block. It was shown that nanoparticles can affect the lamella size.[18] The best ordered arrangement of nanoparticles in multilayered block copolymer films was obtained for the films prepared under nonequilibrium conditions that provided the possibility for highly asymmetrical nanoparticles to be formed.[19, 20]

Sometimes, particle formation in the nanoreactor causes significant changes in the reaction conditions. For instance, cobalt ferrite ($CoFe_2O_4$) is usually obtained by high-temperature synthesis from corresponding hydroxides. If $CoFe_2O_4$ nanoparticles are formed inside the block copolymer domains,[21] the reaction can proceed at room temperature.

2. Metal nanoparticles in block copolymer micelles

a. Formation of metal nanoparticles in block copolymer micelle cores

Amphiphilic block copolymers dissolved in selective solvents (they dissolve only one block) form micelle. The size and shape of these objects depend on the nature of the blocks, the type of solvent (to a first approximation, a hydrophilic or hydrophobic one) and on the molecular mass of the blocks.[9, 11] If, in the case of diblock and triblock copolymers, the micelle core comprises a block containing certain groups capable of being involved in reactions with metal compounds to give metal complexes or salts, this core can be loaded with the corresponding metal constituent of the complex or salt and then used as a nanoreactor for metal nanoparticle formation. Appropriate block materials include, *e.g.*, poly(2-vinylpyridine) (P2VP) or P4VP, polymethacrylic acid (PMAA) or PAA, PB or PI and some other polymers. The micelle corona must be built of a block that contains no functional groups but provides the solubility and stability of micelles in corresponding solvents. Materials appropriate in this case include PS, poly(ethylene oxide) (PEO), polyisobutylene (PIB) and other polymers.

The synthesis of metal nanoparticles in block copolymer micelle cores was nearly simultaneously employed by several research groups.[13, 22–25] Studies on the formation of gold, palladium, platinum and other metal nanoparticles in PS-*block*-P4VP-based micelles revealed that the nanoparticle morphology strongly depends on the type of the reducing agent. With 'sluggish' reducing agents only one particle can be formed in the micelle core in the absence of inter-micellar exchange reactions. Using 'fast' reducing agents, the nucleation and growth of a large number of particles occur simultaneously; therefore, each micelle contains many small particles. This morphology is most preferable for catalysis (Fig. 2).[26] Both morphologies are schematically shown in Fig. 3. To prevent inter-micellar exchange, the micelle cores can be cross-linked. Then, variation of the reducing agent permits fine control of not only the particle morphology but also the particle size.[27] Using micelle cores as nanoreactors, both monometallic and bimetallic nanoparticles can be synthesised; their morphologies depend on the nature of the metal employed.[28] Adsorption of nanoparticle-containing micelles onto different substrates results

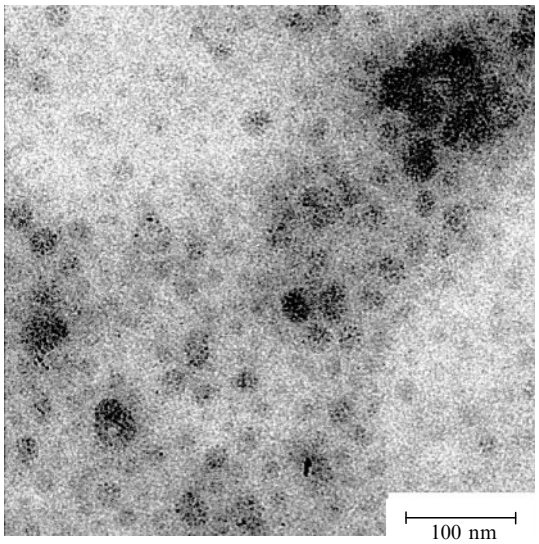


Figure 2. TEM image of bimetallic Pd – Pt nanoparticles formed in PS-*block*-P4VP-based micelles.[26]

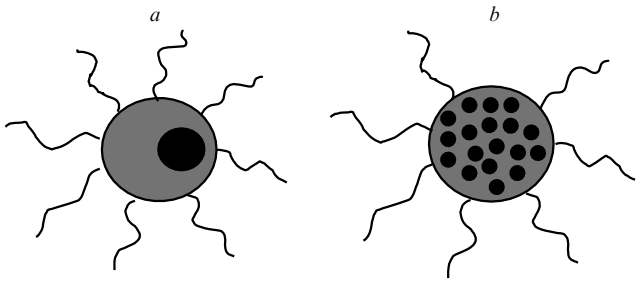


Figure 3. Schematic representation of nanoparticles with 'cherry' (*a*) and 'raspberry' (*b*) morphologies.

in the formation of monomolecular layers; this phenomenon is used in nanolithography.[29]

Nanoparticles confined within micelle cores can also be prepared using star-like block copolymers. For instance, block copolymer micelles based on star-like block copolymers with a P2VP core and PS shell were used [30] to form gold nanoparticles with a narrow size distribution. It is believed [30] that star-like polymer micelles are more stable, thus being responsible for the nanoreactor stability and improved control of particle growth.

When using a triblock copolymer in which only the middle block can be coordinated by metal compounds, and nanoparticles can be formed within the outer layer of the core rather than the entire core space when the middle block and one of the two terminal blocks are insoluble in the reaction medium. This can be exemplified by the synthesis of gold nanoparticles in PS-*block*-P2VP-*block*-PEO micelles in aqueous solutions.[31] Such systems can be of particular interest for catalysis, because nanoparticles present in the outer layer of the core are better accessible to substrates.

Analogously to the synthesis of nanoparticles in block copolymer micelle cores in organic media, metal nanoparticles can be produced in aqueous media; however, only a few block copolymers are available in this case, *e.g.*, PEO-*block*-P2VP and PEO-*block*-PB.[32, 33] In the former system, the situation is complicated by the fact that micellisation of the polymer depends on the pH value of the medium (at pH < 5, the PEO-*block*-P2VP micelles undergo disassembling). Nevertheless, in the presence of metal compounds or after formation of nanoparticles micelles are retained even in acid media; however, they become very loose. The reverse situation is observed in the case of PEO-*block*-PB. In water, this block copolymer forms very dense micelles that can act as both nanoreactors for the formation of palladium, platinum or rhodium nanoparticles and excellent templates for mesoporous silica formation.[33] Such systems are of great interest as promising heterogeneous catalysts of various reactions.

Not only micelle cores (see above) but also the inner micelle corona layer can be cross-linked to stabilise the nanoreactor. Triblock copolymers comprised of PEO, poly(glycerol monomethacrylate) (PGMA) and poly(diethylaminoethyl methacrylate) (PDEAEMA) blocks [poly(2-hydroxyethyl methacrylate), PHEMA, was also used as the middle block] completely dissolved in water at low pH values but formed multilayered onion-like micelles with PDEAEMA cores at pH > 7–8.[34] The middle block in the micelles was cross-linked by reaction with divinyl sulfone. These micelles were used as nanoreactors for the formation of gold nanoparticles. The authors [34] believe that the micelles cross-linked in the corona interior provide the stability of nanoparticles and prevent inter-micellar reactions. Yet another possible advantage of these micelles is a substantial increase in their loading without deterioration of sedimenting stability; however, this has not been confirmed so far.

Another approach was employed to form ferrous oxide nanoparticles in PI–poly(2-cinnamyl methacrylate)–poly(*tert*-butyl acrylate) (PI-*block*-PCM-*block*-PtBA) cross-linked triblock copolymer micelles in a THF–hexane mixture.[35] These micelles are comprised of a PI corona and two core layers with PCM as the outer layer and PtBA as the inner layer. The PCM layer was cross-linked by exposure to UV radiation, which resulted in the formation of stable nanospheres. Subsequent hydroxylation of the PI block to impart hydrophilic properties to the nanospheres was followed by removal of the *tert*-butyl groups to allow the nanosphere cores to react with metal compounds. The possibility of using such nanospheres as nanoreactors was demonstrated by taking the formation of magnetic ferrous oxide particles with a narrow size distribution as an example. However, this technique is very labour-consuming and seems to be of little promise.

We believe that targeted synthesis of block copolymer micelles opens up great prospects for the design of materials suitable for the fabrication of various devices. However, anionic polymerisation employed for the synthesis of most block copolymers is a quite expensive method. Besides, it is very sensitive to external factors, which hampers progress in this area of research. Another method, namely, charge transfer radical polymerisation, is thought to be a cheaper and more reproducible method of synthesis of block copolymers with a narrow molecular mass distribution.[36, 37]

b. Double hydrophilic block copolymers. Micellisation during complexation

In some cases, a metal compound incorporated into a polymer matrix can induce nanostructuring of the matrix. This is observed when using, *e.g.*, the so-called 'double hydrophilic' block copolymers comprised of blocks with similar hydrophilicities. One block must contain functional groups while the other block must be inert towards metal compounds. Dissolution of such a block copolymer in water results in a true solution, but the addition of some metal salts can induce micellisation due to coordination of the metal by one of the blocks (Fig. 4).[38] In this case micelles are formed and exist due to the coordination between the metal ions and functional groups of the polymer. Such block copolymers can be obtained by simply coupling two blocks after relevant functionalisation.[39] Another 'double hydrophilic' block copolymer, poly(ethylene oxide)-*block*-poly[(*N*-carboxymethyl)ethyleneimine] (PEO-*block*-PCMEI), was designed for controlled mineralisation (control of formation of $CaCO_3$ nanoparticles), because PCMEI can interact with calcium ions.[40]

Poly(ethylene oxide)-*block*-polyethyleneimine (PEO-*block*-PEI) was proposed for the synthesis of transition metal nanoparticles in aqueous media because the PEI block readily interacts with these metal ions affording coordination compounds.[38] The

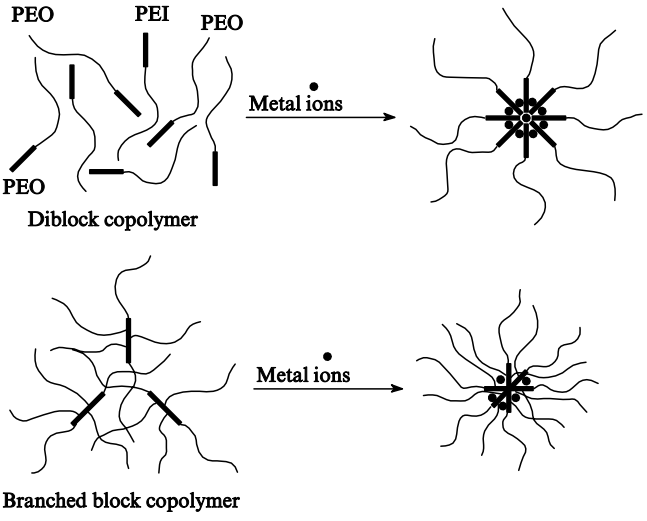


Figure 4. Scheme of micelle formation in PEO-*block*-PEI due to the interaction with metal ions in aqueous solution.[38]

PEI blocks undergo aggregation, thus formng the micelle core, while the PEO blocks form the micelle corona. These micellar systems can control the nucleation and growth of nanoparticles analogously to the amphiphilic block copolymer micelles described above. Moreover, a typical amphiphilic block copolymer, PEO-*block*-P2VP, also becomes soluble on the molecular level at pH < 5 and behaves like PEO-*block*-PEI in the reactions with metal compounds. Reduction of the metal ions is accompanied by the formation of nanoparticles, yet the PEO-*block*-PEI micelles do not decompose; only their hydrodynamic characteristics are changed (Table 1). This block copolymer was successfully used to form CdS nanoparticles [41] which exhibited oxidative stability for many months due to the polymeric environment. By varying the polymer concentration and the type of the solvent the nanoparticle size was varied from 2 to 4 nm.

Table 1. Hydrodynamic diameter (D_h) and its standard deviation (σ) for Pt-containing PEO-*block*-PEI micelles.[39]

Polymeric system	Molar ratio PEI : Pt	D_h /nm	σ (%)
PEO-*block*-PEI + H_2PtCl_6	8 : 1	138	32
	4 : 1	154	29
	2 : 1	176	32
	1 : 1	201	30
PEO-*block*-PEI + Na_2PtCl_6	8 : 1	210	29
PEO-*block*-PEI + K_2PtCl_4	8 : 1	578	115
PEO-*block*-PEI + H_2PtCl_6 reduced with $N_2H_4 \cdot H_2O$	4 : 1	110	24
PEO-*block*-PEI + H_2PtCl_6 reduced with H_2	4 : 1	149	27

To control the morphology of nanoparticles formed, one can use the relations described for amphiphilic block copolymer micelles. The nanoparticle morphology is affected by the nature of the reducing agent, the concentration of the metal compound and the pH value of the medium. Unlike amphiphilic block copolymer micelles, the micelles obtained *via* complexation are loose, which favours inter-micellar exchange of metal ions and prevents control of the growth of nanoparticles.

c. Nanoparticle formation in micelle coronas

Metal nanoparticles can be synthesised in coronas of amphiphilic block copolymer micelles. If the micelle corona contains no groups suitable to coordination by metal compounds, nanoparticles are stabilised only by the hydrophobic interactions with the core. This procedure was employed to synthesise palladium, platinum and gold nanoparticles stabilised in aqueous solutions of PS-*block*-PEO and PS-*block*-PMAA.[42, 43] It was shown that the reduction of metal compounds results in the formation of small nanoparticles and that stabilisation of the nanoparticles exclusively due to hydrophobic interactions with the PS micelle cores is insufficient for obtaining solutions with high sedimenting stability. At the same time, accessibility of the nanoparticles in the micelle corona can play an important role for applications of such systems in catalysis.

To make the nanoparticles located within coronas of amphiphilic micelles more stable, it was proposed to design hybrid systems comprising amphiphilic block copolymers and surfactants.[44–46] It was assumed that the hydrophobic surfactant 'tails' would penetrate hydrophobic PS-*block*-PEO micelle cores while the charged groups of the surfactant would be arranged at the core surface (Fig. 5). Exchange of the surfactant counterions by platinum, palladium or rhodium ions was assumed to enable the loading of the corona with metal ions.

Light scattering and ultracentrifugation experiments showed that hybrid systems PS-*block*-PEO–surfactant have a complex structure and comprise micelles, micellar clusters and supermicellar aggregates. The addition of positively or negatively charged

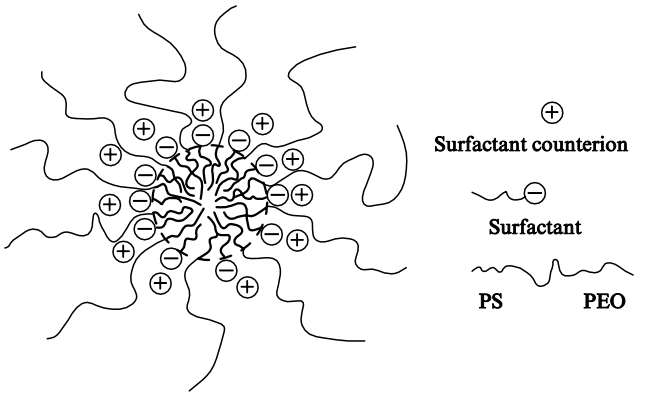


Figure 5. Schematic illustration of PS-*block*-PEO micelles containing anionic surfactant.[38]

surfactants to the PS-*block*-PEO micellar solutions causes an increase in the size and mass of micelles and micellar clusters. This holds until a certain surfactant concentration is reached, which depends on the type of the surfactant. An increase in the concentration [as a rule, above the critical micelle concentration (CMC)] causes a decrease in the size of micelles and micellar clusters. ^{1}H NMR studies revealed that the addition of surfactant significantly enhances the mobility in the PS core, which confirmes co-micellisation of the block copolymer and cationic (or anionic) surfactant molecules. Ion exchange of cetylpyridinium chloride (CPC) counterions by $PtCl_6^{2-}$ or $PdCl_4^{2-}$ ions in the system PS-*block*-PEO/CPC leads to saturation of the micellar structures with palladium or platinum ions. Subsequent reduction of the metal-containing systems thus obtained with sodium borohydride or dihydrogen is accompanied by the formation of (mostly) micelle-encapsulated metal nanoparticles. The morphology and stability of the palladium and platinum nanoparticles synthesised in these systems depend on the type of the reducing agent and on the metal salt concentration. Reduction with $NaBH_4$ results in breakdown of micellar clusters and formation of micelles containing encapsulated nanoparticles (Fig. 6). These systems exhibited very high stability for one year, provided that the metal salt concentration was at most 1.24×10^{-2} mol litre^{-1}. Reduction with dihydrogen results in the formation of metal nanoparticles both in micelles and in micellar clusters. In this case, colloid solutions were stable at the metal salt concentrations of at most 3.36×10^{-3} mol litre^{-1}. Platinum particles formed using the reducing agents

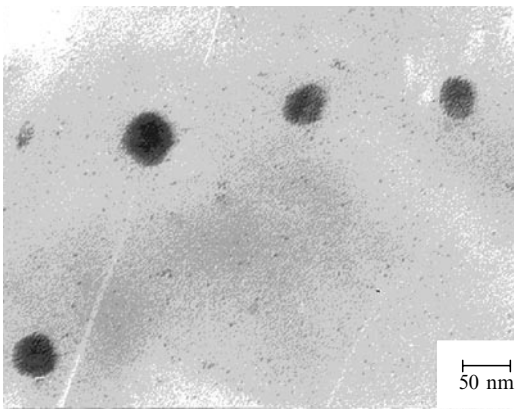


Figure 6. TEM micrograph of platinum nanoparticles obtained *via* reduction of $H_2PtCl_6 \cdot 6H_2O$ (1.24×10^{-2} mol litre^{-1}) with sodium borohydride and stabilised in the PS-*block*-PEO/CPC hybrid micelles in water.[44]

mentioned above were 2–4 nm in diameter, while palladium particles were somewhat larger (4 to 6 nm in diameter).

If the metal salt ions exist only in the form of cations, one can use hybrid systems containing an anionic surfactant, sodium dodecyl sulfate (SDS). For instance, the hybrid system PS-*block*-PEO/SDS allows sodium counterions to be exchanged with rhodium ions generated during dissociation of $[Rh(Py)_4Cl_2]Cl \cdot 6\,H_2O$. Reduction of the system thus obtained with sodium borohydride also leads to saturation of micelles with rhodium nanoparticles of sizes 2–3 nm. Thus, by adding surfactants to 'inert' (containing no functional groups) amphiphilic micelles, one can use them as a good stabilising system for the formation of metal nanoparticles of size 2 to 6 nm. The drawback of this approach is the absence of direct methods of varying the nanoparticle size.

An interesting method of transformation of core-embedded nanoparticles into corona-embedded ones has been reported.[47] When a solution of PS-*block*-P2VP–CdS micelles in an organic solvent was placed in an aqueous medium characterised by a low pH value, the PS block collapsed and a PS core was formed (in the organic medium, the core consisted of the P2VP block). Simultaneously, protonation-induced dissolution of the P2VP block occurred. Protonated (charged) P2VP formed the micelle corona and stabilised the CdS nanoparticles grown in the P2VP core in organic solvent. This permitted fine control of the growth of nanoparticles.

III. Formation of metal nanoparticles in polyelectrolyte systems with regular morphologies

1. Formation of nanoparticles in polystyrenesulfonate microgels

Microgels are spherical particles several nanometres in diameter.[48,49] Taking into account the structure-stabilising factors, *viz*., the size and cross-linked structure of microgels, they can be treated as nanoreactors, or molecular containers that allow the growth of nanoparticles to be controlled. Taking the reduction of gold compounds in these microgels as an example, the nanoparticle formation was studied.[50] The effects of the reduction rate and of the characteristics of the microgel on the nanoparticle parameters was studied. It was found that fast reduction of gold compounds with sodium borohydride in water results in the formation of small gold particles (4.5 nm in diameter according to X-ray diffraction data) in microgels. Slowing down the reduction using sodium borohydride in alkaline solution (0.1 M NaOH) changed the nanoparticle morphology, namely, long 'filaments' (according to X-ray diffraction and TEM data) were formed from the particles 7 nm in diameter. Very slow reduction with hydrazine hydrate led to the formation of large particles (25 nm), which were found only in 15% of the microgel (85% of the microgel contained no gold particles at all). Apparently, in the case of sluggish nucleation, small clusters and metal ions non-uniformly migrate towards disordered microgel domains and then easily undergo aggregation. Clearly, microgels with disordered morphologies cannot be used to control nanoparticle growth.

Yet another parameter, which strongly affects both the nanoparticle and the entire sample morphology, is the degree of cross-linking of the microgel. The larger this parameter, the higher the probability of formation of spherical metal nanoparticles encapsulated in microgels. A high resolution TEM study confirmed the fact that nanoparticles grew from the same core and that the exterior of the particles was governed by the microgel environment. In the experiments with $NaBH_4$, the particle growth was controlled by the elasticity of the surrounding gel matrix. This means that particles grow along a given direction until the surrounding polymer chains become completely aligned in this direction. Thus, the system ensures the 'cage' effect though the 'cage' itself is not rigid.

In addition to gold nanoparticles, this method was employed to synthesise palladium and platinum nanoparticles.[51] Microgel-grown nanoparticles and amphiphilic PS-*block*-PEO copolymers were used as templates for obtaining mesoporous silica. Hence, microgels can have two functions, namely, to act as nanoreactors for the formation of metal nanoparticles and to serve as pore-forming templates in the formation of mesoporous silica.

2. Polyelectrolyte gel–surfactant complexes as nanostructured media for the interaction with metal ions and formation of metal nanoparticles

Polyelectrolyte gel complexes with oppositely charged surfactants are highly ordered self-organised nanostructures. They have been the subject of intensive research in the last decade.[52–57] The SAXS spectra of the cationic gel–anionic surfactant and anionic gel–cationic surfactant complexes exhibit very sharp and intense peaks indicating the presence of large ordered surfactant domains in gel. Statistical disorder in gel has no effect on the regular ordered arrangement of surfactant aggregates. Moreover, at the same surfactant concentration the surfactant molecules in oppositely charged gels are better ordered compared to aqueous media.[57] Spatial ordering in the gel–surfactant complexes is of interest from the standpoint of preparation of a nanostructured medium for the formation of metal nanoparticles.

It was established that sorption of metal ions by hydrogel–surfactant complexes occurs when the charges of the ions and of the charged groups of the gel are opposite in sign.[58–60] The ions sorbed form metal compound clusters arranged between the charged groups of the polymer chain and the head groups of the surfactant molecules (Fig. 7). These clusters serve as the nucleation centres of metal nanoparticles. In the case of fast reduction, particles are formed in an ordered environment. Moreover, the surfactant molecules in the immediate vicinity of the growing particles are even more ordered (though generally the growth of nanoparticles makes the surfactant more disordered), thus providing an extra means for control of the particle growth, which results in a narrow particle size distribution (Fig. 8).[60] This effect is observed for various metal compounds and hydrogel–surfactant complexes. In the case of slow nucleation, small clusters and metal ions non-uniformly migrate towards the disordered region of hydrogel and then undergo aggregation into large particles characterised by a broad size distribution. Polyelectrolyte gels without nanostructured morphologies cannot be used to control the growth of metal nanoparticles.

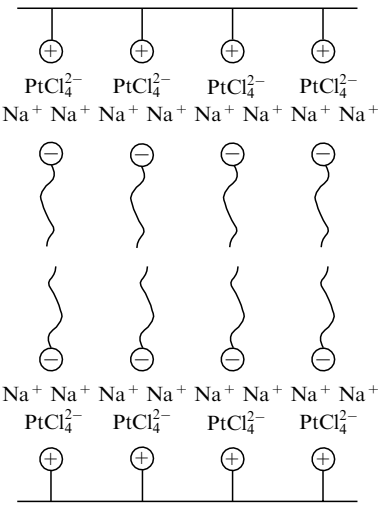


Figure 7. Schematic view of hydrogel–surfactant complexes with a sorbed metal salt.

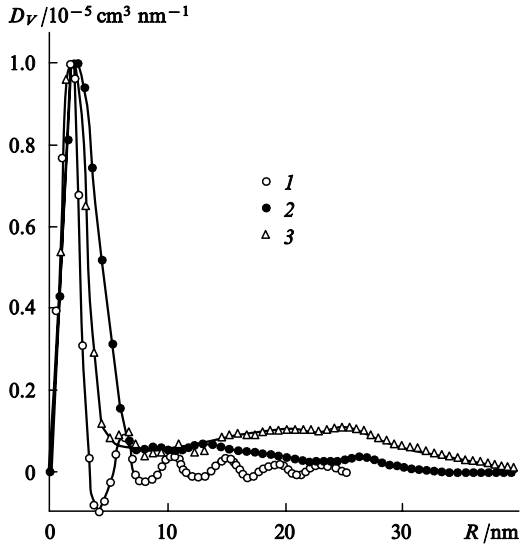


Figure 8. Volume distribution functions obtained for poly(diallyldimethylammonium chloride) hydrogel – sodium dodecylbenzosulfonate complex containing $H_2Pt(OH)_2Cl_4$ clusters (*1*) and encapsulated platinum nanoparticles reduced with $NaBH_4$ (*2*) and $N_2H_4 \cdot H_2O$ (*3*).[60]
R is the particle radius.

3. Nanoparticle formation in thin layers of supported polyelectrolytes

Thin polyelectrolyte layers are prepared by depositing a polyelectrolyte layer onto a charged substrate. This can be followed by layer-by-layer deposition of oppositely charged polyelectrolytes (Fig. 9).[61] Nanoparticles can also be used as 'substrates.' This permits preparation of various core – shell materials or hollow spheres.[62,63] These multilayered materials are treated as nanostructured systems in which each layer is a nanoreactor. For instance, cadmium sulfide nanoparticles were prepared[64] by sequential deposition of cadmium polystyrenesulfonate and polyvinylpyridine layers on PEI-modified silica or other substrates. Then, the multilayered film was exposed to H_2S for 30 min at room temperature, which resulted in a hybrid system containing CdS nanoparticles. Silver nanoparticles were produced in multilayered polyelectrolyte films based on PAA and protonated polyamine.[65] Repeated treatment with the silver salt (carboxyl groups are released after formation of nanoparticles on exposure to UV radiation) permitted an increase in the metal content in the film from 4% to 24%.

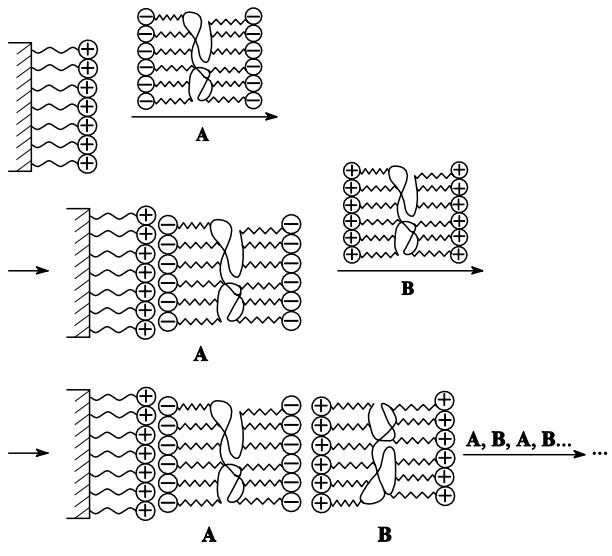


Figure 9. A scheme showing the formation of polyelectrolyte layers involving layer-by-layer adsorption of cationic and anionic polyelectrolytes (counterions are not shown).[61]

In order to provide better control of the particle growth, nanoparticles are sometimes prepared in surfactant micelles, which are then incorporated into polyelectrolytes to give multilayered films containing nanoparticles.[66] In this case, nanoparticles grow outside the polymeric system, which goes beyond the scope of this review. However, this approach is noteworthy. Indeed, recent studies revealed that, in contrast to amphiphilic block copolymers, multilayered composites are characterised by the presence of broad transient regions between each pair of electrolytes. As a consequence, the 'nanoreactor' size changes appreciably. In this case, it is difficult to synthesise particles with narrow size distribution, though their arrangement is governed by the particular polyelectrolyte layer.

Nanoparticles can also be formed using Langmuir – Blodgett polymer films, which resemble thin homopolymer films considered above. Only a few studies on the subject are available. Usually, nanoparticles were prepared separately and then mixed with an amphiphilic polymer before film formation.[67] Interesting results were reported in the article[68] concerned with the formation of CdS nanoparticles in the Langmuir – Blodgett film based on nonacosa-10,12-diyne acid after polymerisation of the acid on exposure to UV radiation. Exposure of the polymerised film containing cadmium ions to H_2S resulted in the formation of nanoparticles 10 nm in diameter. The photochemical and electrochemical properties of these films were described.[68] Another example of similar approach was also reported.[69] Here, cadmium sulfide nanoparticles of different size were prepared in Langmuir – Blodgett films formed by a polymer based on the octadecyl ester of polymaleic acid with different carboxyl group/hydrocarbon chain ratios. This permitted variation of the nanoparticle size and the photochemical properties of the films. Clearly, the systems developed cannot be used for fabrication of bulk materials or thick films, because ordered nanostructures in these amphiphilic homopolymers are formed under specific conditions (*e.g.*, at the air – water interface).

Controlled growth of nanoparticles can be performed in any thin homopolymer films. For instance, bimetallic Au/Cu nanoparticles of different composition were obtained by evaporation of metals in thin nylon-11 films.[70] The composition of bimetallic particles and their sizes were changed by varying the amount of metals evaporated. Experiments led to preparation of bimetallic nanoparticles of different composition with a narrow size distribution.

IV. Synthesis of dendrimer-encapsulated metal nanoparticles

The formation of dendrimer-encapsulated metal nanoparticles can be treated as a specific kind of nanoparticle synthesis in loose cores of block copolymer micelles. At the same time, there are significant differences between these processes (see below). In most cases researchers use commercially available poly(amidoamines) (PAMAM) dendrimers. By varying the dendrimer size (or dendrimer generation) and the metal compound loadings one can control the metal nanoparticle size. All publications on the subject are quite recent. It was Bar *et al.*[71] who pioneered the use of dendrimers as stabilisers in the formation of gold and silver nanoparticles. More recently,[72] it was shown that hydroxyl-terminated PAMAM dendrimers can be used as templates and stabilisers for the preparation of monodisperse transition metal nanoparticles possessing catalytic properties (Fig. 10). It is believed that the dendrimer macromolecule has an internal cavity, which is used for the formation (stabilisation) of a nanoparticle. However, broad nanoparticle size distribution when metal ions

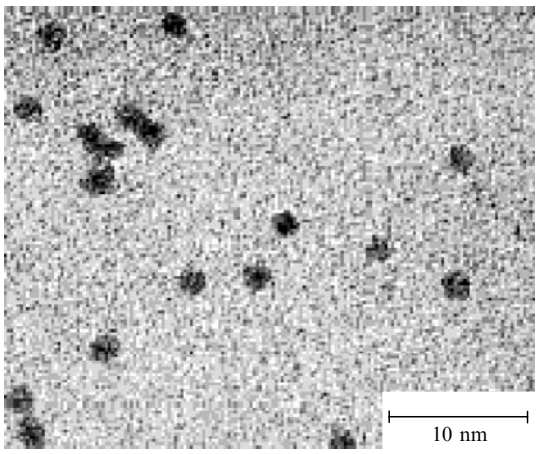


Figure 10. A HRTEM image of hydroxyl-terminated G4 dendrimer containing a total of 60 Pt atoms in each dendrimer.[72]
Platinum nanoparticles are monodisperse in size and shape.

exchange between dendrimer macromolecules (the metal compound migrates from one dendrimer to another) suggests that this cavity plays an insignificant role in the limitation of nanoparticle growth. These materials are prepared *via* sorption of metal ions into dendrimers followed by complexation with amino groups. Subsequent chemical reduction results in the formation of dendrimer-encapsulated metal nanoparticles comprising exactly the same number of atoms as that pre-'loaded' into the dendrimer. If no exchange of metal ions between dendrimer macromolecules occurs, the nanoparticle size distribution is narrow and fine control of the particle growth is possible. Nanocomposites thus obtained are water soluble and retain their stability for months. They exhibit a high catalytic activity towards alkene hydrogenation in water.[73] What is more, the catalytic activity can be controlled by varying the dendrimer size (generation), *i.e.*, the dendrimer acts as a nanofilter. Dendrimers are used as nanoreactors for the formation of not only monometallic but also bimetallic particles.[3]

When using PAMAM dendrimers containing amino groups at the surface, the size of the gold nanoparticles synthesised by exposing the dendrimer solutions to UV radiation was strongly dependent on the amino group/metal compound concentration ratio.[74,75] The particle size distribution was much broader than in the case of hydroxyl-terminated PAMAM dendrimers. Probably, the presence of the surface amino groups favours ion exchange between dendrimers during the formation of gold nanoparticles. By using penetration of hydroxyl-terminated PAMAM dendrimers into PHEMA followed by the formation of dendrimer-encapsulated nanoparticles one can prepare novel hybrid materials containing nanostructured polymer fragments and encapsulated nanoparticles.[76]

The effect of the dendrimer generation in systems with surface hydroxyl groups on the nanocomposite morphology has been studied in detail.[77] It was shown that low dendrimer generations undergo aggregation upon stabilisation of metal nanoparticles, whereas G6–G9 dendrimers can stabilise one nanoparticle per dendrimer and the particle size can be controlled with ease by varying the number of metal atoms. These results are consistent with the published data.[74] Experiments with G10 dendrimers revealed the formation of several small metal particles per dendrimer. To increase the stability of metal nanoparticles in various media, dendrimers can be modified by attaching PEO chains to the terminal amino groups of PAMAM macromolecules.[78] This has no effect on the ability of dendrimers to control the nanoparticle growth but provides better compatibility with a broad range of solvents and with a number of polymers. When using dendrimers with terminal glucose residues, the reduction of gold and silver ions and subsequent formation of nanoparticles from them is performed in an alkaline medium. Oxidation of hydroxyl groups does not require the use of additional amount of the reducing agent; however, nanoparticles thus obtained are characterised by a very broad size distribution.[79,80] Apparently, here we deal with facilitated exchange of metal ions between the dendrimer molecules because the terminal groups are involved in the reduction of metal ions.

Hydrophobically modified PAMAM dendrimers were used to form gold nanoparticles of size 2 to 4 nm in toluene and chloroform.[81] Recently, polypropyleneimine-based dendrimer modified by adamantyl groups have been reported.[82] The idea of these experiments was to involve hydrophobic groups in the interaction with amphiphilic block-cyclodextrin (the inner cavity of this molecule also possesses hydrophobic properties) and thus to prevent inter-dendrimers reactions during the sorption of metal ions and formation of nanoparticles. However, in spite of the complexity of this approach, the degree of control of nanoparticle growth was the same as that achieved using hydroxyl-terminated PAMAM dendrimers. Namely, no stabilisation of nanoparticles was observed with low-generation dendrimers, whereas higher-generation dendrimers permitted formation of nanoparticles with a narrow size distribution.

Another type of hydrophobic modification is to use polypropyleneimine-based dendrimers with stearyl terminal groups.[83] In toluene, they form inverse micelles with collapsed cores; however, sorption of metal salts causes the formation of cylindrical multidendrimer structures with swollen cores containing no metal salt. The action of the reducing agent leads to the formation of spherical gold nanoparticles and to the breakdown of cylindrical structures. These composite materials are thought to be of interest as catalysts and in the design of materials with specific optical properties (though these properties were not studied). Higher generation PAMAM dendrimers are commercially available but their synthesis is a multistage process. Because of this, the use of dendrimers seems to be no more promising compared to block copolymers.

Analogously to other nanostructured polymer matrices (*e.g.*, block copolymers or microgels), dendrimers containing encapsulated nanoparticles can be used as templates for the formation of mesoporous materials containing nanoparticles in pores. For instance, dendrimers containing Cu^{2+} ions were used[84] as templates for the formation of mesoporous silica. However, these templates provided no high SiO_2 porosity and ordered pore structure. Structural ordering is of great importance for the manifestation of optical properties while low porosity is inappropriate for catalytic applications (those materials containing encapsulated CuO nanoparticles were assumed to be efficient catalysts). We believe that only those templates that allow interpenetrating pores to be formed are promising for the fabrication of mesoporous materials containing encapsulated nanoparticles.

Introduction of metals and synthesis of nanoparticles can also be performed with carbosilane dendrimers[85] as well as nitrogen-containing and phosphorus-containing dendrimers[86,87] that offer the possibility of sorption of mixed transition metal clusters.

Thus, the use of dendrimers provides a means for fine control of nanoparticle growth under particular conditions. However, multistage synthesis of these macromolecules and the necessity of purification in each stage of the process complicate practical implementation of these systems as nanoreactors.

V. Metal nanoparticle formation in cavities (pores) of a polymer matrix

Controlled growth of metal nanoparticles in a polymer matrix is possible if it occurs in cavities or pores. In this case, the size of the growing particles can be limited to the cavity size. In the text below we consider two cases: (1) cavities contain no functional groups interacting with metal compounds and with the surface of nano-

particles and (2) cavities contain reactive groups favouring sorption of metal compounds into the polymer.

The first case can be illustrated taking the synthesis of metal nanoparticles in pores of crazed polymers [88] and in pores of hyper-cross-linked polystyrene (HPS) developed at the A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.[89,90]

1. Nanoparticle growth in pores formed as a result of delocalised crazing of polymers

Delocalised crazing of polymers upon mechanical tension in adsorption active media (solvents) permits preparation of polymers containing reactant accessible open interpenetrating pores 3–6 nm in diameter. These pores can be used as templates for metal nanoparticle formation after introduction of corresponding reactants.[91,92] This procedure was employed to obtain nickel nanoparticles in porous polypropylene (PP) and poly(ethylene terephthalate) (PETP). A study of the reduction of nickel perchlorate with sodium borohydride in polymers with different morphologies and pore structures showed that the pore sizes govern the growth of nanoparticles. An interesting aspect of development of a crazed morphology is deformation of the polymer in a solution containing the corresponding metal complex. The synthesis of copper nanoparticles in high density polyethylene (HDPE) matrix was reported.[93] HDPE was crazed in monoethanolamine (MEA) solution containing complex copper salts and MEA. The formation of cavities in HDPE was accompanied by sorption of the copper compound into them. Subsequent heating of the composite material resulted in the formation of metal nanoparticles. However, this technique is inappropriate for preparation of nanoparticles with a narrow size distribution.

2. Metal nanoparticle formation in pores of hyper-cross-linked polystyrene

Hyper-cross-linked polystyrene is the first representative of a new class of cross-linked polymers characterised by unique topology and unusual properties. The internal morphology of HPS is schematically shown in Fig. 11.[94]

Hyper-cross-linked polystyrene has a rather large inner surface area (usually nearly 1000 $m^2\ g^{-1}$) and the ability to swell in any liquid medium including precipitating agents of the starting polymer. The HPS matrix used to form cobalt and platinum nanoparticles was characterised by a formal degree of cross-linking of 200%, an inner surface area of 833 $m^2\ g^{-1}$ and a narrow pore size distribution with a maximum at about 2 nm.

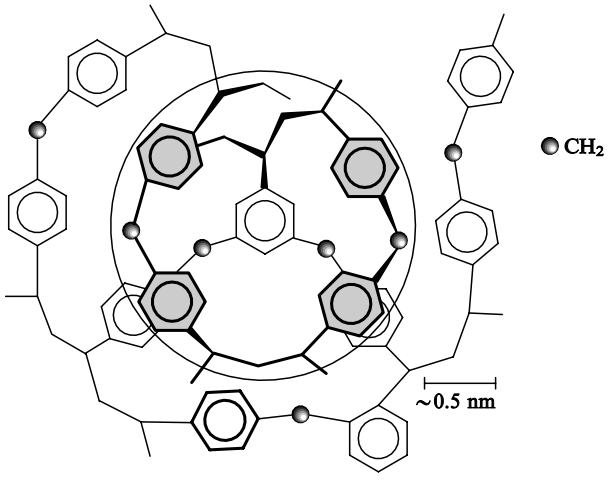


Figure 11. Schematic view of the HPS morphology.[94]
Shaded phenyl rings are in the foreground and bright phenyl rings are in the background. The circle denotes an individual pore of the hyper-cross-linked network.[94]

a. Cobalt nanoparticles in hyper-cross-linked polystyrene

The formation of metal nanoparticles in the HPS matrix was studied taking cobalt particles as examples, because the size and shape of cobalt nanoparticles are known to be related to their magnetic characteristics. Changes in the magnetic properties of the particles manifest themselves in changes in the spectral parameters of ferromagnetic resonance (FMR).[95] Particles of size less than 1 nm do not possess any magnetic properties. Particles 1 to 10 nm in diameter possess superparamagnetic properties. Larger particles are ferromagnetic. Moreover, the width of the signal of spherical particles in the FMR spectrum (ΔH) depends on the particle size while the position of the absorption maximum (H_0) is related to the shape of the cobalt nanoparticles.[95,96] Thus, information on the size and shape of cobalt nanoparticles can be extracted from their FMR spectra.

A cobalt compound, $Co_2(CO)_8$, was introduced into the HPS matrix from solutions in DMF and isopropyl alcohol. The reaction of $Co_2(CO)_8$ with DMF results in a relatively stable complex, $[Co(DMF)_6]^{2+}[Co(CO)_4]^{2-}$, while in isopropyl alcohol, a molecular solution is formed. Both materials were heat-treated at 200 °C. The H_0 and ΔH values for the HPS–Co samples prepared using the starting compound $Co_2(CO)_8$ in isopropyl alcohol and $[Co(DMF)_6]^{2+}[Co(CO)_4]^{2-}$ are listed in Table 2. As can be seen, an increase in the Co content to 8 mass % has little effect on the FMR spectral parameters and they are independent of the type of the starting Co-containing compound used in the experiments. The position of the absorption maximum, H_0, for all the samples under study indicated the formation of spherical cobalt nanoparticles.[95] According to TEM data, the average particle diameter was 2.1 ± 1.0 and 2.6 ± 1.6 nm for the samples with a cobalt content of 5.07 mass % and 10.08 mass %, respectively.[94]

Table 2. H_0 and ΔH values for HPS–Co samples prepared from different starting metal compounds.[94]

Co content (mass %)	H_0 /Œ	ΔH /Œ
Starting compound — $Co_2(CO)_8$ in isopropyl alcohol		
0.85	3100	125
2.58	3050	125
3.41	3100	200
5.69	3100	200
7.09	3125	200
Starting compound — $[Co(DMF)_6]^{2+}[Co(CO)_4]^{2-}$		
0.26	3100	125
1.85	3050	150
5.07	3075	160
8.22	3090	200
11.22	3105	350

Thus, it is the nanoscale voids in HPS that are responsible for controlled formation of Co nanoparticles in the relatively wide range of cobalt concentrations (from 0.9 mass % to 8.0 mass %). The most probable reason for controlled growth of Co particles in the HPS matrix is non-specific interaction between the phenyl rings and the metal surface, which must result in steric stabilisation of the cobalt nanoparticles. At cobalt concentrations exceeding a certain limiting value (> 8 mass %), growth of large nanoparticles begins. In this case, the particle size can reflect either the HPS pore size distribution statistics or the rearrangement of HPS morphology caused by the presence of the metal.

b. Formation of platinum nanoparticles in hyper-cross-linked polystyrene pores

Hyper-cross-linked polystyrene is an interesting object for the creation of novel catalytic systems. This compound can act as a

nanostructured matrix, which governs the particle growth, and as a carrier of catalytically active particles. Moreover, HPS can swell in almost all solvents. This can provide access to catalytic sites in virtually all reaction media.

A model study was carried out taking the formation of platinum nanoparticles in HPS pores as an example. Platinum was introduced into the polymer matrix by sorption of H_2PtCl_6 from solutions in THF or methanol. In contrast to the synthesis of cobalt nanoparticles, the formation of platinum nanoparticles involved the reduction of platinum compounds with hydrogen gas at moderate temperatures (the case of restricted migration of these compounds within the HPS matrix). In Fig. 12 we present a TEM micrograph of HPS containing encapsulated platinum nanoparticles (sorption of H_2PtCl_6 was conducted in THF) and a nanoparticle size distribution histogram. As can be seen, the average particle size is 1.3 ± 0.3 (*cf.* the average size of Co nanoparticles in HPS is ~ 2 nm). This difference can be explained by different mechanisms of formation of metal nanoparticles. At 200 °C, cobalt clusters can readily migrate into the HPS pores, thus forming particles that match the pore size. In the case of platinum, reduction with H_2 proceeds at room temperature (no migration of the platinum atoms or clusters or the molecules of the starting metal compound occurs); therefore, the nanoparticle size exactly matches the number of metal ions in the pores.[97] Thus, in the formation of cobalt nanoparticles the HPS matrix directly controls the metal nanoparticle size by physically limiting the particle size to the pore size (2 nm). In the case of platinum nanoparticles the pores impose restrictions on the amount of the starting metal compound that fills an individual pore; the reduction causes the volume of this compound to decrease (particle density increases) down to the volume of a single particle.

We believe that nanoporous polymers are promising as matrices for creation of efficient heterogeneous catalysts. However, they are inappropriate if the goal is to form thin films or homogeneous solutions.

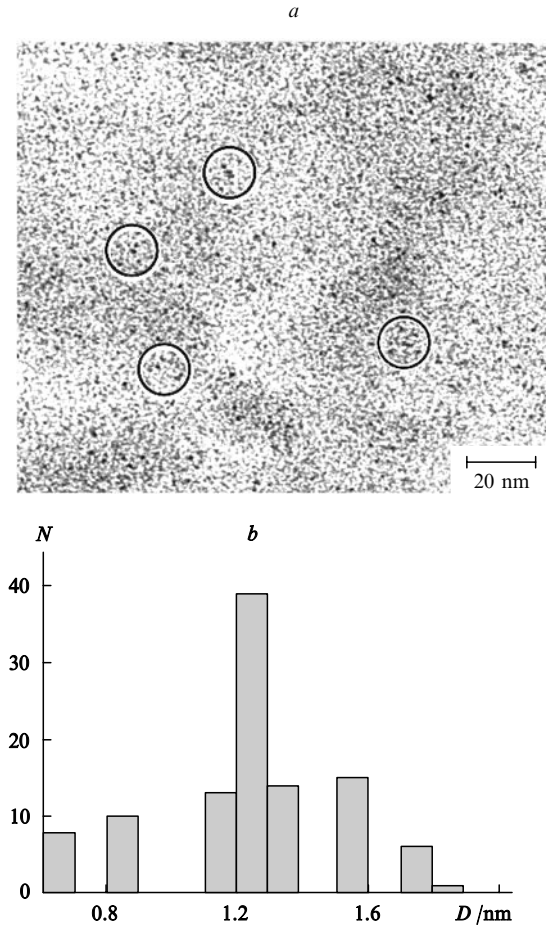


Figure 12. TEM micrograph of HPS containing encapsulated platinum nanoparticles (sorption of H_2PtCl_6 was conducted in THF) (*a*) and a histogram of nanoparticle size distribution (*b*).[97]
D is the particle diameter and *N* is the number of particles.

3. Formation of metal nanoparticles in cavities of nanostructured polyoctadecylsiloxane

Yet another example of control of the growth of metal particles confined in a cavity is provided by the formation of nanoparticles in the bisiloxane layers present in polyoctadecylsiloxane (PODS).[98, 99] This polymer is obtained by hydrolytic polycondensation of octadecyltrichlorosilane in water. The reaction results in a polymeric condensate comprising lamellar microcrystallites in which inorganic siloxane chains form periodically arranged layers separated by crystalline domains (alkyl chains). It was assumed that (i) placing the polymer in a metal salt solution would lead to the sorption of the salt into the hydrophilic layer of the polymer and (ii) subsequent reduction must result in the formation of metal nanoparticles regularly arranged within the material (see Fig. 13). However, it was found that sorption of metal compounds into this nanostructured polymer strongly depends on the type of the metal compound employed.[101] Ions with a planar structure (*e.g.*, $PtCl_4^{2-}$) easily penetrate into the interior of the thin layer (2–3 nm), while the penetration of octahedral ions $PtCl_6^{2-}$ is hindered. The penetration of metal ions is assumed to be entropy driven; namely, an increase in entropy results from the formation of hydrogen bonds between the Cl atoms of the salt anions and the silanol groups (each $PtCl_4^{2-}$ ion can replace up to four water molecules). The formation of nanoparticles in the siloxane double layer occurs upon the reduction of platinum and palladium compounds. The process is independent of the type of the reducing agent and the metal compound and on the concentration of the latter and is governed exclusively by the growth of the metal particles confined within the siloxy bilayer cavity. The particle size distribution for platinum particles obtained in this polymer is shown in Fig. 14. Figure 15 presents a TEM micrograph of a material containing palladium nanoparticles.[100] As can be seen, the metal particles are located exclusively within the siloxy bilayers.

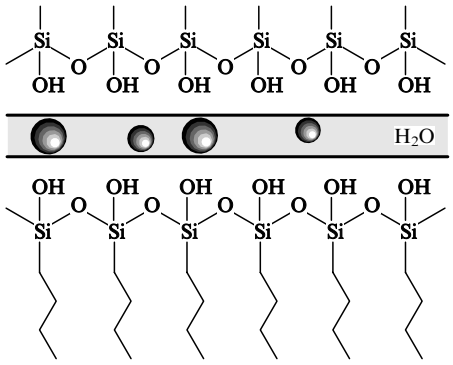


Figure 13. Scheme of nanoparticle formation in the siloxy bilayer of PODS.[100]

Thus, the presence of voids in nanostructured polymers permits control of the nanoparticle growth while the presence of functional groups ensures efficient and uniform sorption of metal compounds into the bulk material. At the same time, the metal content in these polymers is low because only the siloxy bilayers contain silanol groups.

The synthesis of novel highly functionalised colloidal polymer particles by hydrolytic condensation of *N*-(6-aminohexyl)aminopropyltrimethoxysilane was developed.[102] Polysilsesquioxane (PSSO) thus obtained is water soluble and has a structure

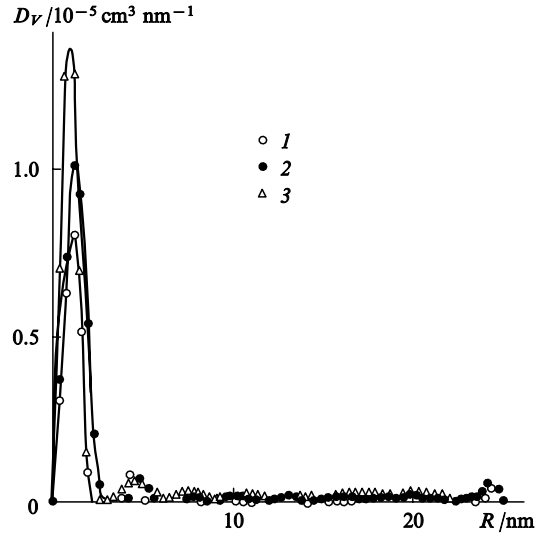


Figure 14. Volume distribution functions of platinum nanoparticles in PODS.[101]
Samples were prepared *via* sorption of K_2PtCl_4 after reduction with silanol groups of PODS (*1*) and *via* sorption of $H_2PtCl_6 \cdot 6\,H_2O$ after reduction with H_2 (*2*) and sodium borohydride (*3*).



Figure 15. TEM micrograph of palladium nanoparticles formed in PODS from Na_2PdCl_4 upon reduction with $NaBH_4$.[100]
Palladium nanoparticles were prepared in the siloxy bilayers of PODS with lamellar nanostructure. Palladium and silicon atoms provide a rather high contrast relative to the alkyl layers.

characterised by high degrees of cross-linking and functionalisation. Functionalised cavities in the PSSO structure act as nanoreactors for nanoparticle formation and provide a high metal loading (up to 35 mass %). The nanoparticles are 1–2 nm in diameter and do not undergo aggregation within the PSSO matrix. Colloidal PSSO particles filled with metals or metal compounds can form surface dendritic structures. We believe these systems are candidates for catalysts and chemical sensors.

VI. Properties of nanostructured polymeric systems containing metal nanoparticles

The unique properties of metal nanoparticles are mainly due to the large total surface area and to the considerable number of surface atoms. For instance, nearly 60% of the total number of atoms in a gold particle 2 nm in diameter are on the surface. In semiconductor and metal nanoparticles, this permits efficient charge transfer from the bulk of the material to the surface and *vice versa* (this manifests itself in, *e.g.*, changes in the optical absorption spectra). The surface of nanoparticles plays an important role in catalysis, being responsible for their selectivity and activity. Therefore, the characteristics of the stabilising polymer (its functionality and nanostructuring) and nanoparticles are of great importance, because they mainly determine the state of the surface of nanoparticles.[103]

1. Catalytic properties

Polymer-stabilised colloidal metal particles have been known to be hydrogenation catalysts for more than five decades. For instance, olefin hydrogenation catalysts based on palladium, platinum,[104,105] rhodium [106] and iridium [107] were prepared using poly(vinyl alcohol) and poly(vinyl acetate) as stabilisers. Most studies are concerned with the synthesis of nanoparticles inside homopolymer matrices that cannot provide a narrow particle size distribution (because of this, particles within the same sample can possess quite different catalytic properties). This reduces the selectivity and activity of a given catalyst.

Taking platinum nanoparticles stabilised by polymer surfactant micelles as an example, it was shown [108,109] that the state of the surface of metal nanoparticles plays an important role. These catalysts prepared within inverse micelles formed by cationic, anionic and non-ionic polymeric surfactants were employed in the isomerisation and hydrogenation of n-butene. The highest activity of the catalyst was achieved using a non-ionic surfactant; however, in all cases, the catalysts were an order of magnitude less active than conventional supported catalysts. Probably, the layer of the surfactant molecules adsorbed on the surface of a metal particle made the catalyst sites inaccessible to the substrate. At first glance, this negative conclusion is quite interesting from the standpoint of improvement of catalyst selectivlty. By choosing an appropriate stabiliser it is possible to achieve a great difference between the diffusion rates of different substrates towards the surface of the catalyst. The effect of surfactant micelles on the hydrogenation of long-chain unsaturated acids (*e.g.*, isomers of undecenoic acid and oleic acid) was studied taking platinum and palladium nanoparticles stabilised with a non-ionic surfactant poly(ethylene glycol monolaurate) as examples.[110] In these systems, the surface of the metal particle is protected by hydrophobic laurate chains while hydrophilic poly(ethylene glycol) chains form the micelle shell.

In this case, the position of the double bond in the substrate governs the hydrogenation rate because the substrate molecule is specifically arranged in the micelle wall. The ordered environment of the metal particle forces the acid molecule to be oriented in such a way that the polar carboxyl group is in the hydrophilic fragment of the micelle and the hydrophobic fragment of the molecule is surrounded by hydrophobic core-forming laurate chains. The acid hydrogenation rates obey the following pattern: undec-10-enoic acid > oleic acid > undec-2-enoic acid. This indicates that the terminal double bond is best accessible to the active sites of the catalyst, whereas the inner double bond has poorer access to the surface of the platinum particles. Platinum nanoparticles stabilised by poly(*N*-vinyl-2-pyrrolidone) (PVP) possessed no regioselectivity except in the cases where sodium salts of unsaturated acids were used. Here, the substrate behaved as a surfactant and the effect of PVP could be ignored.

Modification of the catalyst properties by forming a stabilising shell surrounding the particle is possible only in the case of metal nanoparticles. This is a great advantage of these particles over other catalysts of polyfunctional substrate hydrogenation. Thus, the use of nanostructured polymers permits not only control of nanoparticle growth but also further modification of the nanoparticle surface, which is of considerable value for catalytic applications.

A somewhat different approch was also developed.[42,43] As described above, corona-embedded metal nanoparticles were synthesised by the reduction of corresponding starting compounds of palladium and platinum in the presence of amphiphilic block copolymers (PS-*block*-PEO and PS-*block*-PMAA) in alcoholic and aqueous solutions. The catalytic activity of nanoparticles was assessed taking cyclohexene hydrogenation as a model

reaction. The particle activity was strongly dependent on the procedure for preparation and on the type of starting compounds. The formation of palladium and platinum nanoparticles in the presence of latex dispersions of different hydrophobicity was studied.[111, 112] In some cases, metal nanoparticles were adsorbed and immobilised on the latex surfaces, which was confirmed by TEM data. These dispersions exhibited catalytic activity in the model reaction of cyclohexene hydrogenation. Highly hydrophobic latexes caused such strong immobilisation of nanoparticles that they remained on the latex surface after performing catalytic cycles.

Silver and platinum nanoparticles synthesised in multilayered polyelectrolyte films[113] possessed electrocatalytic properties in methylene bromide reduction; however, these catalysts are less efficient than pure silver electrode because polymer films are insulators. These data are consistent with the results obtained by Zhao and Crooks[72] who used dendrimer-encapsulated platinum nanoparticles deposited on an electrode as a catalyst for an electrocatalytic reaction. Clearly, in spite of some catalytic activity these polymeric systems with encapsulated metal nanoparticles are of no promise as electrode coatings in electrocatalytic reactions, because the insulating properties of the polymer reduce the catalyst efficiency.

Hydrogenation of dehydrolinalool (DHL, oct-6-ene-1-yne-3-ol) is an industrially important reaction in fragrance chemistry. Using catalysts based on palladium nanoparticles synthesised in PS-*block*-P4VP micelles, a selectivity of 99.5% in hydrogenation of the triple bond in DHL to a double bond was achieved.[114] Probably, modification of the metal surface by pyridine units of the P4VP core also contributes to the reaction selectivity. The use of bimetallic nanoparticles Pd/Au, Pd/Pt and Pd/Zn causes a modification of the electronic structure and surface geometry of palladium, which additionally enhances the selectivity up to 99.8%.[28]

Palladium nanoparticles stabilised by PS-*block*-P4VP micelles were used as catalysts of cross-coupling reactions between aryl halides and alkenes (Heck reaction).[115] These hybrid systems exhibited nearly the same efficiency as low-molecular-mass palladium complexes (conventional catalysts of the Heck reaction), being at the same time much more stable.

Direct catalytic L-sorbose oxidation into 2-keto-L-gulonic acid is an intermediate stage of the synthesis of ascorbic acid (vitamin C). At present, direct sorbose oxidation is not used on industrial scale because of the low selectivity of the process. Another synthetic route involves transformation of sorbose into di-*O*-isopropylidenesorbose followed by oxidation of the latter to give di-*O*-isopropylidene-2-keto-L-gulonic acid and then 2-keto-L-gulonic acid. Direct L-sorbose oxidation into 2-keto-L-gulonic acid was performed using the HPS–Pt samples described above. They were obtained by sorption of H_2PtCl_6 from methanol and THF both before and after the reduction with H_2, and contained different amounts of platinum.[97] It was found that the yield of 2-keto-L-gulonic acid (*i.e.*, oxidation selectivity) is strongly dependent on the conditions for preparation of catalysts. In particular, the highest yield (nearly 98%) was achieved with the HPS–Pt(H_2PtCl_6 + THF) samples. Additional reduction of the samples with H_2 reduced the selectivity by 8%–10%. A study on the structure of HPS–Pt before the catalytic reaction, after the induction period and after the catalytic reaction revealed transformations of H_2PtCl_6 and THF in the HPS pores, which resulted in the formation of mixed clusters comprised of $Pt^0/Pt^{II}/Pt^{IV}$ and ligands. Reduction with H_2 increases the proportion of Pt^0 in the sample, which can upset the optimum composition of the complex.

The $\ln\tau_{0.1} - 1/T$ Arrhenius plot constructed using the experimental data obtained at different temperatures gave a value of 34 kJ mol^{-1} for the apparent activation energy, E_a. This is lower than the activation energy for the reaction conducted with the conventional catalyst Pt/SiO_2 ($\sim$45 kJ mol^{-1}).

Metal nanoparticles are widely used in the important catalytic reaction known as the Suzuki reaction. The effect of the stabiliser matrix on the catalytic properties and stability of transition metal nanoparticles in solution was studied.[116] Palladium nanoparticles were prepared *via* the reduction of metal salt in the presence of three different polymer stabilisers, namely, hydroxyl-terminated PAMAM dendrimers (Gn–OH, where Gn is the *n*th dendrimer generation), PS-*block*-PANa (PANa is sodium polyacrylate) and PVP. The nanostructured systems obtained were used to study the effect of the matrix type on their catalytic activity and stability in the catalytic cross-coupling reaction between phenylboronic acid (or 2-thienylboronic acid) and iodobenzene in aqueous medium. The stability of palladium nanoparticles was evaluated using the data on the formation of palladium black after catalytic cycles. The Suzuki reaction is a good test for the stability of nanoparticles, because it proceeds at 100 °C for 24 h. Palladium nanoparticles stabilised by PAMAM-G3 dendrimer and PVP were found to be efficient catalysts of the Suzuki reaction. The G4 dendrimer was found to be a very efficient stabiliser; however, strong encapsulation of palladium nanoparticles in the dendrimer led to reduction of the catalytic activity. The two properties were found to be interrelated, namely, the higher the stability, the lower the catalytic activity (due to inaccessibility of the nanoparticle surface to the substrate). Both palladium- and platinum-containing PAMAM exhibited catalytic activity in the electrochemical reduction of oxygen.[117]

2. Magnetic properties

If the critical distance responsible for a physical property becomes comparable with the nanoparticle size, the magnetic properties of the nanomaterials change significantly. Changes in the magnetisation of a material always require the overcoming of an energy barrier, while any physical mechanism proposed for the description of the corresponding energy barrier includes a relevant linear parameter (length or distance). The main linear parameters used to describe the magnetic properties are as follows: the linear crystalline anisotropy, l_k, the action range of the applied field, l_H, and the magnetostatic distance, l_s; they are defined by the respective equations[118]

$$l_k = \sqrt{\frac{J}{K}},$$

$$l_H = \sqrt{\frac{2J}{HM}},$$

$$l_s = \sqrt{\frac{J}{2\pi M^2}},$$

where J is the constant for intradomain exchange, K is the anisotropy constant, H is the magnetic field strength and M is the saturation magnetisation.

If there is more than one energy barrier, the magnetic properties are determined by the shortest characteristic distance. For the most widely used magnetic materials these values are of the order of 1 to 100 nm (*e.g.*, $l_H \approx 19$, $l_k \approx 45$ and $l_s \approx 8$ nm for nickel in a magnetic field of 1000 Œ at room temperature).

The most interesting magnetic properties of nanoparticles are manifested in the case of monodomain nanoparticles. (Remind that a domain is a group of aligned spins that act in a concerted way and are characterised by the total magnetic moment.) In bulk materials, domains are separated by domain walls characterised by their thickness and formation energy. The reversible magnetisation effect is due to the domain wall motion. The formation of domain walls in bulk metal is energetically favourable but a decrease in the particle size down to a certain critical value, R_c, makes the formation of domain walls energetically unfavourable. This is the case for monodomain particles.[119, 120] Here, the magnetisation changes are due to synchronous spin rotation

resulting in a large coercive force rather than domain wall motion. Further decrease in the particle size causes the spins to be more sensitive to the influence of thermally induced fluctuations. Finally, all spins become completely disordered as the external magnetic field is switched off. Such systems possess properties of superparamagnetics and are characterised by zero remanent magnetisation and zero coercive force.

If magnetic nanoparticles were formed inside a polymer matrix, the nanocomposites obtained possess unique magnetic properties and can be used for electromagnetic shileding and for creation of novel magnetic and magneto-optical devices.[118, 119]

Metallic cobalt is often used in the fabrication of various magnetic devices. Cobalt nanoparticles less than 60 nm in size are monodomain particles characterised by a nonzero total magnetic moment. If the particle size lies between 10 and 60 nm (these values are rough estimates and depend on the particle shape), the total magnetic moment dominates the thermal motion of particles and they form linear chains due to the dipole–dipole interaction. Such materials are the best candidates for production of permanent magnets, magnetic pigments, coatings for magnetic data storage devices, *etc*.[119, 120]

Nearly monodisperse cobalt nanoparticles with controlled morphology were synthesised [121] using PS-*block*-P4VP micelles in organic solvents. Metallic cobalt particles were produced in two ways, by the chemical reduction of $CoCl_2$ and by the thermal decomposition of $Co_2(CO)_8$. The amount of the block copolymer was kept constant but the concentration of the starting metal compound was varied. This permitted the preparation of non-magnetic, superparamagnetic or ferromagnetic materials. Experiments with the ferromagnetic samples allowed the conditions for obtaining very high specific coercive forces (with respect to the cobalt concentration in the sample) to be chosen. Apparently, this is mainly due to the very narrow size distribution of the cobalt nanoparticles. These particles are characterised by high magnetisation and extremely high stability in air, which can be explained by the high degree of adsorption of pyridine units on the particle surfaces.

The magnetic properties of γ-Fe_2O_3 nanoparticles formed inside microdomains of an optically transparent block copolymer based on $[NORCOOH]_{30}[MTD]_{300}$ (NORCOOH is 2-norbornene-5,6-dicarboxylic acid; MTD is methyltetracyclododecene) have been reported.[122, 123] The nanoparticle size was 5 nm. The magnetic properties of the material were strongly dependent on the quantum effects, *e.g*., co-operative magnetisation and superparamagnetic relaxation. It was shown that these nanocomposite films exhibit superparamagnetic properties and possess no remanent magnetisation and coercive force at room temperature. At low temperatures, the coercive force of these films was 530 Œ.

3. Optical properties

The synthesis of manganese- and terbium-doped ZnS nanoparticles in the microsegregated films of diblock copolymers containing carboxyl groups in one block has been reported.[124] The concentration of dopant ions in the microdomain containing the carboxyl groups was controlled by varying either the concentrations of aqueous solutions of the metal salt or the exposure time of the polymer film in solution. The doped ZnS nanoclusters were formed during subsequent treatment of the films with hydrogen sulfide. These films exhibit photoemission characteristic of the dopant ions (manganese and terbium). The synthetic procedure has no features and can be used for the preparation of doped semiconductor nanoparticles involving combinations of various metal salts.

Optically stable CdS nanoparticles were synthesised within a hydroxyl and amino group terminated G4 PAMAM dendrimer.[125] The UV spectra and luminescence spectra showed that the dendrimer stabilises nanoparticles whose optoelectronic properties differ from the corresponding properties of bulk CdS. Dendrimers are prone to aggregation, which depends on the temperature and particle concentration; however, the characteristics of the cadmium sulfide nanoparticles remained unchanged. Studies of the solutions stored at -10 °C revealed that the dendrimers did not undergo aggregation over a period of several months and that the solutions also possessed photoluminescent properties.

Another procedure for the formation of analogous nanocomposites involves PEI as the polymer stabiliser.[126] The optical properties of the particles thus obtained were similar to those of the particles described above (emission in the blue spectral region) but the quantum yield of luminescence was lower. The authors [126] believe that high local concentration of chelating nitrogen atoms (in the dendrimer or PEI) is the major factor affecting the formation of small nanoparticles with perfect morphology.

A XANES study of nanocomposites based on CdS nanoparticles and G4 PAMAM dendrimers was also reported.[127] Investigation of the structure of CdS nanoparticles revealed the presence of sulfates and oxides. A joint X-ray induced optical luminescence–XANES study also revealed correlations between the optical properties and the structure of CdS nanoparticles.

An interesting nanocomposite was obtained by incorporating CdTe nanoparticles into thin films prepared by layer-by-layer deposition of an anionic polyelectrolyte containing a poly(*para*-phenylenethynylene) (PFE) chain and poly(allylamine hydrochloride) (PAAHC) as the polycation.[128] The CdTe nanoparticles were stabilised by poly(ethylene glycol) (PEG)-containing reactive terminal groups. Nanoparticles were incorporated into the multilayered composite *via* chemical bonding to the stabiliser (PEG). The interaction between polyconjugated polymer and nanoparticles provided conjugation transfer, which manifested itself as changes in the optical properties. The luminescence spectrum exhibited a new peak at 600 nm due to the emission of CdTe nanoparticles. The excitation spectrum of CdTe–PEG-*block*-PFE recorded at 600 nm exhibited a new intense band at 400 nm corresponding to the absorption band of the multilayered composite. This is evidence of energy transfer between PFE and the nanoparticles. By varying certain structural parameters of the composite (*e.g*., the PEG chain length) one can change the optical properties. This system is expected to be suitable for fabrication of multilayered optical devices.

4. Electrical properties

A trend towards miniaturisation and high integration of elements of electric circuits has been a salient feature of modern microelectronics. As a rule, the shorter the distance between the elements of a device, the higher the performance of the device. Lithography techniques permit fabrication of working elements of size up to 100 nm, which has opened new prospects for their application using quantum effects. At present, using the Coulomb effect in electric circuits (including submicrometre-sized tunnelling junctions) allows one to control single charge carriers. Research in this field serves as the basis for fabrication of the so-called single-electron devices (SEDs).[129]

The Coulomb effect has long been known, however, studies on SEDs have been a particular avenue of scientific research only recently. Fifteen years have passed since the beginning of intensive studies into ultrasmall sandwich structures of the type metal–insulator–metal (tunnelling junctions).[130] It was shown that the electric charge discreteness becomes significant under particular conditions. Namely, quantum electron tunnelling in the system of tunnelling junctions is affected by the Coulomb inter-electron interaction, which can in turn be varied by applying an external voltage. This phenomenon is called single-electron tunnelling. It serves as the basis for the operation of any SED.

A practical implementation of the SED idea in systems with characteristic capacities of the order of 10^{-15} to 10^{-16} F (these values are typical of modern lithography techniques) requires that the samples be cooled down to a few thousandths of a Kelvin. Room-temperature operation of the SED dictates a reduction of the characteristic capacity by at least two orders of magnitude, which can be achieved using nanometre-sized metal nanoparticles.

Recent advances in lithography, made due to miniaturisation of electronic devices, cannot meet all the requirements from room-temperature operation of SEDs.[131] This problem can be solved by using ligand shell stabilised metal nanoparticles. These particles are thought to be promising as structural elements of novel nanoelectronic devices. A challenge is to develop novel methods for the fine adjustment of such elements in SED design at different scales of integration. Therefore, the use of the principles of self-organisation and controlled intermolecular interaction favours progress towards the design and fabrication of new electronic devices.

The use of dendrimers for the synthesis of metal nanoparticles can simplify some engineering aspects of SED fabrication. The dendrimer macromolecules are characterised by very narrow particle size distribution and an exact number of functional groups. This allows single nanoparticles to be synthesised within individual macromolecules. In contrast to low-molecular-mass ligands, dendrimers have particular chemical structures characterised by the absence of exchange and relaxation processes, provided that the surface functional groups are protected by hydrophobic groups. This permits fine control of the nanoparticle parameters and the thickness of the insulating layer, which is impossible in the case of conventional low-molecular-mass ligands. Dendrimer molecules can self-assemble in the course of, *e.g.*, adsorption from solutions onto appropriate surfaces. Block copolymer micelles with cross-linked cores or coronas can also be used for these purposes. In these systems, micelles are characterised by a very narrow size distribution, which allows a single nanoparticle per core to be generated under particular conditions.[27] A necessary condition for proper SED operation consists in self-organisation of such filled micelles on the surface (this is usually employed in nanolithography [29]). Because of this, we believe that the use of the unique properties of nanoparticles formed in nanostructured polymeric systems for fabrication of SEDs is a promising field of application.

* * *

There are a variety of nanostructured polymeric systems that can provide control of the formation of nanoparticles, stabilise nanoparticles and modify their surface due to the effect of the polymer chains. Among them, prospects for particular systems are determined by the possible fields of application. We believe that block copolymer micelles and dendrimers are the best candidates for use as nanostructured polymeric systems providing the possibility of nanoparticle formation in solutions. It should be noted that block copolymer micelles can form films and coatings, which is of particular importance for application in catalytic, magnetic and optical systems. Block copolymer micelles and dendrimers can adsorb on surfaces to form monolayers. Nanoporous materials are thought to be the most promising for the formation of nanocomposite catalysts of heterogeneous processes. These materials are simple and cheap, they permit control of particle growth, accessibility of reactive sites to substrates and do not require additional heterogenisation.

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