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Formation of ordered nanoparticle assemblies by block copolymer lithography methods

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Abstract. The results of experimental studies devoted to the formation of highly ordered nanoparticle assemblies on planar substrates of various nature using block copolymer lithography methods are presented. The structure and properties of such assemblies and the design of thin-film polymer – metal composites based thereon are discussed. The attention is focused on the assemblies obtained by nanoparticle synthesis in the micelles of amphiphilic diblock copolymers. The bibliography includes 234 references.

I. Introduction

Ordered monolayer assemblies of nanoparticles of metals, semiconductors and other substances formed on various substrates possess unique optical, catalytic, magnetic, electronic and other properties, which depend on the particle composition, size and shape and on the distance between the particles. In recent years, such nanostructured systems have been used more and more often as working elements in the design of solid-state chemical and biological sensors, catalytic systems and optical and other devices.[1 – 3]

The design of such systems often requires not only precise control over the packing density of nanoparticles in the assembly but also creation of a two-dimensional structure with a strictly defined geometry on a substrate. There exist quite a lot of methods for solving this problem: deposition from the gas phase through a mask with a specified shape,[4, 5] adsorption of nanoparticles from colloidal solutions onto substrates modified by self-assembling monolayers of functionalized silanes and thiols,[6 – 8] microcontact printing,[9] *etc.*[10 – 12]

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In our opinion, most promising is the approach called block copolymer lithography based on the use of substrate-deposited thin films of block copolymers (see, for example, Refs 11, 12).† Owing to limited block compatibility, microphase separation takes place in these systems, resulting in some cases in the formation of ordered structures, which represent, in a first approximation, domains of one block distributed in some way in the matrix of the other block.[15 – 17] The size, shape and orientation of the domains can be controlled by varying the relative and absolute lengths of the blocks, the nature of the substrate, conditions of film formation, film thickness and other parameters (see a review[17] and references cited therein). This provides a large set of two- and three-dimensional structures.

It is known (see, for example, the studies[11, 12, 15, 18, 19]) that block copolymers can not only serve as the basis for modification of substrates followed by the formation of ordered nanoparticle assemblies on them by the selective adsorption mechanism, but they can also serve as nanoreactors in the nanoparticle synthesis. In this case, either one of the copolymer blocks (*e.g.*, when organometallic monomers are used[20, 21]) or a compound that specifically reacts with one of the blocks[18, 19] serve as the precursor.

Particular researchers' interest is aroused by amphiphilic diblock copolymers that form micelles of different shape (spheres, rods and so on) in a solvent selective for one block (see, for example, the studies[22, 23]). This interest is caused by several factors. First, this is the possibility to control the size of micelle nanoreactors by varying the copolymer molecular mass (M) and the ratio of the block lengths. In addition, spherical micelles are able to form highly ordered two- and three-dimensional structures.[24 – 26]

The problem of forming quasi-2D structures using block copolymers is studied fairly intensively, and a large amount of experimental results has been accumulated. Nevertheless, despite the topicality of the problem, there are almost no reviews generalizing the information accumulated in this field (an exception is provided by several works that con-

† In some cases, homopolymer blends are also used.[13, 14]

sider particular aspects of formation of nanocomposites using diblock copolymers).

This review presents the results of investigations devoted to the preparation of ordered nanoparticle assemblies on planar substrates of various nature using block copolymer lithography techniques, study of their structures and properties, and design of thin-film polymer–metal composites based thereon. The attention is focused on the assemblies obtained by synthesis of nanoparticles in monolayer films of amphiphilic diblock copolymer micelles.

II. Synthesis of nanoparticles in the diblock copolymer micelles

Most often, micelles of vinylpyridine and styrene (or ethylene oxide) block copolymers with a polyvinylpyridine (PVP) core and a polystyrene (PS) or poly(ethylene oxide) (PEO) corona formed in organic and aqueous medium, respectively, are used as reactors in the synthesis of nanoparticles.[11,12,18,26–34] This is largely related to the ability of the pyridine groups of PVP to form complexes with various metal ions[18,28,29,35] and to the relative simplicity of preparation and commercial availability of these copolymers. Note that water-soluble PEO–PVP block copolymers are mainly used for the synthesis of nanoparticles in solution, whereas PS–PVP copolymers act most often as micellar templates in the synthesis of highly ordered nanoparticle assemblies on solid substrates.

1. Micellar solutions and films of diblock copolymers

A key condition for the use of block copolymer micelles for the preparation of nanoparticles with narrow size distribution and their ordered assemblies is the knowledge of the micelle shape and size and of the effect of various factors (copolymer molecular mass, the ratio of the lengths of the blocks, the nature of the solvent, pH of the medium, *etc.*) thereon. These issues have been the subjects of a number of publications including reviews (see, for example, the studies[26–28,36–41]). Antonietti *et al.*[27] studied the structure of micelles of styrene–4-vinylpyridine (PS–P4VP) copolymer by static and dynamic light scattering. They showed that the aggregation number of the macromolecules in solution (Z), which characterizes the size (and to an extent the shape) of micelles, depends not only on the copolymer M and the block length ratio but also on the thermodynamic quality of the solvent with respect to PS and PVP, as this factor affects appreciably the interfacial tension at the micelle core/corona interface.[42] In particular, the Z value decreases as the solvent quality with respect to the PVP block increases. Meanwhile, the use of a good solvent for the PS block can result in both increase in the micelle size and change in the micelle shape.[27] In addition, the results of the work cited[27] suggest that in some solvents (for example, in butyl acetate), the PS–P4VP micelles form ordered structures. This was also indicated by Park *et al.*,[26] who studied self-organization of PS–P4VP micelles with different molecular masses in solution and on a substrate by small-angle X-ray scattering and transmission electron microscopy (TEM). According to this publication,[26] in concentrated (30 mass %–40 mass %) solutions, PS–P4VP micelles form a face-centred or body-centred cubic lattice (packing type depends on the polymer molecular mass), while upon deposition on the solid substrate, they can form hexagonally ordered assembly (see also the studies[43–46]). The atomic-force microscope (AFM) images of such 2D assemblies deposited from solutions of various concentrations are summarized in Fig. 1. Note that micellar films of block copolymers can also be used as lithographic masks.[43,45,47] The structure of these films can be controlled both during their preparation by varying characteristics of the block copolymer macromolecule, solution concentration, deposition conditions on the substrate, nature of the solvent, the structure and the nature of the substrate and other factors[37,43–46,48–51] and *post factum*, for example, by annealing of the film or its exposure to a given solvent or solvent vapour.[37,46,52–54] It was shown, in particular, that an increase in the molecular mass of the block copolymer or a decrease in the concentration of its solution results in a substantial increase in the distances (L) between the micelles in the film.[43,44,46]

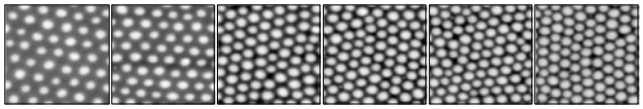


Figure 1. AFM images of micellar PS–P2VP films deposited by spin-coating (5000 rpm) from solutions in *o*-xylene with a concentration of 0.5 mass %–1 mass % (from left to right, a concentration step of 0.1 mass %).[45]
Scanning area 1×1 μm^2.

Upon the introduction of the metal precursor into a solution of a diblock copolymer, the critical micelle concentration considerably decreases.[29,55,56] Indeed, the addition of $HAuCl_4$ [molar ratio (W) per the PVP monomer unit is 0.25–1] to a molecular solution of styrene block copolymer with 2-vinylpyridine (PS–P2VP) gives rise to spherical micelles.[55,56] According to authors,[55] this is caused by the fact that $HAuCl_4$ reacts with the pyridine group of PVP according to the acid–base mechanism to give the pyridinium salt, which is much less soluble in toluene than the initial polymer. However, in our opinion, an alternative mechanism of $AuCl_4^-$ reaction with PVP should also be considered. This is the replacement of the Cl ligands in the $AuCl_4^-$ anions by non-protonated pyridine rings of PVP.[29,35,57] This may result in metal 'binding' to several pyridine groups (including those belonging to different block copolymer molecules), which also facilitates micelle formation. The assumption of 'multicentre' binding is supported by the fact that even after long-term storage of the monomicellar film formed from a block copolymer solution containing $HAuCl_4$ in ethanol (selective solvent for PVP blocks), no micelle inversion takes place.[46] However, in the case of unloaded (or $AgNO_3$-containing) film, this process occurs rather fast.

On the addition of a precursor to a micellar solution of a diblock copolymer, metal ions are solubilized in the micelle cores due to interaction with PVP nitrogen atoms according to the acid–base or electrostatic mechanism.[29] As a rule, this results in an increase in the micelle diameter (D). The effect is largely determined by the increase in the interfacial energy at the boundary between the corona and the metal-ion containing core of the micelle.[49,58] The tendency at minimizing the number of contacts between PS and PVP blocks (and, hence, the free energy of the micelle) makes both copolymer blocks unfold (straighten). The micelle

aggregation number simultaneously increases. Consequently, D increases.

Thus, it is obvious that the size of micelles of a block copolymer depends on its molecular mass, the relative length of the blocks, the aggregation number and the amount of precursor added (W).

However, the results of experiments indicated [59] that in some cases, the size of micelles almost does not depend on W. Indeed, Spatz *et al.*,[49] who studied by dynamic light scattering (DLS) the dependence of micellar size of symmetrical PS(19.76)–P2VP(19.95) diblock copolymer ‡ on the amount of the introduced $HAuCl_4$, showed that in the range of W values from 0.01 to 1, the size of micelles barely changes. We obtained a similar result for PS(48.5)–P2VP(14.5).[59] Note that an attempt of the researchers [49] to interpret this effect in terms of segregation and change in the extension (degree of unfolding) of copolymer blocks does not appear quite convincing. Indeed, according to another publication,[28] the structures of micelles of the block copolymers used by Spatz *et al.*[49] and in our experiments [59] should be considerably different. The former has approximately equal lengths of the blocks and tends to form highly segregated micelles, whereas the latter having shorter P2VP block compared to the PS block forms poorly segregated micelles.[28] However, despite this difference, the effect is the same in both cases.

Probably, in this case, a significant role is played by the cross-linking of PVP chains in the micelle core by $AuCl_4^-$ ions by the mechanism of their simultaneous coordination to the nitrogen atoms of two (and more) pyridine groups. This cross-linking may be both intra- and intermolecular and should lead to the opposite effect: compactization (shrinkage) of the micelle core (and increase in its stiffness), especially in the case of cross-linking of PVP blocks of different molecules by the precursor, *i.e.*, formation of the network structure in the core. In turn, the shorter the PVP-blocks, the higher the probability of formation of intermolecular cross-links (at a specified ratio of the pyridine rings and the $AuCl_4^-$ ions in the micellar core). In addition, this becomes more and more probable (for micelles of the same copolymer) as W increases. Evidently, the effects of unfolding of the PS block and shrinkage of the P2VP block counterbalance each other, resulting in the lack of noticeable dependence of D on W.

As regards the introduction of precursors into micellar solutions of diblock copolymers, two problems deserve mention. First, in some cases, the mechanism of their solubilization remains unknown. Second, what is more important, the distribution of precursors of various nature between the dispersion medium and the micelles of some diblock copolymers has been scarcely studied.

Block copolymer micelles loaded with a metal precursor are used as nanoreactors for nanoparticle synthesis; this process can be carried out both in solution and directly on the solid substrate.

A series of works by Bronstein *et al.*[28, 29, 34, 57, 60–64] and other works [19, 65] are devoted to the regularities of formation of nanoparticles (Au, Pd, Pt, Co, *etc.*) in aqueous and organic micellar solutions of various block copolymers. As reducing agents, the authors used sodium borohydride,[34, 61, 62] hydrazine,[57, 61, 63, 65] hydrogen [34, 60] and other compounds.[61] The experimental results indicate that the nanoparticle size and morphology depend on the nature of the reducing agent,[19, 34, 61, 66] and in the case of aqueous solutions, also on the pH.[29, 62] It was shown, for example, that bubbling of hydrogen through precursor-containing solutions of PS–PEO [34] or butadiene–ethylene oxide copolymer [60] results in the formation of metal nanoparticles in the micelles. Metal ions can also be reduced by exposure to excimer laser radiation at 308 nm (Ref. 28) or to an electron microscope beam.[29, 49, 66]

Note that the synthesis of nanoparticles in micellar solutions of block copolymers is a rather promising line of research, especially as regards the preparation of catalytically active systems,[40, 61, 67] targeted drug delivery agents,[40, 63] information carriers [65] and so on (detailed consideration of this issue is beyond the scope of this review).

Meanwhile, the results of some studies (see, for example, Refs 46, 68, 69) indicate that upon film formation from a block copolymer solution containing a metal precursor, the micelles can form a hexagonally ordered monolayer. This opens up the way for the preparation of highly ordered nanoparticle assemblies on various substrates.

2. Formation of ordered assemblies of nanoparticles on solid substrates

Ordered assemblies of nanoparticles are fabricated most often using PS–PVP block copolymers.

Generally, the algorithm of the design of ordered nanoparticle assemblies with the use of block copolymer micellar nanoreactors includes several key steps (Fig. 2).

1. Preparation of a micellar solution of a block copolymer in a solvent selective with respect to one of the blocks. As noted above, upon dissolution of amphiphilic diblock copolymers in a solvent selective for one of the blocks at a

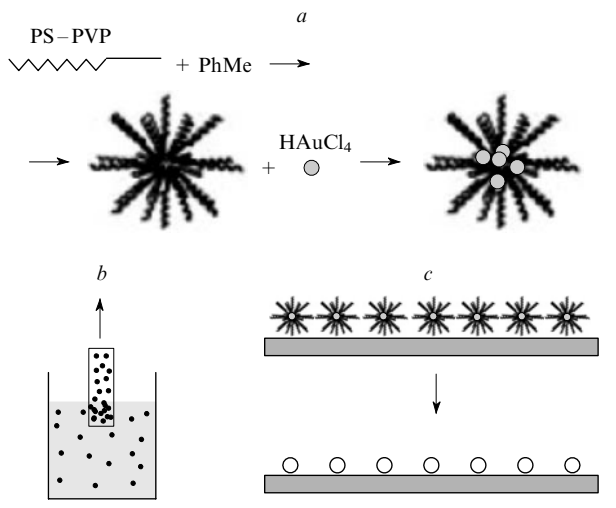


Figure 2. Chart of preparation of hexagonally ordered assemblies of gold nanoparticles.[69]
(*a*) Formation of reverse PS–PVP micelles filled with $HAuCl_4$; (*b*) formation of monomicellar PS–PVP film by vertical withdrawal of the substrate from a solution of precursor-loaded micelles; (*c*) removal of the polymer matrix in plasma with simultaneous reduction of metal ions.

‡ Here and below, the values in parentheses are the molecular masses of the blocks /kDa.

certain ratio of the copolymer block lengths and at concentrations above the critical micelle concentration, spherical micelles are formed in solution.

2. The addition of a metal nanoparticle precursor and its solubilization in the micelle core. The precursor ions are coordinated by the chains of one block of the copolymer (in most cases, the block forming the micelle core). For example, when the PS–PVP block copolymer is used, gold ions are bound to the pyridine groups.

3. The preparation of a monolayer film of block copolymer micelles onto a solid substrate surface by the solution spin coating or by a substrate vertical withdrawal from the solution (dips coating). The purpose of this step of the experiment is to form a monolayer film of hexagonally ordered micelles. The structure thus obtained serves as the template for the synthesis of two-dimensional nanoparticle assembly. The geometric characteristics of the monolayer micellar film determine the parameters of the nanoparticle assembly.

4. The reduction of metal ions and removal of the polymer. This is the final step of formation of highly ordered planar assemblies of nanoparticles on the substrate surfaces. It can be conventionally divided into two parts: reduction of the metal precursor whose ions are coordinated in the micelle cores and removal of the polymer matrix. For obtaining an assembly with hexagonally packed nanoparticles, these two processes should be carried out under as mild conditions as possible.

Note that depending on the requirements imposed on the final nanoparticle assembly, this algorithm may vary considerably. In particular, in some cases, metal nanoparticles are obtained in a micellar solution of the block copolymer and only after that, the film is cast [68] (the introduction of the precursor into the pre-formed micellar film is even possible [44]).

Spatz, Möller and co-workers [68, 69] were among the first to prepare two-dimensional nanostructures of Au, Pt, Pd, Co and Ni nanoparticles on substrates of various nature (made of silicon, mica, diamond, *etc.*) using the algorithm described above. The authors reduced the precursor ions to the metal and simultaneously removed the polymer by treating the sample in an oxygen, hydrogen or CF_4 plasma. As a result, a hexagonally ordered assembly of monodisperse nanoparticles of the metal (*e.g.*, gold) was formed on the substrate surface. Emphasize that the packing of this assembly exactly reproduces the two-dimensional structure of the initial micellar film. This is indicated by comparative AFM analysis of the surface of samples before and after their plasma etching and comparison of the autocorrelation functions obtained by processing of AFM images.[68, 69]

For studying the effect of the type of plasma on the rate of reduction and the size and chemical composition of the particles formed upon etching of the PS–P2VP/$HAuCl_4$ film and for ascertaining the completeness of removal of the polymer, Spatz and co-workers [68, 69] used X-ray photoelectron spectroscopy (XPS) and TEM. The experimental results indicated [69] that the etching rate of the polymer virtually does not depend on the type of plasma used and after $\sim$30 min, it is completely removed from the sample surface. Also, it was shown that upon oxygen plasma etching, nanoparticles are formed more rapidly than in the hydrogen plasma. It is clearly seen in the micrographs shown in Fig. 3 that after a 2-min hydrogen plasma treatment of the sample, the micelle cores contain single particles

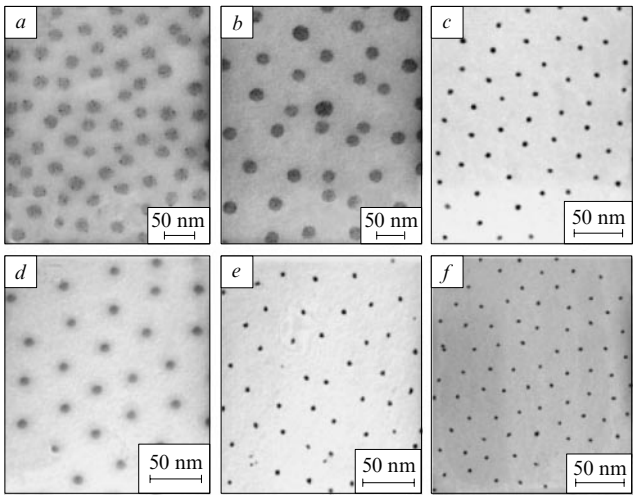


Figure 3. TEM images of micelles in the PS–P2VP samples containing $HAuCl_4 \cdot 3H_2O$ after hydrogen-plasma (*a*–*c*) or oxygen-plasma (*d*–*f*) etching for 2 (*a*, *d*), 10 (*b*, *e*), 20 (*c*) and 40 min (*d*).[69]

of very small size, which completely coalesce only after 20 min of etching (see Fig. 3 *a*–*c*). However, when oxygen plasma is used, as soon as after 1–2 min of etching, rather coarse nanoparticles are formed (Fig. 3 *d*–*f*). However, in this case, nanoparticles may be composed of a mixture of metallic gold and the unstable oxide Au_2O_3. This is confirmed by XPS data. It was shown that [69] for reducing the oxide to the metal, it is sufficient to keep the sample in air at room temperature for several days (this process can be markedly accelerated by annealing or hydrogen plasma treatment of the sample). A TEM analysis of the obtained assemblies showed that the nanoparticles are spherical.

Argon [44] or even air plasma [46, 56] can also be used for the formation of ordered nanoparticle assemblies. The use of air plasma is of obvious practical interest, in our opinion, as this does not require special gas pretreatment. In addition, air plasma allows milder conditions of etching than oxygen plasma, which may be useful for the formation of nanoparticle assemblies of relatively easily oxidizable metals: Ag, Co, Cu and so on.

However, oxygen plasma etching is now the most widely used method of treatment of micellar films of block copolymers aimed at the preparation of various nanoparticle assemblies.

The size of micelle nanoreactors (and hence, of nanoparticles formed therein) and the distances between them in a two-dimensional assembly can be changed by varying the molecular mass of the copolymer and the ratio of block lengths. The results of several publications [44, 68–71] attest that an increase in M and in the length of the PS block leads to greater distance between nanoparticles. Meanwhile, the nanoparticle size depends first of all on the length of PVP blocks, which form the micelle cores (the longer these blocks, the larger the particles formed upon plasmochemical etching of the monomicellar film), and on the amount of the precursor added to the micellar solution. In particular, when the PS(48)–P2VP(70) block copolymer is used, an increase in the amount of $HAuCl_4$ from 0.25 to 1 molecule per P2VP monomer unit leads to increase in the particle diameter from 4 to 17 nm.[71] The structure of a nanoparticle

assembly is also considerably affected by the conditions of formation of the monomicellar film of the block copolymer (see above).

Not long ago, approaches were proposed for controlling the nanoparticle packing density in the two-dimensional assembly by varying the temperature [72] or the composition of the micellar solution of a block copolymer.[73, 74] One of these approaches is to introduce homopolymer molecules of the same nature as the block that forms the micelle corona into the micellar solution of the block copolymer.[73] The homopolymer chains are incorporated in the micelle corona, which thus becomes larger and, hence, the distance between the micelles in the film being formed increases. For the styrene copolymer with acrylic acid (PS – PAA), it was shown [73] that the addition of the homopolymer PS(8.5) to a PS(16.4) – PAA(4.5) solution results in 6- and 9-fold increase in the L value at PS : PS – PAA molar ratios of 4 : 1 and 10 : 1, respectively. Unfortunately, this disrupts the hexagonal packing of the micelles, and it is impossible to obtain an ordered assembly of nanoparticles (in the given case, Fe_2O_3).

An approach consisting in mixing of two micellar solutions, one containing the metal precursor [73] or metal nanoparticles [74] and the other containing unloaded micelles, is also used. According to Bennett *et al.*,[73] this method is suitable not only for varying the nanoparticle packing density on the substrate surface but also for producing assemblies composed of particles of different metals (see below). However, two issues should be taken into account. First, the structure (degree of ordering) of the monomicellar film formed from a mixed solution is affected by a number of factors.[73, 74] In particular, when the solution is kept for a long period, the unloaded and loaded micelles can combine, and also redistribution of metal ions or nanoparticles between them can take place. It was shown [74] that the probability of these processes can be reduced by using mixed micellar solutions, for example, unloaded PS – PAA micelles and gold nanoparticle-containing PS – P4VP micelles.

Second, using mixed solutions, it is virtually impossible to control the mutual arrangement of the unloaded and loaded micelles in the film, and, hence, to obtain an ordered nanoparticle assembly. (Meanwhile, it is the ordered nanoparticle assemblies that are of most practical interest. Hence, the applicability of these approaches is limited.)

Turning back to the problem of preparing nanoparticle assemblies using micelle nanoreactors, note that the key advantage of the plasmochemical etching is the possibility of simultaneous removal of the polymer and reduction of the metal ions. The use of excimer laser could serve as an alternative. Indeed, according to another work,[75] exposure of a PS – P2VP film saturated with $HAuCl_4$ to laser radiation at 193 nm in oxygen or air results in ablation of the polymer; however, in this case, several small gold nanoparticles are formed within each micelle, while no ordered assembly can be obtained.

A large number of fine (1 – 2 nm) gold nanoparticles is also formed in the micelle cores upon the reaction of Au(III) ions with a strong reducing agent, sodium borohydride, directly in the solution of PS – P2VP.[59] The nanoparticle-containing micellar film obtained from this solution has a clear-cut two-dimensional structure, which is, however, destroyed upon plasma treatment. When a mild reducing agent, hydrazine, is used, rather large single particles are formed in the block copolymer micelles. Therefore, the structure of the film deposited from this solution remains the same after plasmochemical etching, and a hexagonally ordered assembly of gold nanoparticles is formed on the substrate.[68] As shown in our experiments,[59] a similar result is attained when a PS – P2VP film containing $HAuCl_4$ is kept in hydrazine vapour (see also Ref. 76).

Aizawa and Buriak [44, 77] proposed an original method for the preparation of nanoparticle assemblies of various metals (in particular, easily oxidizable Ag and Cu) using micelles of PS – P2VP and PS – P4VP diblock copolymers on semiconductor substrates (Si, Ge, InP, GaAs). This method is based on the electrochemical process called galvanic displacement where the reduction of target metal ions occurs at the expense of oxidation of the substrate material. The experimental results [44, 77] showed that the process is almost completed 10 min after deposition of the block copolymer film containing the metal precursor onto the substrate (note that the reaction was carried out under nitrogen). To remove the block copolymer, the sample was washed in toluene.

In addition, it was demonstrated that the precursor can in principle be introduced into the pre-formed monolayer film of block copolymer micelles [44, 77] (see also the studies [45, 53]). For this purpose, the substrate bearing the PS – PVP film was immersed into an aqueous solution of the precursor. Solubilization of the precursor by the micelle cores and its reduction occur almost simultaneously, and the structure of the two-dimensional nanoparticle assembly being formed depends appreciably on the contact time of the block copolymer film with the precursor solution.[44]

According to some researchers, the introduction of a precursor into a monolayer film of block copolymer micelles allows the subsequent preparation of highly ordered nanoparticle assemblies with much fewer defects.[44, 45, 53] This is largely related to the fact that the structures of films with unloaded block copolymer micelles are controlled much more easily than in the case of loaded micelles. As noted above, there is a wide range of expedients for doing this.

In particular, a publication [53] indicates that exposure of a monolayer film of PS(47.6) – P4VP(20.6) micelles formed on a freshly cleaved mica to tetrahydrofuran vapour promotes the formation of almost defectless structure.§

A TEM analysis of a block copolymer film before and after this annealing and construction of the Voronoi diagrams demonstrated that in the non-annealed film, the fraction of the micelles that do not occupy hexagon vertices (*i.e.*, with a number of neighbours other than 6) is 30% of their total number (Fig. 4 *a*). Meanwhile, the fraction of such micelles in the film annealed in THF vapour does not exceed 5% (Fig. 4 *b*). Simultaneously, the average diameter of the micelle core decreases, being 24 ± 3.9 nm before the annealing and 13.0 ± 1 nm after the annealing. Keeping of the annealed film in an alcohol solution of $HAuCl_4$ followed by treatment with oxygen plasma affords a two-dimensional hexagonally ordered assembly of gold nanoparticles with very few defects (0.5% to 1%).

§ For PVP, tetrahydrofuran is not a solvent; however, it has higher solvation capacity toward PVP than toluene. This ensures mobility of PVP chains sufficient for the formation of an equilibrium structure.

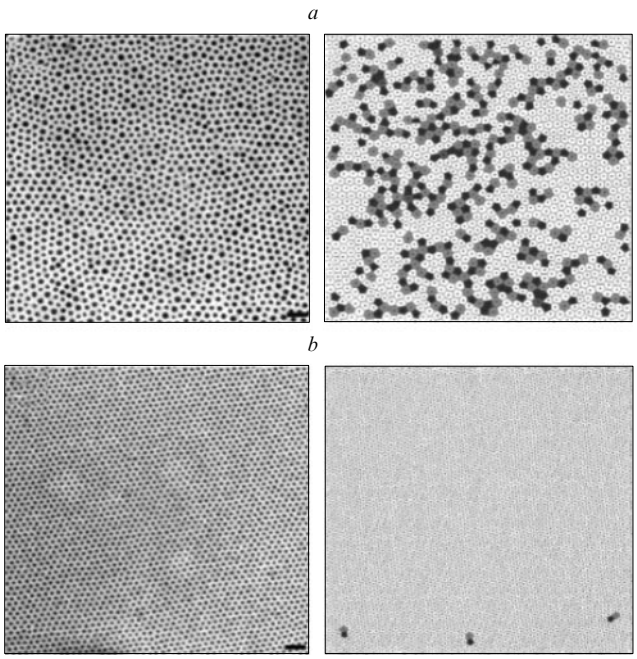


Figure 4. TEM images (on the left) and Voronoi diagrams (on the right) of the micellar PS – P4VP film before (*a*) and after (*b*) keeping in THF vapour.[53]
In the Voronoi diagram, the cores of micelles with <6 neighbours are coloured black and those with >6 neighbours are coloured grey.

The assemblies of nanoparticles (first of all, Au, Ag and Pt) obtained using block copolymer micellar templates can be used for the design of various sensors [78, 79] and catalysts and chips used to analyze biological systems.[55, 74, 80–89] For example, the two-dimensional structures of gold nanoparticles formed on an optically transparent substrate are fairly convenient 'platforms' in cell adhesion experiments.[80, 82] In addition, gold nanoparticles are able to catalyze electrochemical oxidation of carbon monoxide,[84–86] nucleation and growth of arrays of unidimensional phthalocyanine crystals,[88, 89] silicon nanowires,[55] carbon nanotubes [83] or zinc oxide nanorods,[74, 82] which are of interest for practical applications.[90] The effect of the nature of the substrate and the size of gold nanoparticles on the catalytic activity of their assemblies has been studied.[85] According to experimental results, the particles with the smallest diameter ($\sim$1.5 nm) are most effective. This was assumed [85] to be due to not only the size effect but also to the fact that the Au_2O_3 layer formed upon etching-out of the block copolymer template by oxygen plasma and playing an important role in the electrochemical oxidation of CO is fairly stable on the surface of these ultrasmall particles. It was also shown that the oxide layer on the surface of gold nanoparticle in the assembly arranged on a conducting or semiconducting substrate (made of $In_2O_3-SnO_2$ or TiO_2, respectively) is much more stable than that on the dielectric substrate (SiO_2).

In recent years, a tendency has been observed toward complication of the structure and/or the composition of nanoparticle assemblies designed using diblock copolymer micelles. For example, a combination of block copolymer lithography with standard photo- (Refs 70, 91, 92) or electron-beam lithography methods (either using a resist [70] or not [70, 82, 93]) and microcontact printing [91] provides highly ordered nanoparticle assemblies with various two-dimensional organizations. The experiments were carried out by the following procedure. First, the substrate surface was

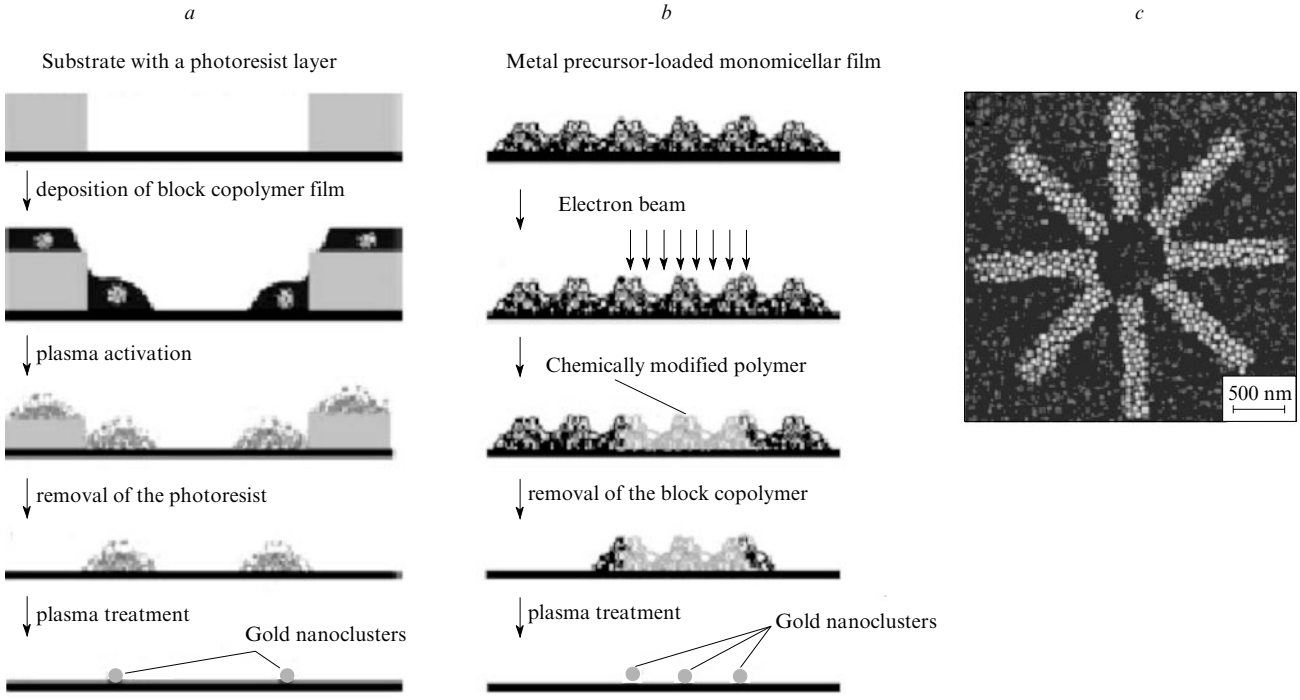


Figure 5. Chart of construction of nanostructures with complex geometry by combining photo- (*a*) or electron beam lithography (*b*) and block copolymer lithography with (*a*) or without (*b*) resist.[70] (*c*) Scanning electron microscope (SEM) image of the two-dimensional structure of gold nanoparticles.

patterned by standard methods.[94,95] As a result, areas coated by a photoresist sensitive to UV radiation and photoresist-free areas appear on the substrate. Then a monolayer film of block copolymer micelles containing a metal precursor was formed, the sample was treated with plasma and washed in a solvent to remove the resist.

The plasmochemical etching was performed in one[91,92] or in two stages.[70] Thus Glass *et al.*[70] treated the sample with plasma before and after removal of the resist layer (see the chart presented in Fig. 5 *a*). According to the authors, the short-term primary etching of the sample results in partial cross-linking of the copolymer, which precludes its dissolution (and, probably, prevents desorption of nanoparticles from the substrate surface) during washing-off of the resist (see below). On repeated etching, the block copolymer is completely removed and the metal ions are reduced.

According to a number of publications,[59,70,82,92,93] the monomicellar film itself containing the metal precursor can serve as a resist. In particular, electron beam irradiation (Fig. 5 *b*) of $HAuCl_4$-loaded PS–P2VP micelles results in partial cross-linking of the monomicellar film and, as a consequence, in deterioration of its solubility and enhancement of the adhesion to the substrate (as compared to non-irradiated regions of the film, which are readily removed by washing the sample in toluene in an ultrasonic bath).[70,82,93] The plasmochemical etching of this sample produces microscopic-sized two-dimensional structures with a complex geometry whose elements are composed of hexagonally ordered gold nanoparticles (Fig. 5 *c*). A similar cross-linking effect of macromolecules is induced by UV irradiation of $HAuCl_4$-containing monolayer films of 2-vinylpyridine–isoprene[92] and PS–P2VP block copolymer micelles.[59,92] According to a publication,[92] pre-modification of the substrate with vinyltriethoxysilane and the addition of photoinitiator (*e.g.*, benzophenone) into a block copolymer solution allow one to increase the cross-linking density.

In some cases, after reduction of the precursor and removal of the block copolymer matrix, the substrate can be subjected to further plasma or ion beam etching. The formed nanoparticle assemblies serve as a sort of mask.[96–101] Thus, this procedure was used to obtain arrays of nanorods of various materials, in particular, gallium arsenide,[96,97] its alloys with indium or aluminium,[98] diamonds,[99] silicon dioxide,[100] free nanoporous gold films[97] and two-dimensional structures of $PbTiO_3$ particles.[101]

The possibility of using microcontact printing for the preparation of two-dimensional assemblies of iron oxide nanoparticles of specified geometry has been demonstrated.[91,102] The flow chart of this experiment is presented in Fig. 6 *a*. Hollows shaped like 2 μm-wide grooves were formed on the poly(dimethylsiloxane) stamp surface by photolithography. Then PS–P4VP[91] or PS–PAA[102] monomicellar film containing Fe(III) ions was applied onto the stamp; by microcontact printing, this film was transferred to the substrate. After separation of the stamp, the sample surface was treated with oxygen plasma. As a result, bands of hexagonally ordered iron oxide nanoparticles were formed on the substrate¶ (Fig. 6 *b*,*c*).

¶ Bands of gold nanoparticles were prepared similarly;[74] however, in this case, the film was deposited from a mixed PS–P4VP and PS–PAA solution.

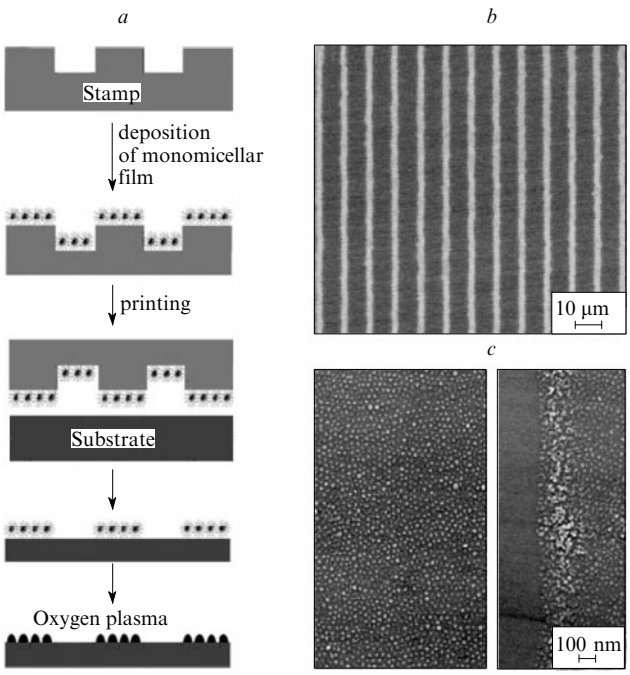


Figure 6. Chart of the preparation of nanostructures of metal particles by combining microcontact printing and block copolymer lithography techniques (*a*) and SEM images of two-dimensional nanostructures of Fe_2O_3 nanoparticles formed according to this chart (*b*, *c*).[91]

It was shown[91,102–114] that in the case of non-noble metals (*e.g.*, Fe, Co, Ni, Mo) and their binary alloys, the nanoparticles formed upon the destruction of block copolymer templates, PS–PVP or PS–PAA, induced by oxygen plasma,[91,102–110,114] UV radiation[111,112] or high temperature[113] are coated by fairly stable films of the corresponding oxides or entirely consist of them (in some cases, they have more complex composition[103]). Perhaps, the only alternative that allows one to avoid the surface oxidation of such nanoparticles is the approach based on the pyrolysis of the film of a styrene block copolymer with ferrocenyl(ethyl)methylsilane.[115] According to the publication,[115] this procedure can be used to prepare pure iron particles. However, in our opinion, these assemblies should be rather easily oxidizable by air oxygen.

Note that depending on the problem to be solved, two-dimensional structures of metal oxide (or oxide-coated) nanoparticles can be immediately used[105,106] or subjected to the subsequent treatment for reduction of the oxide and in some cases, for removal of the oxide.[106–114]

Special mention is deserved by the study[105] devoted to the synthesis of Fe_2O_3 nanoparticles with diameters of 6 to 25 nm in PS–P4VP monomicellar films formed on silicon substrates. The Fe_2O_3 nanoparticle diameter was varied by increasing the amount of the precursor ($FeCl_3$) in the micelle cores ($W = 0.2–1$). An interesting effect was detected: in the obtained assemblies, particles with a mean diameter of 25 nm exhibited ferrimagnetic properties, whereas 6 nm particles were superparamagnetic. It is also of interest that according to field emission scanning electron microscopy,[105] the Fe_2O_3 particles are hemispheres, unlike gold nanoparticles formed in a similar way, which are spherical (see above).[69] The researchers cited believe[105]

that this is due to higher chemical affinity of iron oxide as compared to gold to native silica, which coats the substrate surface.

Bhaviripudi *et al.*[106] reported the preparation of gallium nitride nanocrystals. The process was carried out in one step (by treating the monomicellar PS–P4VP film containing a metal precursor with nitrogen plasma) or in several steps. In the latter case, oxygen was used to remove the block copolymer. The substrate with ordered Ga_2O_3 nanoparticle assembly formed thereon was placed in an ammonia-saturated chamber ($T = 500-750$ °C); in some cases, the sample was pre-treated in a hydrogen atmosphere to reduce the oxide. Consequently, GaN particles were also formed. Similar methods were used[106] to obtain indium nitride nanocrystals.

The annealing under hydrogen or a hydrogen mixture with argon at 800–900 °C results in reduction of the oxides to give nanoparticles of individual metals[102, 107, 108, 110–114] or alloys.[105, 110, 112] The assemblies of cobalt nanoparticles obtained in this way can be used to design memory cells.[107] In addition, two-dimensional assemblies of some metal nanoparticles are efficient catalysts for decomposition of methane and some other compounds,[102, 104, 108–115] they promote the formation of arrays of multiwalled and single-walled carbon nanotubes on the solid substrate, which have found wide use in recent years.[116] In most cases, this is done using two-dimensional structures of iron nanoparticles;[102, 104, 108–115] however, it was shown[110–112] that assemblies consisting of Co, Ni, Mo particles or binary alloys exhibit much higher catalytic activity.

Templates based on monomicellar films of PS–PVP,[117–121] PS–PEO[122, 123] or 2-vinylpyridine – butadiene[117] block copolymers are also used to prepare silicon oxide[117] and titanium oxide[118–123] nanoparticle assemblies (the latter are quite promising for the design of sensors, catalytic systems for water decomposition, *etc.*). These particles are formed by the sol–gel mechanism. Note that in the case of synthesis of SiO_2 particles, prior to the addition of the precursor, tetraethoxysilane (TEOS), which is rather readily soluble in organic solvents, aqueous hydrochloric acid was added to a micellar solution of PS–PVP in toluene, and it was solubilized in micelle cores.[117] As a result, TEOS hydrolysis and the formation of particles took place just in the block copolymer micelles.

According to published data,[118–123] TiO_2 nanoparticles can be synthesized either in solution with the subsequent deposition on the substrate[118, 123] or directly on the substrate surface.[119, 120] It was noted[118] that with increase in the amount of the precursor in solution, the particle size and shape change (if $W < 1$, spherical micelles are formed, and for $W > 1.2$, ribbon-like micelles are produced). In the latter case, it is almost impossible to prepare a sufficiently ordered nanoparticle assembly.

Original methods for the production of highly ordered TiO_2 nanoparticle assemblies have been proposed.[119, 120] In particular, in one work,[119] titanium chloride ($TiCl_4$) serving as the precursor was introduced into the PS–P2VP film predeposited on a silicon substrate. For this purpose, the sample was first kept in water (the micelle cores consisting of hydrophilic P2VP blocks sorbed some water) and then in dried argon saturated with $TiCl_4$ vapour. As a result, hydrolysis of the precursor and the condensation of the resulting compounds took place in micelle cores. After removal of the polymer by UV irradiation or plasmochemical etching, hexagonally ordered assemblies of TiO_2 nanoparticles were formed on the sample surface.

Weng *et al.*[120] introduced pre-hydrolyzed precursor [as $Ti(OH)_2^{2+}$] into PS–P4VP micelles by mixing a solution of the block copolymer in toluene with an aqueous solution containing $Ti(OH)_2^{2+}$. Note that in this two-phase system, solubilization of the $Ti(OH)_2^{2+}$ ions in micelle cores occurs at a markedly lower rate than in a single-phase system.[118] The mechanism of this process is barely discussed in the paper cited,[120] but in our opinion, the block copolymer molecules can act in this case as 'phase-transfer agents' by analogy with low-molecular-mass amines[124] (this feature of PS–PVP was indicated in another publication[125]). High-temperature annealing of the micellar film containing $Ti(OH)_2^{2+}$ *in vacuo* afforded TiO_2 particles. For the removal of the block copolymer, the sample surface was treated with oxygen plasma.

The next stage was demonstrating the possibility of enlargement (seeding growth) of the TiO_2 nanoparticles thus obtained in their ordered two-dimensional assemblies. The sample was kept for a certain period in an aqueous solution of the precursor with specified pH. According to field emission SEM, the seed nanoparticles were enlarged (and acquired needle shape) and no new particles were formed.[120]

In recent years, publications appeared dealing with the preparation of a fundamentally different class of nanoparticles, semiconductor quantum dots[126, 127] and their two-dimensional assemblies using the PS–PVP micelles. Thus Anthony and Kim[126] synthesized nanoparticles of cadmium selenide. The process was carried out in a two-phase system by mixing a toluene solution of the block copolymer containing $CdCl_2$ with an aqueous solution of sodium hydrogen selenide (NaHSe). This yielded CdSe particles 1–3 nm in diameter in PS–PVP micelles. It was found that an increase in W from 1 to 20 affected not only the particle size but rather their structure: at small W values, the particles were amorphous, and at large W values, the particles were crystalline. According to AFM data, the monomicellar films deposited from such systems had a relatively ordered structure, which was retained both after removal of the block copolymer matrix on exposure to UV radiation and after annealing of the samples at 250 °C. It was assumed[126] that assemblies of other semiconductor particles (for example, PbSe and ZnSe) can also be obtained in this way.

Turning back to the enlargement (or seeding growth) of nanoparticles in their two-dimensional assemblies, note that this approach is used rather often to prepare metal nanoparticles, including bimetallic composite particles with the core/shell structure both in solutions and on solid substrates.[128–130] The approach is based on the ability of metal nanoparticles to catalyze the reduction of ions of the same or another metal. A mild reducing agent is used. As a consequence, only enlargement of the nanoparticles already present in the system takes place (and no formation of new ones).

By combining this approach and block copolymer lithography methods, one can vary the structure of an ordered assembly of nanoparticles (first of all, their size) over a broad range using the same block copolymer. This is indicated by a number of publications.[56, 131, 132] Thus it was reported[131] that keeping the substrate bearing an ordered assembly of Au, Pt or Pd nanoparticles in a

solution containing corresponding metal ions and hydroxylamine results in an increase in the particle diameter from 6 to ~50 nm (see also Ref. 56). The particle growth rate depends on the type of metal (being maximum for gold). As an example, Fig. 7 *a*–*c* shows the TEM images of two-dimensional structures of gold nanoparticles before and after the seeding growth.

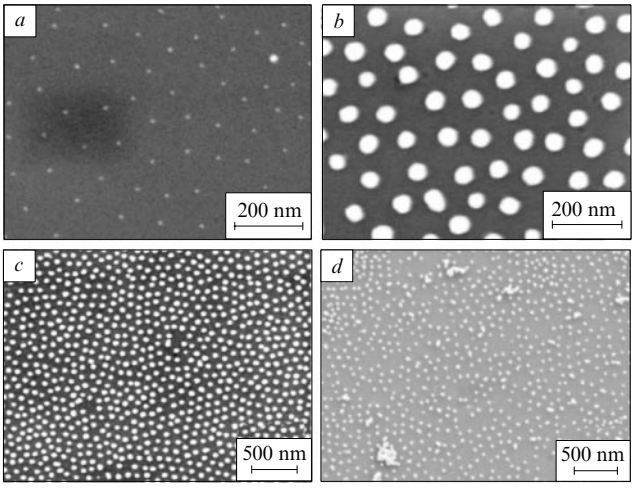


Figure 7. SEM images obtained before (*a*) and after (*b*, *c*) seeding growth of gold particle assemblies formed on hexadecyltrimethoxysilane-modified (*b*, *c*) and 'pure' substrate (*d*).[131]

The results of experiments[56, 131, 132] showed that during seeding growth, some fraction of particles is desorbed from the substrate surface, which causes violation of the hexagonal packing of the assembly (Fig. 7 *d*). In the opinion of the researchers,[131, 132] this effect is caused by weak interaction of the particles with the substrate surface and to some extent by their Ostwald ripening during the seeding growth. The contribution of the latter process appears insignificant in view of the temperature and temporal conditions of the experiment.

In our opinion, the main cause for particle desorption is that after plasmochemical treatment of the sample, fragments of PVP blocks may remain under the formed metal nanoparticles. Indeed, according to some works,[49, 133, 134] during the deposition of the PS–PVP film from solution, a brush-like ultrathin adsorption layer of free block copolymer molecules is first formed on the substrate, and micelles are attached to this layer. Complete removal of this adsorption layer during the plasmochemical etching is difficult. However, it is sensitive to the pH of the medium. It is known[135] that at low pH values (3–4), the PVP pyridine groups are protonated, which results in pronounced swelling of the polymer, and in the case of relatively low molecular mass, to its dissolution in the aqueous medium.

Note that for the seeding growth of nanoparticles, hydroxylamine[56, 131] or ascorbic acid[132] was used as the reducing agent. In our experiments,[56] pH was ~4 (presumably, in the other two cases,[131, 132] the aqueous medium was also acidic). This provides the conclusion that desorption of nanoparticles from the sample surface and disruption of the initial geometry of the assemblies are due, at least partly, to the dissolution of the PVP layer remaining between the particles and the substrate. This assumption is also supported by the fact that even on long-term storage of the substrate with the nanoparticle assembly formed thereon, no particle desorption takes place in an alkaline solution.[59]

The particle desorption can be prevented (or considerably retarded) by increasing pH of the medium[59] or by chemical modification of the substrate.[131] In particular, modification of the sample surface (after formation of an ordered assembly of gold nanoparticles) with hexadecyltrimethoxysilane was used[131] to bind more strongly the seed particles to the substrate and to retain the assembly structure during the seeding growth (*cf.* Fig. 7 *c* and 7 *d*). The authors did not discuss the nature of this effect. In our opinion, this is due to hydrophobization of the substrate with silane, which hampers the penetration of the growth solution to the nanoparticle contact region with the surface and, hence, prevents swelling (dissolution) of the PVP layer remaining in this region after plasma etching.

For enlargement of the nanoparticles directly in the monomicellar PS–PVP films, an $HAuCl_4$-containing film formed on a substrate surface was subjected to short-term plasma treatment.[131] As a result, seed gold particles were formed in the micelle cores, whereas the polymer matrix was destroyed only partly, which allowed fixing the particles on the substrate upon their seeding growth; after completion of the seeding growth, the sample was once again treated with plasma to remove the remaining block copolymer.

In our opinion, the seeding growth technique can be successfully used also for the preparation of highly ordered assemblies of nanoparticles with a core/shell structure. Note that it is rather difficult to synthesize these particles in block copolymer micelles. Indeed, despite the large number of papers devoted to the synthesis of bimetallic particles in monomicellar film templates,[64, 73, 110–112, 136–140] only one publication,[136] to our knowledge, demonstrates the possibility of controlling the structure of bimetallic Fe/Pt particles by varying the sequence of introduction of the precursors into PS–P2VP micelles. In one case, first $FeCl_3$ and then H_2PtCl_6 were added to a solution of PS–P2VP in toluene, in the second case, these compounds were added in the opposite order, and in the third case, they were added simultaneously. The PS–P2VP film containing the precursor was treated with oxygen plasma and then (to remove the oxide layer from the particles) with an Ar^+ ion beam. As a result, hexagonally ordered assemblies of Fe/Pt particles of ~21 nm diameter formed on the substrate, the distance between the particles was ~100 nm. XPS analysis of the resulting assemblies showed that successive addition of the precursors into the micellar solution gave rise to core/shell particles. The cores were composed of the metal whose precursor was added first to the solution. The simultaneous addition of the precursors gave the Fe—Pt alloy.

However, according to Ethirajan *et al.*,[137] nanoparticles of the Fe—Pt alloy can also be obtained by successive addition of the precursors into the PS–P2VP micelles; chloroplatinic acid is the first to be added, and only after that, ferric chloride should be added. Otherwise, $FeCl_3$ solubilized in the micelle cores prevents chloroplatinic acid from penetrating inside and no bimetallic nanoparticles are formed. (Note that Qu *et al.*[136] used exactly this order of introduction of these precursors in their later works.[138, 139])

It was found[137, 138] that the nanoparticles of disordered Fe/Pt alloy synthesized in monomicellar PS–PVP films have initially a face-centred cubic lattice and, hence, they

are superparamagnetic. However, ferromagnetic particles with a face-centred tetragonal lattice are of much higher practical interest, as they have very high energy density of the magnetocrystalline anisotropy, namely $(6.6-10) \times 10^7$ erg cm^{-3} (Ref. 136). The assemblies of such particles can be used to produce magnetic data carriers with very high recording density. It was shown [138] that high-temperature (700–750 °C) annealing results in recrystallization of nanoparticles to give assemblies with rather high coercive force (10 kŒ).

The structure of a micellar film template (and, hence the nanoparticle assembly based thereon) can be varied not only by varying the nature of the block copolymer or parameters of its macromolecules but also by selecting the appropriate solvent.[140, 141] Sohn *et al.*[141] used the ability of the micellar PS–PVP film to be inverted (PVP chains pass to the corona, while PS chains pass to the micelle core) upon storage in ethanol (a solvent selective toward the PVP block) for controlling the two-dimensional distribution of silver nanoparticles in the free-standing PS(21.4)–P4VP(20.7) thin film.

The TEM images of the monomicellar PS(21.4)–P4VP(20.7) film containing silver acetylacetonate before and after it is kept in ethanol are shown in Fig. 8.[141] The reduction of Ag^+ ions and the formation of metal nanoparticles was induced by the microscope electron beam. It can be seen that in the former case, silver nanoparticles located in the P4VP cores of the micelles form isolated islets, whereas in the latter case, they form a quasi-continuous assembly. The authors believe [141] that this change in the assembly structure is accompanied by the change in the physical properties, first of all, conductivity.

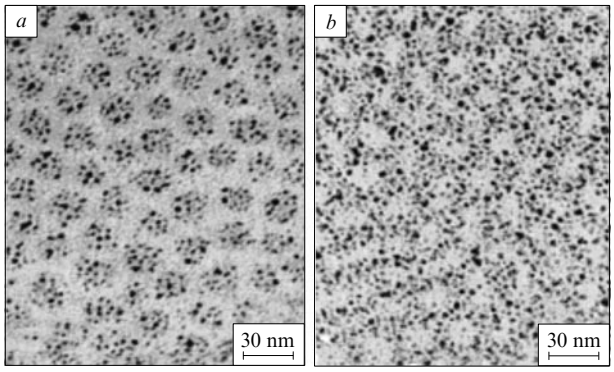


Figure 8. TEM images of the monomicellar PS–P4VP film containing silver nanoparticles obtained by electron beam treatment before (*a*) and after (*b*) micelle inversion.[141]

The possibility of formation of ring structures of nanoparticles was demonstrated.[142–145] For this purpose, a toluene sol of gold,[142] whose dodecanethiol-coated particles (5.4 nm) were synthesized by the procedure reported by Tiranishi *et al.*,[146] was added to a solution of PS–P4VP in toluene. The thiolated gold particles were selectively incorporated into the PS corona of the micelle. Finally, after the film formation, gold nanoparticles were arranged around the micelle cores and had a short-range hexagonal order caused by the interaction of dodecanethiol chains (Fig. 9 *a*). Hybrid structures consisting of particles of different metals were prepared in a similar way.[142–144] For this purpose,

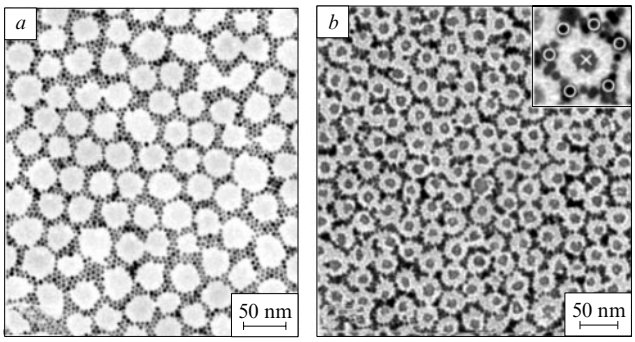


Figure 9. TEM images of two-dimensional assemblies of gold nanoparticles (*a*) and mixed assembly composed of hexagonally ordered iron oxide nanoparticles surrounded by gold nanoparticle (*b*).[142] For explanation, see the text.

apart from thiolated gold nanoparticles, ferric chloride [142, 143] or silver acetate,[144] which were noted above to solubilize in the micelle cores, were introduced into a micellar solution of block copolymer. Oxygen plasma treatment [142, 143] or annealing (200 °C) [144] of the film obtained from this solution gave rise to an assembly comprising ordered Fe_2O_3 or silver nanoparticles surrounded by gold nanoparticles. This is indicated, in particular, by the results of energy dispersive X-ray microanalysis.[142, 143]

It was shown [144] that in the assembly composed of silver and gold nanoparticles, the corresponding localized plasmon resonances (LPR) are hybridized. By varying the relative length of the PS block (*i.e.*, the distance between the micelles in the film) and/or the concentration of gold nanoparticles, one can adjust the position of the overall LPR peak to a specified wavelength in the range of 440–560 nm. For example, as the molecular mass of the PS block increases from 19 000 to 122 000, the distance between the micelles increases from 40 to 90 nm and the position of the LPR peak of the assembly shifts from 500 to 550 nm.[144]

Moreover, according to Bae *et al.*,[145] by using block copolymers of different molecular mass for the formation of monomicellar films, it is possible to control the resonance fluorescence energy transfer between the donor and the acceptor in the two-dimensional assembly. The CdS core/ZnS shell composite quantum dots stabilized by oleic acid and tri-n-octylphosphine served as the donors, while the sulforhodamine dye was the acceptor. Upon the addition to a PS–P4VP micellar solution, the latter was solubilized in micelle cores, while the CdS/ZnS nanoparticles were incorporated in the shell. A TEM analysis of the monomicellar films obtained out of such solution showed that semiconductor particles form ring structures similar to those presented in Fig. 9 *a* (see also Ref. 147). As the molecular mass of the block copolymer increases, the efficiency of the energy transfer from the nanoparticles to the dye decreases due to the increase in the distance between the donor and the acceptor.[145]

To conclude this Section, consider several more methods for the preparation of hybrid assemblies consisting of different types of nanoparticles. A method based on mixing of micellar solutions of block copolymers containing different precursors was suggested by Bennett *et al.*[73] and later studied systematically.[148–150] The experimental results

obtained for unloaded micelles of PS–PVP copolymers of different molecular mass [148] indicate that the structure of the monomicellar film depends appreciably on the order of mixing of the components. In addition, by varying the molecular masses of copolymers, *i.e.*, the micelle sizes and numerical ratio of different micelles in the mixed solution in the appropriate way, it is possible to obtain films with a honeycomb structure in which hexagonally ordered larger micelles are surrounded by smaller micelles (Fig. 10).[148] Highly ordered assemblies of gold and platinum nanoparticles were prepared by this procedure.[150] However, when using a block copolymer of a single molecular mass, control over the mutual arrangement of nanoparticles is impossible.[149]

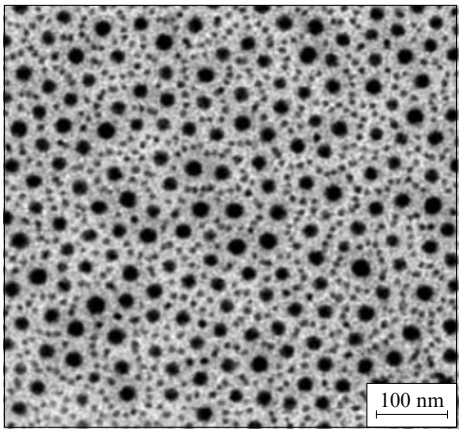


Figure 10. TEM image of ordered micelle assembly obtained from a binary mixed solution of PS–P4VP copolymers with different molecular mass.[148]

In addition, hybrid structures can be prepared in monomicellar film templates of styrene, vinylpyridine and ethylene oxide triblock copolymers; however, it was rather difficult [151, 152] to ensure the formation of any ordered assemblies of nanoparticles.

Thus, analysis of works devoted to the formation of two-dimensional ordered assemblies of nanoparticles using monomicellar films of diblock copolymers as the templates demonstrated that the block copolymer micellar lithography technique is applicable to the preparation of assemblies of various nanoparticles by varying both the nature or characteristics of block copolymer macromolecules and the experimental conditions. However, it should be noted that most of the publications have similar drawbacks. First, the authors evaluate the degree of order of the assemblies by visual examination of their images obtained by different procedures. Only in several studies were quantitative techniques used for this purpose, in particular, Fourier transform image processing [105] or, what is more informative, Voronoi diagrams.[53, 59, 71] Second, the polydispersity of nanoparticles in the obtained assemblies is seldom reported.

Turning back to the problem of development of two- and three-dimensional nanoparticle assemblies and using them for the design of nanocomposites with specified structure, note that the use of somewhat thicker block copolymer films (non-micellar films) provide new possibilities.

III. Formation of ordered assemblies of nanoparticles using non-micellar thin films of block copolymers as templates

1. Structure of thin films of block copolymers and ways for controlling it

The capability of block copolymers for microphase separation and, as a consequence, for the formation of highly ordered two- and three-dimensional domain structure of different shape (spherical, cylindrical, lamellar, *etc.*) makes them quite attractive as versatile templates for the formation of nanoparticle assemblies on solid substrates of various natures.[17, 153–170]

The publications devoted to experimental and theoretical investigation of the phase behaviour of block copolymers have been comprehensively analyzed in the reviews [17, 58, 153, 154] (see also references cited therein and the studies [155–170]). In the first approximation, their phase behaviour is governed by several key factors: the Flory–Huggins parameter, which describes the interaction of blocks, the total degree of polymerization ($N = N_A + N_B$) and the 'symmetricity' (the ratio of block lengths) of copolymer macromolecules. Depending on the temperature and/or pressure, two types of 'phase' (morphological) transitions are possible: from one ordered state to another ordered state or from an ordered to a disordered state.[153] It should be borne in mind that in the case of relatively thin film (*i.e.*, under restricted geometry), their structure depends considerably on the interfacial energy at the block copolymer interfaces with the substrate and air. For example,[155] it was shown in relation to the styrene block copolymer with methyl methacrylate (PS–PMMA) that the preferred wetting of the silicon substrate with the PMMA block promotes the formation of films with lateral (parallel to the substrate plane) orientation of the domains. If the film thickness exceeds some critical value, the effect of the substrate is mitigated and the domain orientation may change (Fig. 11).

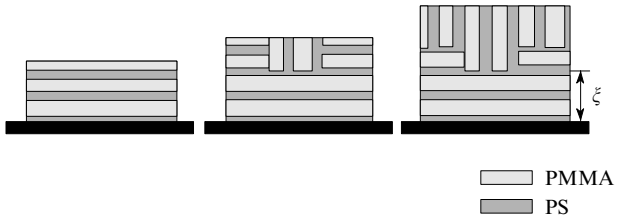


Figure 11. Schematic view of the PS–PMMA film cross-section.[155] ξ is the correlation length characterizing the degree of influence of the substrate surface on the domain orientation.

According to published data,[156–172] pre-modification of the substrate by random copolymers (of the same monomers) of a definite composition [157–172] or by some other compounds, in particular, octadecyldimethylchlorosilane,[156] may minimize the difference between the interaction energies of the two blocks with the substrate. Indeed, it was shown that interaction energies of the silicon substrate coated by grafted [157] or adsorbed [158–161] statistical PS–PMMA copolymer (styrene mass fraction $\sim$0.6) with the homopolymers PS and PMMA are nearly equal. This modification allows preparing a film with controlled ori-

entation of the domains for the PS–PMMA block copolymer.

Apart from those mentioned in the Introduction, there is a broad range of other methods for controlling the structure of block copolymer films.[158–172] The size of domains and/or the distance between them can be increased by adding a homopolymer of the same nature as one of the blocks or of a different nature to the block copolymer template.[158, 159, 161, 162] The magnitude of the effect depends on the nature and the molecular mass of the homopolymer.[158]

Considerable attention is paid to the order–order and order–disorder transitions in block copolymer films during their annealing in the vapour of a selective solvent [162, 163] or at high temperature [164–171] aimed at obtaining templates with a specified structure. In some cases, these transitions occur under additional external treatment (radiation at a specified wavelength [165] or applied stress [166–171]). For example, the transformation of spherical PMMA domains in the PS matrix to cylindrical domains was observed [168] under the action of electric field (simultaneously, their hexagonal ordering took place). The process was carried out at a temperature above the glass transition temperature in order to increase the mobility of macromolecules. Then the film was rapidly cooled to room temperature and thus the formed structure was frozen.

Oxygen plasma etching of such structured films of block copolymers,[173, 174–179] their UV irradiation with subsequent washing in acetic acid [52, 158, 159, 166, 170, 172, 179, 180] or keeping in an alkaline alcohol solution [171] result in the destruction and removal of one of the blocks. In particular, UV irradiation of the PS–PMMA film induces the destruction of the PMMA block (accompanied by partial cross-linking of the PS chains) the products of which are removed rather easily when the sample is kept in glacial acetic acid. Finally, a sort of template is formed on the substrate as a system of hexagonally ordered nano-sized pores (grooves) oriented perpendicular (parallel) to the substrate surface. These templates are used as masks in the preparation of assemblies of gold, chromium,[175] cobalt [177] and silicon dioxide [174, 176] nanoparticles and arrays of cobalt [170] or copper oxide [171] nanowires and nanoporous films made of various materials.[160, 175, 177, 180] This is done using electrodeposition,[170, 171] vacuum evaporation,[175, 178] ion beam treatment of the surface [160, 177] and other methods.[180]

Rather recently, the preparation of arrays of polypyrrole nanorods and other conducting polymers by monomer electropolymerization in a template film of PS–PMMA block copolymer fabricated on a conducting substrate was reported for the first time.[161] The experimental results showed that, owing to the high degree of orientation of macromolecules in nanorods, these arrays have higher conductivity than thin film of the same polymer. This opens up the way for their use in the design of highly sensitive sensors, nanoantennas and photovoltaic devices.

This Section considers the ways for controlling the structure, orientation of blocks and characteristic sizes in thin non-micellar films of amphiphilic diblock copolymers used as templates for the development of polymer–metal nanocomposites with selective localization of nanoparticles in the domains formed by a particular block. It was shown that by using these methods, one can control fairly efficiently parameters of the films and, hence, of the final materials.

Along with those mentioned above, there are also other methods for the formation of ordered assemblies of nanoparticles using thin films of block copolymers as templates: the synthesis of nanoparticles directly in one of the copolymer blocks, introduction of pre-synthesized particles into the template bulk or deposition of such particles on the surface of the structured film. These methods have been briefly surveyed in the literature.[180, 181] Below they are considered in more detail.

2. Template synthesis of nanoparticles in thin films of copolymers

As noted above, block copolymers can act as nanoreactors in the synthesis of nanoparticle assemblies on various substrates. In the case of non-micellar thin films, the use of copolymer in which one block is organometallic seems to be the most obvious way of solving this problem.[20, 21] However, it should be borne in mind that the synthesis of such compounds is a fairly complicated task. Consequently, the set of structures obtained in this way is quite limited.

An alternative approach is more widely applicable. This method includes saturation of one block of the copolymer that forms the initial template film or the structured film (obtained from the former by the above-described procedure) with the metal precursor and its subsequent reduction by chemical, plasma, heat or UV treatment.[182–198] In most cases, this is done using PS–PVP,[182–187, 191–194] and copolymers of 2-vinylpyridine with isoprene (PI–P2VP).[188–190] As noted above, this is largely caused by the ability of pyridine groups of PVP to coordinate metal ions. As a result, nanoparticles are formed in the PVP domains of the block copolymer. Note that with rare exceptions, films of these copolymer have lamellar structure, the lamellas being oriented parallel to the substrate plane. In the case of PS–PVP, the PS layer having lower surface energy is located at the interface with air and the PVP layer is located near the substrate.

Saito *et al.*[182–184] were among the first to apply the above approach to synthesize gold nanoparticles in the PS–P2VP film by reduction of Ag^+ ions with hydroquinone. The process was carried out by a rather complicated multistage route comprising film deposition, cross-linking of the P2VP lamellas, quaternization of the pyridine nitrogen atoms, film swelling in the solvent with simultaneous introduction of the precursor, reduction of metal ions and evaporation of the solvent.

In later studies,[185–198] this flow chart was considerably modified. For example, loading of the precursor into the PS–PVP film was carried out [185–187] 'directly' (*i.e.*, without preliminary cross-linking of PVP blocks). For this purpose, the sample was kept in ethanol [185, 186] or in a slightly acidified aqueous solution of the precursor.[187] The metal ions were reduced by treating the film with an aqueous solution of sodium borohydride [185, 186] or oxygen plasma.[187]

The structure of the PS–P2VP film was found [187] to change considerably during loading of the precursor. In the authors' opinion, this is caused by protonation of the pyridine nitrogen atoms of the PVP groups. Oxygen plasma treatment of the film saturated with the precursor gives rise to metal nanowires with a length from several hundred nanometres to several micrometres, which are arranged on the substrate according to a pattern resembling fingerprints (Fig. 12 *a*). This procedure was used to prepare assemblies of platinum, gold, palladium and other metal nanowires.[187]

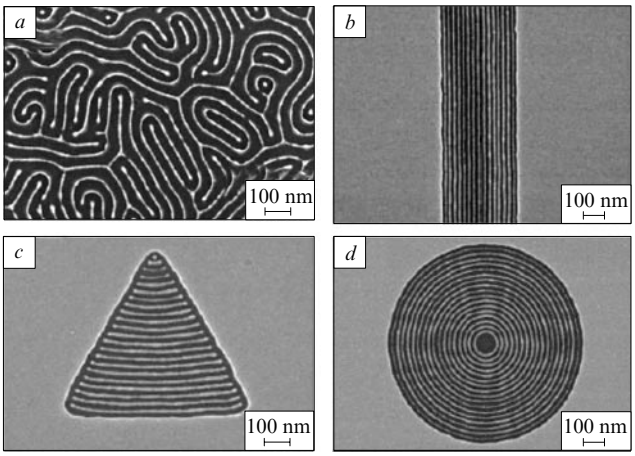


Figure 12. SEM images of platinum nanowires obtained in PS–P2VP block copolymer film templates formed on a smooth (*a*) or structured (*b*–*d*) silicon substrate.[187]

It was shown that the distance between the nanowires and their diameter can be varied by varying block copolymer characteristics: relative and absolute lengths of blocks. In addition, the possibility of preparing diverse highly ordered two-dimensional structures upon deposition of the block copolymer film onto the substrate structured in an appropriate way was demonstrated (Fig. 12 *b*–*d*).

However, according to other works,[185,186] the lamellar structure of the PS–P4VP film does not change during the experiment. The precursor ($HAuCl_4$) and then the reducing agent easily diffuse through PS layers and are selectively accumulated in the P4VP phase where the gold nanoparticles are formed. This gives rise to a multilayer nanocomposite consisting of alternating unloaded and metal particle-containing PS and P4VP domains, respectively (Fig. 13).

The characteristic features of preparation and distribution of palladium nanoparticles in the PI–P2VP matrix were studied.[188–190] The process was carried out at elevated temperature (140 °C) using a concentrated solution of PI–P2VP in benzyl alcohol, which served simultaneously as the reducing agent for the metal ions.[188,189] During the reaction, the solvent was gradually evaporated, and a polymer film containing nanoparticles was formed. It should be emphasized that palladium nanoparticles were formed only in P2PV lamellas. As a consequence, the resulting nanocomposite film had a layered structure similar to that presented in Fig. 13.

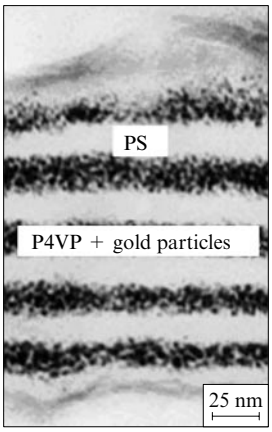


Figure 13. Cross-section TEM image of the PS–P4VP film with gold nanoparticles selectively localized in P4VP lamellas.[186]

Analysis of the published data[182–200] indicates that particles of metals (gold,[185–187,191] palladium,[187–190,192,195,196] platinum,[187] silver,[182–184,197] iron,[187,194] cobalt[187,194]), bimetallic alloys,[194] oxides[198] and semiconductors[199,200] can be prepared in the films of block copolymers. However, it should be borne in mind that it is multilayered nanocomposites that are formed in most cases.[182–186,188–195,199,200] It was shown[191,192] that oxygen plasma etching of cross-sections of these composite films allows one to produce metallic (gold or palladium) nanowires. In our opinion, this approach is very complicated for practical implementation. Note that such multilayered materials are of considerable interest for the design of electronics and non-linear optics devices; however, they are rather three-dimensionally ordered structures, and their detailed consideration is beyond the scope of this review.

Turning back to the problem of design of two-dimensionally ordered assemblies of nanoparticles by the reduction of metal ions in block copolymer film templates, we would like to note a number of publications.[196–198]

Yin *et al.*[196] solved this problem by keeping a film of the methyl methacrylate and 2-hydroxyethyl methacrylate block copolymer (PMMA–PHEMA) in palladium acetylacetonate vapour at 180 °C. Nanoparticles were formed in the PHEMA domains. The subsequent oxygen plasma treatment of the PMMA–PHEMA film containing palladium nanoparticles resulted in the removal of the copolymer matrix. In the authors' opinion,[196] the nanoparticle assembly obtained in this way is applicable as a mask for reactive ionic etching of the substrate. In addition, according to the experimental results, the structure of this assembly can be changed by varying the nature of the solvent from which the copolymer film is formed.

The preparation of highly ordered assemblies of silver[197] and zinc oxide[198] nanoparticles by UV irradiation and heat treatment of the precursor-saturated block copolymer template, respectively, was reported.

3. The introduction of pre-synthesized nanoparticles into a block copolymer thin film

It should be emphasized that the introduction of pre-synthesized nanoparticles into a thin film of block copolymer affords polymer–metal nanocomposites with 3D-ordered structure. Nevertheless, we considered it expedient to briefly survey the works devoted to this approach, in particular, to elucidation of the relationships between the characteristics of the block copolymer and nanoparticles and the morphology of the composite film, as this knowledge is significant for the design of ordered two-dimensional assemblies of nanoparticles using block copolymer templates.

Experiments are usually carried out according to the following chart. A colloidal solutional containing nanoparticles is mixed with a copolymer solution and a composite film is cast and then annealed at a specified temperature to remove the solvent and form an equilibrium structure.

According to a number of theoretical [201–204] and experimental [205–224] studies, the structure of a nanocomposite depends considerably on the copolymer molecular mass, the ratio of block lengths,[208, 210, 213, 214] the size,[202–204, 216–218, 220] the shape,[221] the concentration [206–210] and the chemical properties of the nanoparticle surface [212–216] and also on the film annealing temperature.[216]

For example, the introduction into the PS–P2VP matrix of CdSe nanoparticles modified by tri-n-octylphosphine oxide and, hence, selectively accumulated in the cylindrical PVP domains results in the change of their orientation from lateral (parallel to the substrate plane) to vertical.[205] Note that a similar domain re-orientation effect is also induced by globular ferritin macromolecules (nanoparticle according to the authors' terminology) in the PEO–P2VP film.[205]

A study of morphological transitions in the PS–PEO [206] and PS–PVP [207–210] films induced by CdSe [206, 207] or Au [208–210] nanoparticles showed that an increase in the volume concentration of nanoparticles (c_{np}) induces transitions: order–order (*e.g.*, of cylindrical PVP domains into a lamellar structure [207]) and/or order–disorder [208] (see also Refs 190, 211) transitions. In this connection, note a publication [210] in which a nanoparticle concentration gradient across the film was observed for the first time in the PS–P2VP/Au system. This was indicated, in particular, by analysis of TEM images of the film cross-sections with nanoparticle contents of about $\sim$0.5 vol.%. The nanoparticles were modified by thiolated PS and were selectively accumulated in the PS domains of the block copolymer. It was shown (Fig. 14) that as the distance from the interface with air increases, the concentration of nanoparticles in the film increases. As a consequence, morphological transitions from the lamellar structure through a disordered structure to a structure composed of spherical domains take place. It was assumed [210] that the concentration gradient of nanoparticles is related to faster evaporation of the solvent from the surface layer of the polymer.

In view of the results, phase diagrams for the PS–PVP/CdSe [207] and PS–PVP/Au [208] systems were proposed. In this connection, noteworthy are two theoretical studies.[202, 203] The calculation showed [202] that the introduction of nanoparticles into the copolymer matrix results in noticeable shift of the order–disorder transition temperature, this effect being more pronounced for smaller particles.

One of the key conditions for nanoparticle incorporation into the domains of a particular block of the copolymer is the minimization of the interfacial energy at the boundary between the polymer forming this block and the nanoparticle. For solving this problem, the particle surface is modified by compounds having affinity to one of the blocks.[205–223] These compounds can be represented by surfactants,[211] low-molecular-mass thiols,[206, 217–219] homopolymers [208–210, 212–214, 220–222] or block copolymers of the same or different nature,[214–216] statistical copolymers [212] and other compounds.[205, 207, 223] For example, thiolated PS or P2VP or a blend of these polymers were used [213] to modify gold nanoparticles. The macromolecules were grafted on the particle surface through the formation of S–Au bonds. The photomicrographs of the cross-sections of PS–PVP/Au composite films cast from a nanoparticle dispersion in a copolymer solution are presented in Fig. 15. It can be seen (see Fig. 15*a*) that the PS-coated particles occur at the centres of PS lamellas (the opposite picture is observed for P2VP–Au particles). Meanwhile, the nanoparticles modified by a mixture of PS and P2VP are adsorbed at the block interface (see Fig. 15*b*). It was assumed [212] that localization of particles in the block copolymer matrix is considerably affected by the grafting density of the modifying macromolecules. If it is high, the particles are located closer to the domain centres and if it is low, they are located at the domain interface.

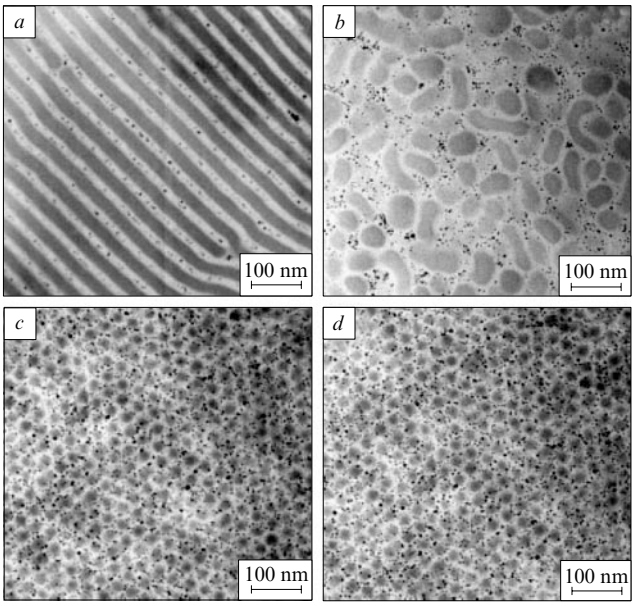


Figure 14. Cross-section TEM images of the PS–P2VP film containing 0.5 vol.% gold nanoparticles obtained at different distances (l) from the sample surface.[210]
l = 27 (*a*), 36 (*b*), 52 (*c*) and 95 μm (*d*).

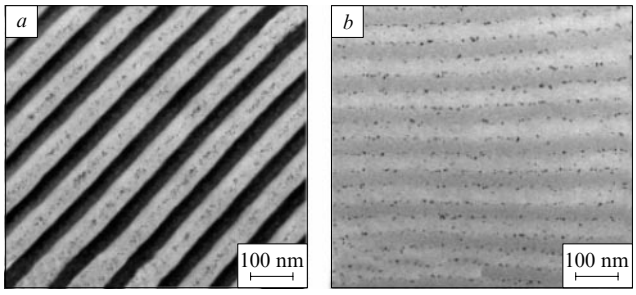


Figure 15. Cross-section TEM images of the PS–P2VP/Au composite films obtained by mixing copolymer with gold nanoparticles modified by PS (*a*) and a 4 : 1 PS–P2VP mixture (*b*).[213]

In the previous Section, we mentioned the possibility of synthesis of palladium nanoparticles in the concentrated solution of PI–P2VP [188, 189] (a similar process can also be carried out in a solution of the P2VP homopolymer [214]). A rather tight adsorption layer is formed on the particle surface as a result of strong interaction of palladium with P2VP chains. The results of some works [190, 214, 215] indicate that being introduced in the film of the PI–P2VP block copolymer, palladium nanoparticles obtained in this way are selectively accumulated in the central region of the P2VP domains. The pattern of distribution of the

PI–P2VP-coated particles inside the domains depends on the ratio of the lengths (degrees of polymerizastion) of the P2VP blocks of the copolymer matrix and the 'stabilizer' (N_m/N_s).[215] If N_m is considerably larger than N_s, the nanoparticles are concentrated near the domain interfaces; otherwise, they are accumulated at the lamella centres; and if $N_m \approx N_s$ the particle distribution over the domain is even.

An original method for the control of the structure of the PS–PMMA/Au nanocomposite film has been proposed;[216] the authors functionalized the surface of Au nanoparticles with thiol-terminated styrene–ethylene glycol block copolymer (PS–PEG). The copolymer blocks were coupled according to the Diels–Alder reaction. In experiments, the film of PS–PMMA with different molecular masses was used. TEM analysis of the cross-sections of the composite films formed from a mixed solution containing PS–PMMA and functionalized gold nanoparticles showed that immediately after the preparation of the PS–PMMA/Au nanocomposite, two types of nanoparticle distribution across the section are observed. In the case of PS(38)–PMMA(37) in which the size of lammelar domains is comparable with the particle diameter, the particles are evenly distributed in the copolymer matrix. In the case of copolymers with high molecular mass [PS(90)–PMMA(90) and PS(170)–PMMA(168)], the particles are located in PMMA domains due to the predominant interaction of PEG with PMMA. Irrespective of the molecular mass of the matrix copolymer, the annealing of the composite films for 24 h at 120 °C resulted in elimination of the PEG block and migration of gold nanoparticles coated with a PS layer from the PMMA domains to the PS domains.

Some publications are devoted to the relationship between the size of block copolymer domains (l), the nanoparticle diameter (d) and the structure of the nanocomposite film [203, 204] (see also the studies [217, 218, 220]). For solving this problem, Thompson *et al.*[204] used a combination of self-consistent field and density functional theory techniques. Analysis of the density profiles showed that large particles (for which $d/l > 0.3$) tend to be incorporated in the centre of the corresponding domain in order to reduce the loss of the conformational entropy of the chains contacting with it and, hence, the free energy of the system. Smaller particles (for which $d/l < 0.2$) are adsorbed at the domain interface, because in this case, the gain in the translational entropy of nanoparticles exceeds the loss in the conformational entropy of macromolecules.

The results of experimental work [217] are in rather good agreement with the above theoretical data. In the system consisting of the symmetric block copolymer of styrene and ethylene-propylene (PS–PEP), silica particles of diameter 21.5 nm ($d/l = 0.26$) and gold nanoparticles of diameter 3.5 nm ($d/l = 0.06$), large particles were concentrated at the centres of PEP lamellas and small particles were concentrated at domain interfaces.

In conclusion of this Section, we would like to note the study by Deshmukh,[221] who succeeded in inserting PEG-modified gold nanorods into the PS–PMMA matrix. It was shown that nanorods are concentrated in the lammelar PMMA domains. By controlling the ratio of the domain size to the nanorod diameter, one can achieve a desired orientation of the nanorods within the domain (when $d \approx l$, they are parallel to the lamellar plane). The sample annealing in the solvent vapour gives rise to a gradient of the nanorod concentration across the composite film (a similar effect was observed in another publication [210]). The c_{np} value is minimum at the air interface and maximum near the substrate. It was assumed [221] that this gradient is caused by faster evaporation of the solvent from the surface layer of the film and by entropy 'pushing out' of nanorods to the substrate.

4. Deposition of nanoparticles from a colloidal solution on the surface of structured films of diblock copolymers

The deposition of nanoparticles from a colloidal solution is a promising method for the formation of two-dimensional assemblies of nanoparticles with a desired structure. An obligatory condition for implementing this method is the presence of some specific interactions (affinity) between the nanoparticles and one of the copolymer blocks. Thus when gold nanoparticles modified by dodecanethiol are deposited on the surface of structured (phase separated) PS–PMMA film from a toluene dispersion,† they are accumulated predominantly in the PS domains.[224] This gives two-dimensional assemblies whose geometry reflects the structure of the initial copolymer film. (Note that composite films based on PS–P4VP containing gold and cadmium selenide nanoparticles were prepared in a similar way.[225])

According to a publication,[226] in the use of gold nanoparticles modified by terpyridinium dodecanethiol derivatives, it is possible to perform their quasi-two-dimensional cross-linking in the formed assemblies by treating the sample with a solution of $[Fe(H_2O)_6](BF_4)_2$. This cross-linking is due to complex formation between the terpyridine groups of neighbouring particles and the iron ion. Owing to the cross-linking, the nanoparticle assemblies can retain their structure even after annealing of the sample in the vapour of a solvent that is 'good' for both copolymer blocks.

An original method consisting of the deposition of a drop of a colloidal solution on a rotating substrate coated by the PS–PMMA film with vertically oriented phase separated structure elements (lamellas or cylinders) was used [227] to prepare ordered two-dimensional structures of spherical CdSe/ZnS or Fe_2O_3 particles, ZnO nanorods, and assemblies of a mixed composition (see also Ref. 228). The flow chart of this experiment is presented in Fig. 16. Prior to the deposition of nanoparticles, the copolymer film was kept in the vapour of a solvent selective toward one of the blocks. As a consequence, the lammelar film acquired a typical nanosized-grooved pattern, and its surface was coated by a thin polymer layer of the corresponding block. In both cases, during deposition in a centrifugal field, the nanoparticles were accumulated exactly in these grooves. Electron beam etching of this sample induces a faster destruction of PMMA backbones (as compared with PS backbones), which may result in reversal of its structure and opens up the way for the design of complex systems by subsequent deposition of a colloidal solution containing particles of a different nature.

In addition, particles can be deposited on nanoporous film templates obtained by etching-out of one of copolymer blocks (see Section II.1). This method has found the widest use. As a rule, this is done using PS–PMMA templates.[228–233] Misner *et al.*[229] were among the first to use this method. Upon immersion of the nanoporous

† Recall that this solvent is selective for the PS block.

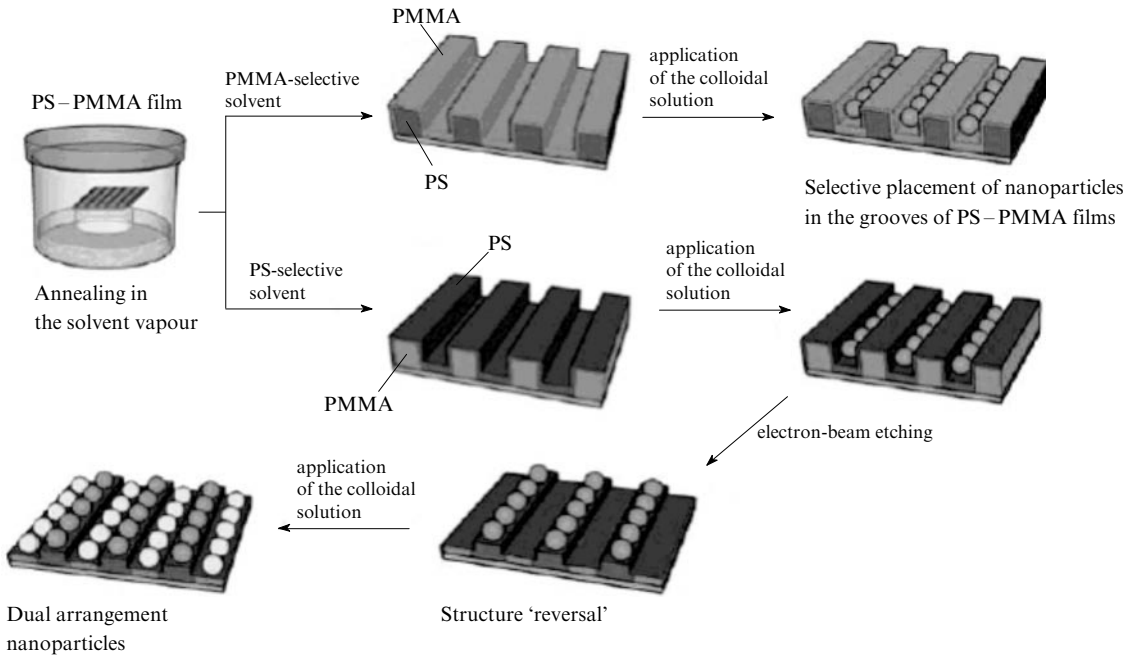


Figure 16. Flow chart of the formation of nanoparticle assemblies in film templates based on PS – PMMA.[227]

PS – PMMA template into CdSe organosol, nanoparticles were incorporated in the pores. It was noted [181, 229] that this process would proceed efficiently if two conditions are met: the particle diameter is smaller than the pore diameter and the affinity of the particles to the template material (in this case, to the PS) is low.

In more recent studies using electrphoretic deposition [230] and flotation [231] methods, two-dimensional assemblies of CdSe nanoparticles were designed on nanoporous PS – PMMA templates. The results of Zhang *et al.*[230] indicate that the coverage of nanopores by CdSe particles can be varied by changing the applied stress, the process time and the concentration of nanoparticle dispersion in aqueous methanol.

According to the approach used by Zhang *et al.*,[231] the nanoporous PS – PMMA template was placed on the surface of a hydrosol containing CdSe nanorods modified by PEG or mercaptoundecanoic acid. The former type of particles was selectively accumulated in the pores or channels formed upon the removal of PMMA blocks. In the researchers' opinion, this is caused by higher 'surface activity' of such particles (obviously, it is more appropriate to speak about the surface activity of PEG coating the nanoparticles). We believe that a certain role can be played by the presence of specific interactions between PEG and functional groups present on the external surface of the pores. Meanwhile, the nanorods of the second type (modified by mercaptoundecanoic acid) show no signs of selectivity.

Relatively recently, aminosilane or oligonucleotide modification of the internal surface (and/or 'the bottom') of the pores of the structured template based on the PS – PMMA block copolymer was reported.[232] In the latter case, the process is carried out in several steps by grafting oligonucleotide molecules on the pre-formed aminosilane. Upon deposition of oligonucleotide-modified gold nanoparticles on this template, they are selectively incorporated into the pores either through electrostatic interaction with the substrate or by the mechanism of hybridization of oligonucleotides.

In conclusion, note a study [234] devoted to the design of ordered two-dimensional assemblies of palladium nanoparticles using template films based on the PS – P4VP block copolymer. The nanoporous template was prepared by introducing a low-molecular-mass additive [2-(4-hydroxyphenylazo)benzoic acid] into a copolymer solution; this additive is able to be solubilized in P4VP domains through hydrogen bonding with the pyridine nitrogen atom. The film formed from this solution was kept in chloroform or 1,4-dioxane vapour, which resulted in the lateral or vertical orientation of cylindrical P4VP domains in the PS matrix. After that, the sample was washed in ethanol to remove the low-molecular-mass additive and immersed into a hydrosol containing palladium nanoparticles. The particles were selectively accumulated in the film pores and grooves, respectively. According to authors, this was due to specific interaction between the pyridine groups of P4VP and nanoparticles and to capillary forces. Oxygen plasma treatment or annealing at 450 °C of this system destroyed the block-copolymer template to give an ordered nanoparticle assembly.

To conclude this Section, note the remarkable diversity of the developed methods for the preparation of heterogeneous polymer – metal nanomaterials using thin non-micellar films of block copolymers. All of the proposed approaches are based on the ability of block copolymers to undergo microphase separation and to form periodic structures of different morphology. Using diblock copolymers, it is possible to vary not only the structure of thin films but also the method of nanoparticle introduction of the polymer matrix: it is possible to synthesize nanoparticles directly in the film bulk, introduce pre-synthesized nanoparticles into the film or adsorb the nanoparticles on the film surface. The extensive experimental and theoretical knowledge accumu-

lated to date enables selective localization of nanoparticles in the films of various block copolymers. All this allows one to obtained ordered thin-film polymer – metal composites with a set of properties controlled at the nanolevel.

IV. Conclusion

The problem of preparing highly ordered two-dimensional assemblies of nanoparticles using block copolymer templates is quite topical. As shown by the analysis of published data carried out in this review, the synthesis of nanoparticles in the micellar films of amphiphilic diblock copolymers is one of the most promising ways of solving this problem. This is largely related to the possibility of controlling the structure and composition of the obtained assemblies by changing the type of the precursor, parameters of the block copolymer macromolecules, preparation conditions of the template film and other factors dicussed above. Many of the arising problems may now be considered solved. As a consequence, more and more applied publications appear devoted to the use of ordered assemblies of nanoparticles obtained by this approach (including those with rather complex hierarchy) for the design of working parts of various devices. The number of such publications will undoubtedly increase; however, many fundamental problems remain unsolved, and further studies are required. First of all, this concerns more in-depth understanding of the quantitative relationships between parameters of diblock copolymer micelles in solution (unloaded and loaded with the precursor), their monolayer films and the finally produced two-dimensional assemblies of nanoparticles of different nature.

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