ADVANCED MATERIALS

Amphiphilic Block Copolymers in Structure-Controlled Nanomaterial Hybrids**

By Stephan Förster* and Markus Antonietti

1. Introduction

Amphiphilic block copolymers (ABCs) represent a new class of functional polymers that are unique building blocks serving a number of applications mainly related to the energetic and structural control of materials interfaces. The chemical structure of ABCs can be programmed such that interfaces between materials with very different chemical nature, polarity, and cohesion energy can be controlled to a much broader extent than currently possible with low molecular weight surfactants. This is the physical basis for the construction of thermodynamically stable materials hybrids with nanoscale structure and order that consist of a polymer on one side and metal or ceramic nanoparticles or nanophases on the other. These hybrids are particularly interesting since they inherit some of the properties of both the polymer and the inorganic materials, such as mechanical performance and magnetic and optical characteristics.

1.1. Amphiphilic Block Copolymers

The interest in the synthesis and characterization of amphiphilic block and graft copolymers has increased enormously in the last years. This is owing to their unique molecular structure, which consists of at least two parts with different chemical natures, constituting an *amphiphilic* (amphi: of both kinds; philic: having an affinity for) character. In fact parallels can be drawn between typical *surfactants* and amphiphilic copolymers having both hydrophilic and hydrophobic blocks. Such amphiphilic copolymers find numerous applications as emulsifiers, dispersants, foamers, thickeners, rinse aids, and compatibilizers.

For ABCs, the notation "amphiphilicity" has a much broader meaning. It includes problems of colloidal solubility in a variety of solvents (as expressed by hydrophilicity/hydrophobicity), questions of interface activity and stabilization between media with different cohesion energies (appropriate adjustment of van der Waals interactions), and the stabilization of dispersed particles (which can also be mediated by specific local chemical interactions). This "generalization of amphiphilicity", i.e., stabilization not only of the oil/water interface, but of any interface between different materials with different cohesion energies, is enabled by the wide variability of the structure of the polymer through choice of the repeat unit, possible copolymerization, and/or the length and structure of both parts. In addition, various copolymer architectures are possible: random, block, graft, star, multiblock, etc. As a consequence, these polymers can substitute low molecular weight surfactant molecules or extend surfactant applications in many heterophase stabilization problems, such as in emulsion polymerization, stabilization of pigments, or the formulation of cosmetics and drugs.

Apart from the wide ranging adaptability of both parts of the polymer, some additional advantages of polymeric amphiphiles are obvious: as high molecular weight stabilizers, additional mechanisms of colloidal stabilization can be invoked, i.e., steric and electrosteric stabilization contributions are added to the standard stabilization by charge repulsion (electrostatic). In addition, the critical micelle concentration (cmc) of polymeric surfactants can be controlled so that it is extremely low, so that the dispersion efficiency is kept, even at high dilution. Because of the low mobility of polymetic amphiphiles, their release into the environment is slowed down. For some technological applications, it is interesting to note that the kinetic stability of the aggregated structures is also sensitive to the chemistry and block length: compared to the millisecond exchange of low molecular weight aggregates, the lifetime of block-copolymer micelles can easily be adjusted to be in the second, minute, or hour region.

It is worth mentioning that to solve heterophase stabilization problems biological systems employ practically exclusively polymer-like amphiphiles (proteins, polysaccharides), and the principle of low molecular weight surfactants as emulsifiers is not found in nature. This is a clear hint to all materials scientists working in the area of interfaces: it is the macromolecular architecture of the amphiphilic copolymers and the different length scales, timescales, and levels of interaction that it entails which makes the use of these compounds very attractive.

Inherent in their various applications is the unique ability of the amphiphilic polymers to self-organize at interfaces

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and in solution, and thus modify interfacial properties and enhance compatibility or partition. For the layout of ABCs, we have to distinguish between all applications based on micellar aggregates (solubilization, use as nanoreactors, templating of mesophases), where very stable assemblies are required, and all other applications that invoke rearrangement of the aggregates (surface stabilization, compatibilization), where weak self-assembly is required. This structural optimization of ABCs with respect to targeted use is described below.

1.2. Metal and Semiconductor Nanoparticles

For a better understanding of the importance of hybrid systems constituting assemblies of ABCs and metal/semiconductor nanoparticles, some introductory words on the world of nanoparticles is also given. The production of particles in the nanometer range is one of the most important challenges of modern materials science for a variety of reasons:

- Technologies have been (and continue to be) developed that use components that are as small as possible, and size reduction of the constituent components plays an important role in the development of these "nanotechnologies".
- Owing to the fact that in nanoparticles the surface/volume ratio can reach very high values, new applications associated with the inner surface have appeared, for example, the development of new catalysts.
- Optical, magnetic, electric, adsorptive, catalytic, and other characteristics of a given material can strongly vary with the size and shape of the particles, even though they may have the same composition or molecular structure. In many cases, these properties change in an abrupt manner below a certain particle size, for example, the electrical conductivity or the type of magnetism. Ferromagnetic specimens are build up from many magnetic domains, and there is a critical size for each material below which the particles are single domain. Small, single-domain particles exhibit an exotic magnetic behavior that allows them to reach a limiting magnetism, i.e., the disappearance of the coercivity and remanence at a very high level of magnetization (superparamagnetism).
- Ultrafine particle properties are normally very different to those of the bulk materials and, at the same time, also different to those of isolated atoms. As improved syntheses lead to highly characterized samples with narrow size distributions and regular shapes, the behavior of single nanocrystals is being examined with increasing rigor and detail. A decade ago quantum-size effects were first recognized in relatively crude 2–4 nm colloidal II–VI semiconductor particles.[1] Weller recently reviewed a number of experiments dealing with these quantum-size effects, where optical transitions and spectral characteristics are linked to the particle size of metal and semiconductor colloids.[2] Such new properties can be continuously tuned-in and allow the exploration of mesoscopic effects ranging from the limits of quantum mechanics to classical phenomena.

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A special task is still the production of particles that are uniform in size and shape, both for academic and applicational reasons. The history of the so-called monodisperse systems is more than a century old, possibly starting with Michael Faraday's gold sols, but systematic studies on the methods to prepare and characterize such dispersions were initiated only about two decades ago. In general, these new synthetic methods can be divided into physical (molecular beam epitaxy, sputter deposition, electron beam lithography, etc.) and chemical methods. Chemical methods include a large variety of different chemical techniques with the common property of using reactions in solutions to produce particles of different materials. In order to control the size and shape of the particles, the synthesis is based on the appropriate control of the parameters that influence nucleation and growth. The use of ligands (stabilizing agents) such as surfactants and polymers is very common in the specific control of growth and in the prevention of agglomeration of the particles once they have been synthesized. These classical approaches to nanoparticle dispersions were recently reviewed in a number of recommendable contributions and include the discussion of new applications of nanostructured materials constructed from these nanoparticles.[3–7]

The disadvantages of the traditional routes to nanoparticles are obvious: the large interface area costs a lot of energy and requires large amounts of stabilizer or embedded surface units. The simple nucleation-and-growth route demands very low in-situ concentrations of the formed colloids, i.e., the mass output is rather low. Concentrating the products or harsh reaction conditions usually leads to the failure of stabilization and the formation of larger aggregates. For those reasons, some modern techniques developed to control the uniformity in size and shape make use of synthesis in mesoscopically confined geometries, such as in vesicles,[8] reverse micelles,[9–12] sol-gel processing,[13] zeolites,[14] Langmuir–Blodgett (LB) films,[15–17] microporous glass,[18] or organic or inorganic gels. Nanoparticle formation in block-copolymer aggregates can be considered to be a further advancement of these techniques. From a technological point of view, wide applications for many types of materials are found, including information storage, magnetic fluids, medical diagnostics, ceramics, and pigments in paints and cosmetics.

In this review, we start by reporting on the synthesis of ABCs via a variety of synthetic routes and compare the advantages of the different methods. Afterwards, the ability to form superstructures such as micelles, lyotropic phases, and mesophases in the solid state is reported. After some remarks about the underlying rules of solubilization and adhesion of ABCs, different ways of forming nanoparticles in ordered ABC assemblies from solubilized precursor states are outlined. We focus on the size and structure control of the particles and report the existing experiments dealing with the special catalytic properties, magnetism, and optical properties of such hybrids. Addressing the next step of a hierarchical structure set-up, the formation of ordered arrays of block copolymer stabilized nanoparticles and other, more complex, superstructures, is a further interesting feature of these materials just beginning to be exploited, the perspectives of which will be discussed at the end.

2. Synthesis of Amphiphilic or Functional Block and Graft Copolymers

The last decade has seen considerable progress in the development of synthetic strategies to prepare block copolymers of various architectures, solubility, and functionality. Architectures comprise diblock, triblock, and multiblock copolymers arranged linearly or as grafts, star, or H-shaped blocks. The solubilities vary from solvents with high cohesive-energy densities such as water to media with very low cohesion energies such as silicon oil or fluorinated solvents. Also, control of functionality has become an important issue, motivated by the necessity to stabilize metallic, semiconductor, ceramic, or biological interfaces.

Many of the classical synthetic routes to block copolymers, for example, living anionic polymerization, have long been known and are summarized in an excellent review by Riess et al.[19] In recent years, new methods such as living cationic and living radical polymerization have become available, allowing the preparation of new classes of amphiphilic or functional block copolymers. Living polymerization techniques have the advantage of yielding narrow molecular weight distributions with predetermined degrees of polymerization N that depend only on the molar ratio of monomer $[m]$ to initiator $[i]$ concentration, $N = [m]/[i]$.

One of the important goals in block-copolymer synthesis has always been the simplification of reaction conditions so that efficient production on larger scales becomes possible. Indeed, besides the well-known Pluronic (BASF Wyandotte) and Kraton (Shell) block copolymers, which are already used as emulsifiers and thermoplastic elastomers, new amphiphilic block copolymers based on polystyrene (PS), poly(ethylene oxide) (PEO), or poly(methylmethacrylate) (PMMA) have also become commercially available (e.g., the SE and ME series from Goldschmidt).

2.1. Living Polymerization

In the following we will mainly review techniques that involve sequential block growth[20] by living polymerization. These comprise living anionic,[21] group-transfer,[22] ring-opening metathesis,[23] cationic,[24] and free-radical polymerization.[25] Among living polymerization techniques, anionic polymerization is the oldest one used for a number of vinyl and cyclic monomers. Group-transfer polymerization is especially suited to acrylates and methacrylates. Living ring-opening metathesis polymerization, first described

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by Grubbs and Tumas,[26] can be used with norbornene derivatives, initiated by special group VI-B transition-metal complexes. Living cationic polymerization is now well-established for vinyl ethers and isobutylenes. Conditions for living radical polymerization have recently been optimized to prepare well-defined block copolymers. Since the radical intermediates are much less sensitive to impurities compared to anions or cations, this technique may become widely used to synthesize amphiphilic block copolymers. As living polymerization occurs only for a limited number of monomers, strategies for using monomers with protected functional groups and polymer-analogue reactions have been exploited to provide a larger variety of block copolymers.

2.1.1. Anionic Polymerization

Among the block copolymers that have been prepared by anionic polymerization are the "classics" PS, polybutadiene (PB), polyisoprene (PI), PMMA, poly(methylacrylate) (PMA), PEO, poly(propylene oxide) (PPO), and poly(dimethylsiloxane) (PDMS) block copolymers. Some of the block copolymers have become commercially available. PS-PB-PS triblock copolymers (Kraton) are used as thermoplastic elastomers, and PEO-PPO-PEO (Pluronics) as surfactants and steric stabilizers. PEO has an unusually wide range of solubility from water to toluene. This is due to specific interactions of the polyether leading for instance to the formation of hydrogen bonds to water molecules. Thus, it can serve as the hydrophilic block, which in combination with some of the other hydrophobic blocks forms amphiphilic block copolymers, e.g. PS-PEO and PS-P2VP-PEO (P2VP = poly(2-vinylpyridine)) and PEP-PEO (PEP = poly(ethylenepropylene)).[27]

2.1.2. Group-Transfer Polymerization

Group-transfer polymerization[28] (GTP) has become a valuable method for the preparation of methacrylate and acrylate polymers. An interesting polymer prepared by GTP is poly(2-(dimethylamino)ethylmethacrylate), a polymer that is directly soluble in water. In combination with hydrophobic methacrylate polymers Billingham and coworkers[29,30] synthesized poly((dimethylamino)ethylmethacrylate-*b*-methacrylate)[31] and poly(2-(dimethylamino) ethylmethacrylate-*b*-*n*-butylmethacrylate)[32] or other methacrylates.[33] Micellization in aqueous media as well as the use as stabilizers for the dispersion polymerization of styrene in alcoholic media[34] has been investigated. GTP is not only useful for preparing block copolymers that stabilize hydrophilic/hydrophobic interfaces, but also biological interfaces. Okano et al.[35] created a highly blood-compatible polymer surface with a poly(styrene-*b*-2-(hydroxyethyl)methacrylate) (PS-PHEMA) block copolymer. If such blood compatibility can be introduced into a polymer with high gas permeability, a new high-performance artificial lung could be constructed. The paper by Ito et al.[36] describes the synthesis of poly(4-(bis(trimethylsilyl)methyl) styrene-*b*-HEMA) (PBMS-PHEMA) via an anionic polymerization technique. PBMS shows high oxygen permeability owing to its high mobility and low cohesion-energy density.

2.1.3. Ring-Opening Metathesis Polymerization

The group of Cohen and coworkers in particular used living ring-opening metathesis polymerization (ROMP) techniques to synthesize block copolymers containing functional groups.[37] Monomers such as norbornene and methyltetracyclodecene (MTD) together with tungsten initiators are commonly used. Functional groups include amino and cyclopentadiene, which form stable coordination complexes with a variety of metals. It is also possible to obtain −COOH groups after hydrolysis of block copolymers containing trimethylsilyl groups.

2.1.4. Cationic Polymerization[38]

Two classes of monomer have been shown to polymerize cationically via a living polymerization mechanism: isobutylene[39,40] and vinyl ethers.[41] The latter has been used to synthesize a number of new amphiphilic block copolymers[42–44] but only a minority of these has been characterized in detail in terms of their aqueous solution properties.[45] Such polymers included poly(isobutylene-*b*-methyl vinyl ether),[46] poly(styrene-*b*-hydroxyethyl vinyl ether),[47] poly(styrene-*b*-ionic acetylene),[48] poly(methyl tri(ethylene glycol) vinyl ether-*b*-isobutyl vinyl ether),[49] poly(α-methylstyrene-*b*-2-hydroxyethyl vinyl ether),[50] poly(2-(1-pyrrolidonyl)ethyl vinyl ether-*b*-isobutyl vinyl ether).[51] Armes and coworkers[49,52] investigated the synthesis by living cationic polymerization of amphiphilic water-soluble diblock copolymers of methyl tri(ethylene glycol) vinyl ether and isobutyl vinyl ether and their aqueous solution behavior, including a systematic variation of block lengths. It is also possible to prepare amphiphilic vinyl ether block copolymers with glycosidic moieties.[53]

2.1.5. Living Radical Polymerization

Living radical polymerization is currently a very rapidly developing field in polymer chemistry.[54] It has been successfully used to prepare block and graft copolymers of styrenes, (meth)acrylates, (meth)acrylonitrile, and dienes at temperatures ranging from 80 to 130 °C in the presence of catalytic amounts of transition-metal compounds (Cu, Fe, Ni, Pd). Molecular weights are controlled in the range $200 < M_n < 200\,000$ g/mol with polydispersities of 1.01

$< M_w/M_n < 1.4$. Synthesis of block copolymers can be accomplished either by addition of the second monomer after the first one is already consumed, or by isolating the halogen-terminated polymer and dissolving it in the second monomer in the presence of a transition-metal catalyst.

Although the number of monomers that can be polymerized by living polymerization techniques is still growing, alternative routes have been investigated to increase the variety of available solubilities and functionalities. Among these are active-center transformations and polymer-analogue reactions.

2.2. Active-Center Transformation

Owing to specific limitations of anionic, cationic, or free-radical polymerization, an alternative approach to block-copolymer synthesis is to devise processes whereby the polymerization mechanism can be changed at will to suit the monomers being polymerized sequentially. All transformations involving anions, cations, and radicals are possible. For example, polystyrene and polyisoprene have been deactivated with a benzoyl peroxide, leading to a polymeric epoxide. In an analogous manner, peroxidized chains have been obtained by addition of a "living" polymer to a tetrahydrofuran (THF) solution saturated in oxygen, or by reaction with 2,2′-azobisisobutyronitrile (AIBN). Starting with these polymeric peroxides or azo compounds, either by thermal or redox decomposition in the presence of a second monomer, diblock copolymers of the type PI-P(S-MA) or PI-P(SAN) (S-MA = styrene-*alt*-maleic anhydride, SAN = styrene-*co*-acrylonitile) have been obtained. This route in reverse order, e.g., free-radical to anionic ring-opening polymerization, has recently been developed on an industrial scale by T. Goldschmidt AG[55] for the preparation of PS-PEO and PMMA-PEO diblock copolymers. This reaction sequence involves the free-radical polymerization of styrene in the presence of mercaptoethanol as chain-transfer agent; the hydroxy functionalized PS is then the starting point for the ring-opening polymerization of ethylene oxide.

The preparation of graft copolymers via polymerization of macromonomers is a classical example of active-center transformations. The synthesis of amphiphilic graft copolymers has recently received much attention, because it is usually possible to scale the synthesis up more easily compared to linear block copolymers. An important class of amphiphilic graft copolymer contains a hydrophobic backbone and hydrophilic poly(ethylene oxide) side chains. Qui et al.[56,57] reported free-radical copolymerization of stearyl-PEO with styrene as the backbone. Ramasami et al.[58] synthesized a similar graft copolymer with PEO side chains and found them to be water soluble and to form micelles. One application of PS-PEO graft copolymers is as supports for solid-phase peptide synthesis, and an extensive review of this topic has recently appeared.[59] Recent work on graft copolymers includes experimental work from Frere and Gramain,[60] where methoxy poly(ethylene oxide) was grafted onto a poly(acrylic acid) backbone. A significant amount of work on PS-PEO based water-soluble polymers has come from the research groups of Berlinova[61–63] and Wesslen.[64–68] Both of these groups have used a variety of synthetic methods, varying the PEO length and grafting density, to control certain properties. The former group specifically measured oil and water emulsion properties. Such PEO graft copolymers are also intended for applications related to the generation of biocompatible surfaces.

Amphiphilic graft copolymers with PEO side chains have become the focus of extensive research because of their ability to undergo microphase separation and micellization. The synthetic routes to amphiphilic graft copolymers of definite side-chain length are the macromonomer and the grafting "onto" methods.[69,70] The disadvantage of the macromonomer method stems from the small macromonomer reactivity ratios. A new synthetic approach to the synthesis of amphiphilic graft copolymers is the "activated ester method".[71] Amphiphilic graft copolymers of definite composition can be obtained by grafting amino-functionalized PEO monoethers onto phthalimidoacrylate homopolymer or its copolymer with styrene.[72] Similarly, amino-functionalized PEO monoethers have been grafted onto poly(styrene-*alt*-maleic anhydride) to obtain amphiphilic graft copolymers.[73] Dialysis from dioxane to water produced micelles that were characterized by light scattering and electron microscopy (EM).

An unconventional form of amphiphilic block copolymers has been synthesized by Meijer and coworkers.[74] They synthesized amphiphilic polymers by coupling PS with poly(propylene imine) dendrimers. Dynamic light scattering, conductivity, and transmission electron microscopy measurements showed that in aqueous media PS-*dendr*-$(NH_2)_{32}$ forms spherical micelles, PS-*dendr*-$(NH_2)_{16}$ forms rod-like micelles, and PS-*dendr*-$(NH_2)_8$ forms vesicular structures, a sequence that can be well understood within classical surfactant concepts such as packing parameter and spontaneous curvature.

2.3. Polymer-Analogue Reactions

In all previous cases, polymerizability and copolymerizability according to a living mechanism restricts the number of monomers. In addition, high purity during the reactions and/or the use of protecting-group chemistry are required. Polymer-analogue reactions broaden the diversity of block copolymer systems.[75–77] Preferably, the reaction starts from a well-defined and readily available block copolymer, e.g., polystyrene-*block*-polybutadiene, which is accessible on an industrial scale in a variety of compositions and molecular weights with narrow molecular weight distribution. With the choice of the polymer, the polymer architecture, its absolute length, and the relative block lengths are predetermined. Subsequent chemical reactions

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only change the chemistry of the two blocks, not the molecular architecture (decoupling of structure and functionality control). An important goal is the development of mild and at the same time effective conditions to transform the precursor block into a block of desired functionality or solubility. The reaction should not lead to any degradation or crosslinking of the polymer.

A commonly used polymer-analogue reaction is the hydrolysis of poly((meth)acrylic ester)s to obtain poly ((meth)acrylic acid). Especially the *tert*-butyl esters are easily hydrolyzed with concomitant elimination of *iso*-butylene.[78] Poly(methacrylic acid) may be prepared via polymerization of the protected monomer benzyl methacrylate and subsequent catalytic hydrogenolysis of the poly(benzyl methacrylate). More recently, Forder et al.[52] and Aoshima et al.[79] independently extended this benzyl protecting group approach to include poly(vinyl ether)s, and so developed routes to near-monodisperse poly(vinyl alcohol). Hydrogenation of polydienes has become a standard technique that is used commercially in the preparation of thermoplastic elastomers (Kraton). Quantitative hydrogenation can be accomplished with tosylhydrazide,[80] by homogeneous catalysis using Wilkinson's catalyst,[81] or by heterogeneous catalysis using $Pd/CaCO_3$.[82] This catalyst can also be used to prepare poly(vinylcyclohexane)s from polystyrenes.[83] Block copolymers with a methacrylic acid block have been prepared from a trimethylsilyl methacrylate block by hydrolysis at room temperature with aqueous methanol.[84] The quaternization of poly(vinylpyridine)s with alkyl or benzyl bromides has become a standard technique for the preparation of polycationic blocks.[85] Poly(styrene sulfonate)s are the most commonly investigated polyanions. Fully sulfonated polystyrenes are conveniently prepared via an H_2SO_4/P_2O_5 complex as described by Vink.[86] Partially sulfonated polystyrenes are preferably synthesized via acyl sulfates.[87] An interesting route to convert polyisoprenes into a biocompatible Heparin analogue uses *N*-chlorosulfonyl isocyanate (CSI).[88] This reactive isocyanate adds to the double bond of the polyisoprene forming a β-lactam that can be subsequently hydrolyzed to obtain a polymer containing sulfonic and carboxylic acid groups.

In many polymer-analogue reactions the precursor blocks are transformed into a reactive intermediate, which can subsequently be reacted with a wide variety of functionalized low molecular weight components, resulting in different amphiphilic block copolymers. An example of a transformation into a reactive intermediate is the epoxidation reaction of the double bonds of the polybutadiene, where epoxidation agents that effect complete conversion with only a minimal amount of side reaction are known.[75,89,90] Following the epoxidation, a variety of oxirane ring opening reactions, such as nucleophilic (Nu = nucleophile) ring opening[91] and reaction with acid chlorides,[92] are applied to introduce different functional side groups. Another possibility of functionalization via reactive precursors is the hydroxylation via hydroboration with 9-BBN (9-borabicyclo[3,3,1]nonane), followed by oxidation with $H_2O_2/NaOH$.[93–95] The hydroxy derivative can simply be esterified with a functional acid chloride or acid anhydride, resulting in the target structure.[96,97] Interestingly, modification with acid chlorides is not restricted to hydrocarbon acid chlorides: perfluorinated derivatives can also be effectively coupled.[76,77] This gives rise to blocks with ultra-hydrophobic character. The polymer-analogue reactions are not restricted solely to one block, but can be performed on both blocks in a different, but selective, manner. This was performed during the synthesis of poly(ethylethylene)-*block*-poly(styrene sulfonate) block copolymers, a very powerful electrosteric stabilizer for emulsion and suspension polymerization.[98]

A summary of common polymer-analogue reactions, solvate blocks, and functional blocks is given in Tables 1, 2, and 3.

3. Mesophases and Micelles of Block Copolymers

The self-assembly of block copolymers leads to a variety of morphologies. In view of the utilization of these structures, control over size and topology has become an important goal. Particulate structures such as micelles of various shapes as well as ordered, continuous morphologies like lamellae, ordered cylinders, or bicontinuous structures can be prepared. This chapter outlines the basic parameters that determine micellization and phase behavior of block copolymers.

3.1. Micelles and Lyotropic Mesophases of Amphiphilic Block Copolymers

3.1.1. Micelles

In solvents that selectively dissolve only one of the blocks, AB-diblock copolymers form well-defined micelles with a core consisting of the insoluble block, A, and a shell or corona of the soluble block, B. Spherical and cylindrical micelles as well as more complex, vesicular structures have been described. Most of the block copolymers that have been investigated form micelles either with the more polar or with the more non-polar block pointing outwards, i.e., regular or inverse micelles, depending on the polarity of the solvent. The area of micellization in non-aqueous media has recently been reviewed by Tuzar and Kratochvil[99] and by Gast.[100] The area of aqueous media was reviewed by Chu[101] and Alexandridis.[102] Two reviews on ionic block copolymers were published by Selb and Gallot[103] and Eisenberg and coworkers.[104]

For all applications based on the micellar aggregates of ABCs, the aggregation number Z, i.e., the number of block copolymers in a micelle, and the related size of block copoly-

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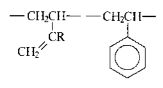
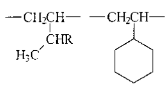
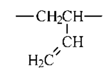
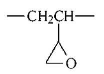
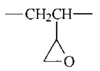
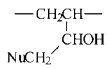
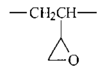
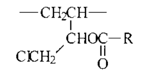
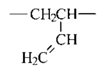
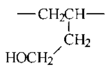
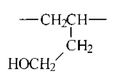
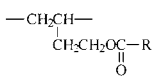
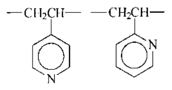
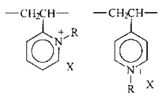
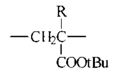
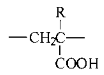
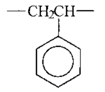
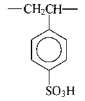
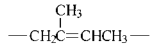
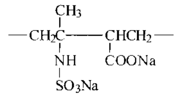
Table 1. Useful polymer-analogue reactions for the preparation of amphiphilic block copolymers.

Chemical Reaction	Precursor Block	Target Block	Comments
Hydrogenation			increase of thermal stability, selective deuteration; [80–83]
Epoxidation			transformation into reactive intermediate; [75]
Ring-Opening I			Nu = 2-mercaptobenzthiazole, 2-mercaptopyridine; [75]
Ring-Opening II			ring opening with acid chlorides; R = benzoyl chloride, phosphine; [75]
Hydroboration/ Oxidation			transformation into reactive intermediate; [76,77,93–95]
Esterification			R = cholesteryl, perfluoralkyl; [76,77]
Quaternization			R = H, Me, Et, Bz, sulfobetain, O (*N*-oxide); X = Cl, Br, I, SO_4; [103]
Hydrolysis			R = H, Me; [78]
Sulfonation			[86,87]
β-Lactam/ Hydrolysis			with CSI [a], blood-compatible Heparin analogue; [88]

mer micelles is an important parameter. Recently, it has been shown that a general relation of the form in Equation 1 holds for many diblock, triblock, and graft copolymers as well as for low molecular weight non-ionic, anionic, and cationic surfactants.[105] N_A and N_B are the degree of polymerization of the insoluble and the soluble block, respectively.

$$Z = Z_0 N_A^2 N_B^{-0.8} \qquad (1)$$

This is shown in Figure 1 where the aggregation number Z is plotted versus N_A for a variety of amphiphilic structures. The parameter Z_0 is related to the interaction parameter χ and the monomer volume and has a direct relation to the packing parameter v/al, introduced by Israelachvili for surfactant micelles, i.e., Equation 2, where υ is the molar volume of the surfactant, a the area per head group, and l the contour length of the alkyl chain.

$$Z_0 = 36\pi N_B^{6\varepsilon} \left(\frac{v}{al}\right)^3 \qquad (2)$$

Z_0 is known for many block-copolymer and surfactant systems,[105] which allows the aggregation number to be adjusted via the molecular weight of the block copolymer. This is of relevance to the size-controlled synthesis of inorganic colloids, which will be discussed below.

Also the internal structure of block-copolymer micelles, as given by the size of core and corona and the density profile in each domain, has been carefully characterized by static and dynamic light scattering[105,106] and by small-angle neutron scattering using contrast variation techniques.[107] The micellar corona has many of the characteristics of a spherical polymer brush. This allows a quantitative understanding of the corona density profile enabling one to improve or adjust the steric stabilization of polymeric or inorganic colloids in a number of applications.[107] Also the interaction potential of block-copolymer micelles has been determined experimentally,[108] which allows the rheological properties and ordering phenomena occurring at large micellar concentrations to be predicted.

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Table 2. Common solvate blocks (S-blocks) covering the range from aqueous to fluorinated media.

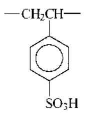
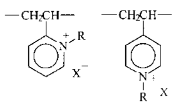
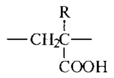
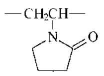
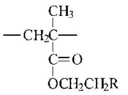
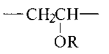
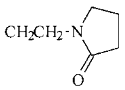
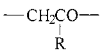
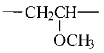
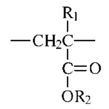
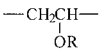
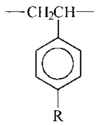
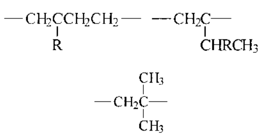
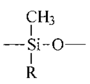
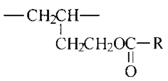
S-Block	Structure	Remarks
PSSH poly(styrene sulfonic acid)		strong polyelectrolyte, very hydrophilic (hygroscopic); also Na, K salts
PQ2VP, PQ4VP poly(*N*-alkylvinylpyridinium halide)		strong polyelectrolyte, very hydrophilic (hygroscopic); R = H, Me, Et, Bz; X = Br, I
PMAc, PAAc poly((meth)acrylic acid)	 $-CH_2\overset{R}{\underset{COOH}{C}}-$	polyelectrolyte, hydrophilic; R = H, Me; also Na salts
PVP poly(*N*-vinylpyrrolidone)		hydrophilic
PHEMA poly(hydroxyethylmethacrylate)	 $-CH_2\overset{CH_3}{\underset{\substack{C=O\\OCH_2CH_2R}}{C}}-$	hydrophilic; R = OH, NMe_2
PVE poly(vinyl ether)s	 $-CH_2\underset{OR}{CH}-$	hydrophilic; R = CH_2CH_2OH, $(CH_2CH_2O)_3CH_3$ 
PEO, PPO poly(ethylene oxide), poly(propylene oxide)	 $-CH_2\underset{R}{C}O-$	amphiphilic; R = H, Me; PEO hydrophilic up to 80°C, PPO hydrophilic up to 20°C
PVME poly(vinyl methyl ether)	 $-CH_2\underset{OCH_3}{CH}-$	amphiphilic; hydrophilic up to 70°C
PMA poly((meth)acrylate)s	 $-CH_2\overset{R_1}{\underset{\substack{C=O\\OR_2}}{C}}-$	hydrophobic; R_1 = H, Me; R_2 = Me, *n*-Bu
PVBE poly(vinyl butyl ether)	 $-CH_2\underset{OR}{CH}-$	hydrophobic; R = *i*-Bu
PS polystyrenes		hydrophobic; R = H, *t*-Bu, $CH(SiMe_3)_2$
PEP, PEE, PIB poly(ethylenepropylene), poly(ethylethylene), poly(isobutylene)	 $-CH_2\underset{R}{C}CH_2CH_2-$ $-CH_2\underset{CHRCH_3}{C}-$ $-CH_2\overset{CH_3}{\underset{CH_3}{C}}-$	hydrophobic; R = H, Me
PDMS poly(dimethylsiloxane)	 $-\overset{CH_3}{\underset{R}{Si}}-O-$	very hydrophobic; (silicon oil) R = Me, Et, Ph
PF partially fluorinated blocks	 $-CH_2\underset{CH_2CH_2O\underset{O}{C}-R}{CH}-$	very hydrophobic; (Freon, sc-CO_2) R = C_4F_9, C_8F_{17}

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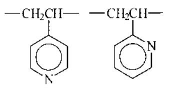
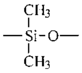
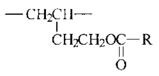
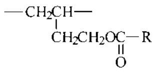
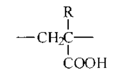
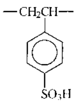
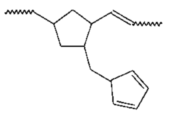
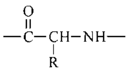
Table 3. Common functional blocks (F-blocks) for the incorporation of inorganic materials into polymer microdomains.

F-Block	Structure	Remarks
P2VP, P4VP poly(vinylpyridine)s		ligand, acid-base reactions
PDMS poly(dimethylsiloxane)	 $-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-$	gas separation, low energy surfaces, biocompatible; R = Me
PF partially fluorinated blocks	 $-\mathrm{CH_2}\underset{\mathrm{CH_2CH_2O\underset{O}{\underset{\Vert}{C}}-R}}{\mathrm{CH}}-$	gas separation, low energy surfaces, emulsion polymerization in sc-CO_2
PEO poly(ethylene oxide)	—CH_2CH_2O—	ion binding, biocompatible
PL specific ligand-containing blocks	 $-\mathrm{CH_2}\underset{\mathrm{CH_2CH_2O\underset{O}{\underset{\Vert}{C}}-R}}{\mathrm{CH}}-$	R = 2-mercaptopyridine, 2-mercaptobenzothiazole: selective binding of transition metals, stabilization of metal surfaces; R = benzoic acid: binding to ceramic surfaces and alkaline earth salts (biomineralization); R = cholesterol: coupling to lipid membranes
PMAc poly((meth)acrylic acid)	 $-\mathrm{CH_2}\underset{\mathrm{COOH}}{\overset{\mathrm{R}}{\mathrm{C}}}-$	ion binding, biomineralization
PSSH poly(styrene sulfonic acid)		ion binding, ion exchange
PCp poly(cyclopentadienylmethyl norbornene)		binding of transition metals via metallocene complexes
PA poly(amino acid) blocks	 $-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\underset{\mathrm{R}}{\mathrm{CH}}-\mathrm{NH}-$	R = $(CH_2)_4NH_2$ (lysine); R = CH_2COOH (aspartic acid); site-specific drug delivery, biomineralization

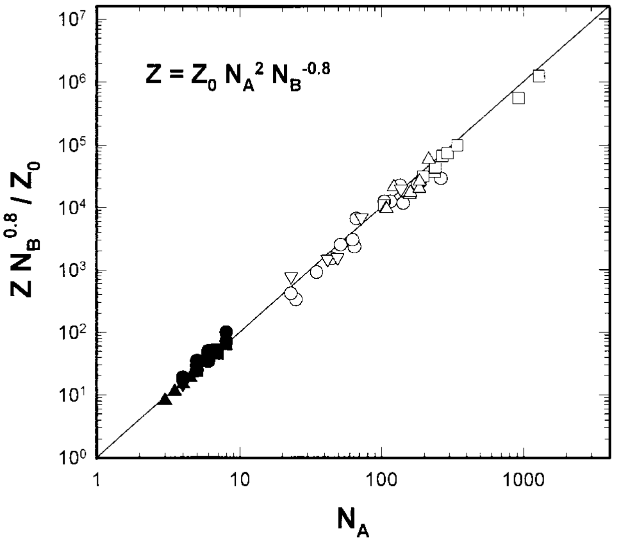


Fig. 1. Aggregation number Z as function of N_A for various block copolymer/solvent systems: poly(styrene-*b*-4-vinylpyridine)/toluene (○), poly(styrene-*b*-methacrylic acid)/dioxane–water (□), poly(methacrylic acid-*b*-styrene-*b*-methacrylic acid)/dioxane–water (△), poly(styrene-*co*-maleic anhydride-*g*-ethylene oxide)/water (▽), alkyl ethylene glycol/water (●), alkylammonium bromide/water (■), alkylsulfonate/water (▲), alkylsulfate/water (▼). The solid line corresponds to the relation $Z = Z_0 N_A^2 N_B^{-0.8}$.

The quality, polydispersity, and stability of block-copolymer micelles can be impressively visualized by electron microscopy. Figure 2 shows a typical picture characterizing the micelles of polystyrene-*block*-poly(4-vinylpyridine); due to a lack of contrast the sample was stained with Pt/C. The spherical shape of the micelles as well as their rather narrow size distribution is easily recognized.

In most cases block copolymers form spherical micelles in dilute solution. In only a few studies was the formation of non-spherical aggregates reported. For example, cylindrical or worm-like micelles were observed for PS-PB-PS triblock copolymers in ethylacetate,[109] PS-PI in *N*,*N*-dimethylformamide (DMF),[110] or PEO-PPO-PEO triblock copolymers in aqueous solutions.[111] Conditions for the formation of non-spherical micelles currently seem to be clear only for ionic block copolymers. Due to enormous interfacial tension these systems are in a thermodynamic state close to the super-strong segregation limit (SSSL).[112] Under these conditions, a sequence of shape transitions from spherical → cylindrical → lamellar is possible. Such transitions can be induced by increasing the ionic strength of the solution or by increasing the relative length of the core block. This can be rationalized in terms of the surfactant parameter *v*/*al*, which

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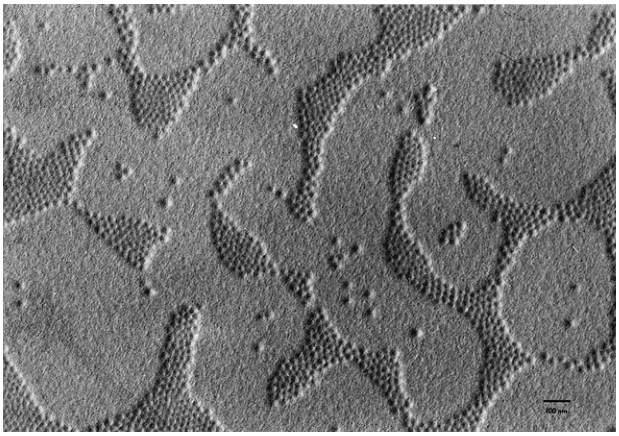

Fig. 2. Electron micrograph of micelles formed by PS-P4VP in toluene. The scale bar corresponds to 100 nm. Due to the narrow size distribution, micelles tend to form ordered domains upon evaporation of the solvent during sample preparation.

increases from 1/3 for spherical structures, to 1/2 for cylindrical structures, to 1 for lamellar or vesicular structures. The ionic strength increases this ratio by decreasing the area per headgroup, a; an increase in the block length increases v/al by decreasing the contour length l. Upon increasing the core-block length, Eisenberg and coworkers indeed found cylindrical and vesicular shapes with ionic block copolymers micelles.[113,114] The exact conditions for shape transitions are still unclear, as the system investigated by Eisenberg and coworkers involved non-equilibrium structures that had been trapped at some stage of the sample preparation procedure. A salt-induced sphere → cylinder transition under equilibrium conditions was recently reported[115] and the investigation of equilibrium micellar properties of ionic block copolymers is just beginning.

3.1.2. Lyotropic Phase Behavior

Early studies on lyotropic phase behavior of amphiphilic block copolymers were performed by Selb and Gallot.[103] They reported the formation of hexagonal morphologies formed by quaternized PS-P4VP block copolymers at high concentrations. Most of the present knowledge on lyotropic phase behavior of block copolymers was obtained from studies of Pluronics, i.e., PEO-PPO-PEO block copolymers and other weakly segregated systems. Phase behavior strongly depends on temperature, which affects the dehydration of the PEO and PPO blocks. PPO dehydrates between 20 and 50 °C, PEO at higher temperatures (ca. 80 °C). Many of the lyotropic properties have been summarized by Hoffmann and coworkers[116] and Chu.[101] In general, these systems form all the different mesophases that are observed for normal hydrocarbon surfactants. The effects of block length could be elucidated. At given PPO block length (insoluble block), a decrease in the PEO block length (soluble block) destabilizes the cubic and the hexagonal phase, so that the whole system is dominated by the lamellar phase. This behavior is completely analogous to the phase diagrams of non-ionic alkyl poly(glycol ether)s when the number of EO groups is reduced. More parallels between block copolymers and low molecular weight amphiphiles have been observed for pure block copolymer melts as shown in the next section.

3.2. Solid-State Mesophases

The bulk block copolymer's microphase separates into a number of different morphologies, depending on block length and interfacial tension. Theories and experiments have been extensively reviewed by Bates and coworkers.[117,118] In the following we will focus on the parameters that control the type and size of morphology. A variety of diblock copolymer mesophase morphologies such as lamellae (LAM), modulated (MLAM) and perforated layers (PLAM), hexagonally ordered cylinders (HEX), arrays of spherical microdomains (BCC), and ordered bicontinuous structures such as the gyroid have been documented.

For AB-diblock copolymers the basic parameters that determine the size and shape of the microdomains are the degree of polymerization $N = N_A + N_B$, the composition $f_A = N_A/N$, and the Flory–Huggins interaction parameter χ_{AB}. Typical dimensions of microdomains are 10–100 nm, depending on the molecular weight of the polymer. Even for such simple architectures as diblock copolymers the phase behavior can be quite complex. The bulk morphologies can be mapped into a phase diagram parameterized in terms of χN versus f, in close analogy to lyotropic liquid crystals, where phase diagrams are given in terms of temperature T versus volume fraction ϕ. These phase diagrams give an excellent overview of the types of morphologies that are available for the construction of the ordered materials described below. An example of such a phase diagram is shown in Figure 3 for poly(styrene-*b*-isoprene) (PS-PI), a system that has been examined in some detail.[119,120]

One notes the rich polymorphism near the order–disorder transition (ODT) in the weak segregation limit (WSL) $\chi N = 10$. In the strong segregation limit (SSL) at larger values of χN it is assumed that only the "classical" morphologies LAM, HEX, and BCC are stable. Recent experiments on strongly segregated fluorinated block copolymers indicate that some non-classical phases known from low molecular weight surfactant solutions (the M and T phases) are stable even at quite large values of χN.[121] Also, in many other aspects there are close similarities to the phase behavior of low molecular weight amphiphiles. Short PEP-PEO block copolymer melts resemble solvent-free non-ionic surfactants and also show complex phase behavior.[122] Phase diagrams are available for PS-PI,[119,120] PEP-PEE (PEE = poly(ethylethylene)),[118] PE-PEE (PE = polyethylene),[123] PS-P2VP,[124] and PS-LC[125] (LC = liquid-crystalline block). A still more complex phase behavior is observed for ABC-triblock copolymers.[126]

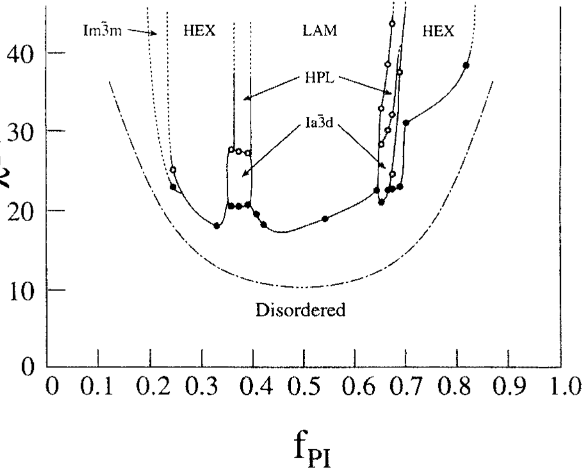

Fig. 3. χN versus f_{PI} phase diagram for poly(isoprene-*b*-styrene) (PS-PI) diblock copolymers. Open and filled circles represent order–order and order–disorder transitions, respectively. Five different ordered microstructures (LAM, HEX, $Im\bar{3}m$, HPL, $Ia\bar{3}d$) together with their inverse topologies are observed.

The morphologies present in diblock copolymers are rather well-defined, i.e., show long-range order, and their characteristic size can be controlled in a systematic fashion between 10 and 250 nm. The possible chemical modifications of such structures as a starting point for the synthesis of advanced materials are numerous, e.g., degradation of one microphase would result in ordered porous materials and crosslinking of one of the components leads to new colloidal structures. The latter aspect has recently been demonstrated by Liu et al.,[127] who crosslinked the microdomains of a cylindrical mesophase to obtain fibers of uniform diameter (30 nm) and lengths of the order of some micrometers.

An overview over the most common structures that are formed by diblock copolymers is shown in Figure 4.

4. Solubilization and Adhesion of ABCs

Solubilization has become an important issue in pharmacy and cosmetics, where micelles or microemulsions are employed as solvating moieties for hydrophobic pharmaceuticals. The enhancement in solubility arises from the fact that the micellar cores and oil droplets of oil/water microemulsions can serve as a compatible microenvironment for the water-insoluble solute molecules. Apart from the solubilization of organic molecules, inorganic substances such metal oxides have also received increased attention, e.g., for the development of UV-protecting agents. Whereas solubilization refers to binding of small molecules in small compartments, adhesion usually refers to the binding of molecules to large surfaces or interfaces. However, on mesoscopic length scales, where solvating agents such as block copolymers and the diameter and surface area of solubilizates such as nanometer-sized colloids are comparable in size, solubilization and adhesion are closely interrelated. Both can be understood and optimized through the underlying physical processes summarized below.

4.1. Solubilization of Hydrophobic Compounds

Recent progress in the understanding of amphiphilic block copolymers for the solubilization of hydrophobic compounds was driven by the great potential of aqueous block-copolymer solutions as environmentally friendly substitutes to organic media. A number of applications such as reaction media, chemical extraction aids in separation processes, and industrial cleaning agents have been discussed. Other potential applications such as tissue-specific drug de-

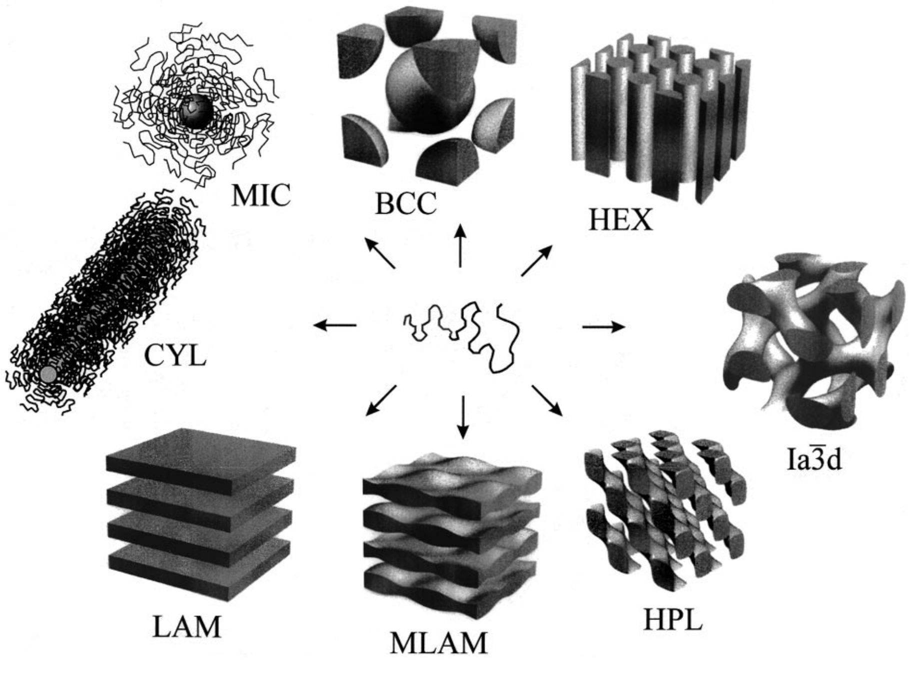

Fig. 4. Common morphologies of microphase-separated block copolymers: body centered cubic (bcc) packed spheres (BCC), hexagonally ordered cylinders (HEX), gyroid ($Ia\bar{3}d$), hexagonally perforated layers (HPL), modulated lamellae (MLAM), lamellae (LAM), cylindrical micelles (CYL), and spherical micelles (MIC).

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livery are also based on the exploitation of the solubilization process.[128]

For a quantification of such effects, one can employ the concept of solubility parameters, which was developed to describe the enthalpy of mixing of simple liquids. The Hildebrand solubility parameter δ is directly related to a number of other relevant interaction parameters such as the Flory–Huggins parameter χ, the interfacial tension γ, and the cohesive energy density ΔE and describes the attractive strength between molecules of the material. In general, the difference of the Hildebrand parameters $(\delta_1 - \delta_2)^2$ of components 1 and 2 must be small to make them miscible.

The solubilization in amphiphilic block copolymer micelles was investigated theoretically by Nagarajan and Ganesh,[129,130] Dan and Tirrell,[131] Cogan et al.,[132] Hurter et al.,[133,134] Linse,[135] and Leermakers et al.[136] Parameters that determine solubilization characteristics include the molecular volume of the solubilizate v_j, its interfacial tension against water χ_j, and the solubility parameter values of the core polymer δ_A and the solubilizate δ_j. For practical applications one is interested in the solubilization capacity η, the volume fraction of the solubilizate molecules within the core of the micelle. Theory predicts that the solubilization capacity increases if the core block is very compatible with the solubilizate and if the molecular volume of the solubilizate is small. For two solubilizates, the capacity η will be larger for the solubilizate associated with a lower interfacial tension towards water. Solubilization is found to increase the micellar core radius and decrease the cmc. The increase in core radius results not only from the incorporation of the solubilizate, but also because of the increasing number of block-copolymer molecules that are accommodated within the micelle. This increase in Z is more dramatic for solubilizates whose uptake by the micelles is large.

Experimental results are often expressed in terms of the molar solubilization ratio, MSR = $\eta/(1 - \eta)$, an important parameter in solubilization studies with low molecular weight surfactants.[137] Results for amphiphilic block copolymers seem to correlate according to Equation 3,[138] where kT is the thermal energy and b an empirical constant.

$$MSR \propto \chi_j^{-b} \propto \left(\frac{\left(\delta_A - \delta_j\right)^2 v_j}{kT} \right)^{-b} \qquad (3)$$

From an experimental point of view, one is interested in the solubilization capacity of the micelles for different hydrophobic substances and in changes to the size and shape of the micelles as a consequence of solubilization. Most experimental studies have been performed on Pluronic-type (PEO-PPO, PEO-PPO-PEO) block copolymers. Nagarajan et al. systematically investigated the solubilization of aliphatic and aromatic hydrocarbons,[138] alcohols, ethyl esters, ketones, and aldehydes (all of which are typical components present in food flavors).[139] Further investigations focused on the selectivity in the solubilization of orange oil components,[140] polycyclic aromatics,[141] benzene,[142] xylene,[143,144] and fluorescent probes.[145] The solubilizates in block-copolymer micelles need not be limited to low molecular weight hydrophobic substances: homopolymers[146,147] and membrane integral proteins[148] have been solubilized in dilute solutions of block-copolymer micelles.

All these experiments show that very large solubilization capacities and high selectivities can be achieved through the use of block-copolymer micelles when compared to micelles formed from conventional low molecular weight surfactants. The 4-fold difference between the solubilization of benzene and hexane in the low molecular weight surfactant sodium dodecylsulfate (SDS) is 17-fold in PEO-PPO block copolymers and 40-fold in the PVP-PS block copolymer (PVP = poly(*N*-vinylpyrrolidone)).[138]

4.2. Solubilization of Inorganic Compounds

Block copolymers are also able to solubilize or adhere to inorganic materials. This is of special relevance to the controlled synthesis of inorganic colloids or the controlled assembly of hybrid materials. The incorporation of inorganic materials into polymeric domains is at first sight not a trivial matter. Since most polymers are low surface energy materials, the adhesion between metals and polymers is usually poor. Only through specific interactions like dipolar interactions, hydrogen bonding, complex formation, or covalent bonding can inorganic materials be incorporated into polymers.

A survey of recent literature shows that indeed many different polymers have been used, for example, to stabilize gold colloids in aqueous media. Among these are Nafion 117,[149] poly(ethylene glycol) (PEG), poly(vinyl alcohol),[150] polyphosphate,[151] polyacrylate,[151–155] poly(ethylene imine) (PEI),[156,157] PVP,[158–160] gelatin,[161] and PMMA.[162] These polymers have to provide solubility in the desired medium (water) and at the same time bond to the metal colloids. With block copolymers each function is provided by one of the blocks and therefore the effectivity of stabilization can be improved considerably.

The solubility of organic molecules can be controlled and adjusted based on the concept of solubility parameters as discussed in the previous section. In order to solubilize inorganic molecules one has to optimize the polymer–metal bonding. In this respect, Pearson's hard–soft acid–base (HSAB) principle has proved to be quite valuable. It relates acid–base and donor–acceptor interactions to solid adhesion and surface interactions[163] and represents one of the important bridges between chemistry and physics of the solid state. In chemistry, the absolute or chemical hardness, η, was introduced by Pearson[164] to be $\eta = -\frac{1}{2}(E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}})$ (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital). On the other hand, in physics the concept of an average energy gap, E_g, as defined by Phillips,[165] $E_g = -(E_{CB} - E_{VB})$ (CB = conduction band, VB = valence band) is used. The average energy gap is generally larger than the minimum energy gap (bandgap). On the basis of this extension, one can classify the following materials according to their chemical hardness as follows: all metals are soft and mostly acidic, all semiconductors are fairly soft and most of them are bases; most insulators, including polymers, are hard. The HSAB principle states that hard acids prefer to bond to hard bases, and soft acids prefer to bond to soft bases. By incorporation of functional groups of appropriate hardness, e.g., by polymer-analogue reactions, one can optimize the binding of a polymer to metals or semiconductors. It is also clear that changes in the band structure of semiconductor colloids (quantum-size effects) also change the stability of the polymer/semiconductor interface.

The HSAB principle allows one to optimize the bonding block for the stabilization of colloids. Metal colloids are well-stabilized by soft bases such as thiols and phosphines (standard "capping agent" for the synthesis of small metal clusters). Most of the polymers mentioned above used to stabilize gold colloids, e.g., polyphosphates, are, however, hard bases, and the stabilization is mainly due to the high local concentration of bases within a polymer chain. A much better stabilization effect could be provided by block copolymers consisting of a water-soluble block and a binding block containing soft bases.

Metal salts of hard acids and hard bases such as hydroxides, sulfates, and phosphates are often water-insoluble substances. To stabilize colloids the appropriate stabilizing polymer should contain hard bases. Up to now, poly(vinylalcohol), poly(styrene sulfonic acid), and polyphosphates have been the frequently used stabilizer systems in the preparation of monodisperse metal oxide sols, see for instance the work of Matijevic.[166]

The HSAB principle also allows the design of appropriate reaction sequences for the controlled assembly of hybrid materials. As discussed in the next section, such an assembly proceeds through a number of steps that involve solubilization of inorganic precursors, chemical reactions, and nucleation/growth processes. One can start from a labile hard–soft bonded precursor salt that is easily incorporated into a polymeric domain via formation of a more stable soft–soft bond. This should not be so stable that it hinders the further transformation (redox reaction, oxide/sulfide formation) of the compound into the desired colloid. Nucleation and growth of the colloid creates a new interface, the structure and stabilization of which again depend on its energy.

4.3. Adhesion

Like molecules to a surface, block copolymers adsorb to interfaces because of the chemically distinct nature of each block. The interface may be formed between two polymers, between a polymer and solid, or between a polymer and air. Thereby most of the chemical and physical properties of the materials change, for example, adhesion, catalysis, corrosion, fracture, lubrication, diffusivity, and wear, which leads to some of the most important applications of block copolymers, namely, as adhesion promoters, compatibilizers, surface modifiers, and blood compatibilizing agents.

As discussed above, the principles of solubilization and bonding are closely related to adhesion phenomena where polymers are bound to surfaces or interfaces. The following example of the adhesion between natural rubber and brass-plated steel for the steel cord tire application is an illustration of such a concept. Because of their difference in hardness (in the HSAB sense), there is only poor adhesion between natural rubber and steel. Interestingly, brass-plated steel was found to bind much more effectively to natural rubber. Sulfur, the crosslinking (or vulcanizing) agent in the natural rubber, actually also functions as a chemical adhesive between natural rubber and brass to form the Cu_xS/ZnS interphase.[167] Alkylsulfides are soft bases, which bind strongly to the soft acid Cu. The binding of rubber to metallic cord fibers in this manner is responsible for the performance of the present generation of tires. This is a good example of the challenges one has to meet when constructing stable nanohybrid materials.

The systematic investigation of the interfacial behavior of block copolymer hybrid systems is still in its infancy. Only over the past few years has an understanding of the mechanism of interfacial toughening by block copolymers been developed.[168] In some cases, graft copolymers or even random block copolymers have been found to effectively stabilize interfaces under certain conditions.[169,170] However, in many cases the concepts developed for the solubilization of inorganic materials can be a guideline for the construction of stable polymer/inorganic nanohybrid materials.

5. Formation of Nanoparticles in ABC Systems

Generally, polymers and inorganic materials are mutually incompatible. In order to prepare stable polymer/inorganic hybrid materials, the polymer/inorganic interface has to be sufficiently stabilized. This becomes a major requirement, if nanostructured hybrid materials with very large interfacial areas have to be prepared. The use of block copolymers makes the construction of such materials straightforward.

- In order to obtain stable polymer/inorganic hybrid materials there has to be sufficient adhesion between the polymer and inorganic microphase. Adhesion can be provided by polymer-bound functional blocks (F-blocks) that bind to the inorganic material. Examples of such functional blocks are summarized in Table 3.
- The mechanical or solution properties of polymer/inorganic hybrid materials depend largely on the properties of the polymeric matrix. These properties are provided

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by the second block (S-block), which is covalently attached to the functional block. An overview of such blocks can be found in Table 2.

- Block copolymers provide a large number of microstructures that can be used in the construction of microstructured hybrid materials. On overview of these structures is given in Figure 4.
- Control over the size and shape of the metal colloids in polymeric materials can be achieved by growing the desired colloids within microdomains of suitable size and shape.

Within the last years, a number of synthetic routes have been developed for the controlled formation of nanoparticles in block-copolymers systems. These are shown schematically in Figure 5.

This basically involves five steps, i.e., preparation of the block copolymers (Pol), loading of the precursor (Ld), micellization (Mic), chemical reaction followed by a nucleation and growth process (CT, N&G), and ordering (Ord). The succession of steps is variable. Different research groups put forward and optimized different sequences, so that a variety of routes are now well-understood. The loading (Ld)–chemical reaction (CT) cycle can be carried out a number of times so that core-shell or onion-type colloidal structures are prepared.

The synthesis of block copolymers (Pol), micelle formation (Mic), and the formation of ordered block-copolymer structures (Ord) have already been discussed in the previous sections. In the following we briefly discuss the remaining steps in the construction of hybrid materials.

5.1. Loading

As a guideline to optimum precursor materials and micellar core blocks one can use the HSAB concept as discussed above. The general strategy is to start from weakly coordinated metals, e.g., $Pd(OAc)_2$ or $Pd(ClO_4)$, which are complexes of a soft acid (the transition-metal ion) and a hard base (acetates, perchlorates, etc.). The formation of a more stable complex with a softer base forming the micellar core, e.g., poly(vinylpyridine), is then the driving force for loading of the precursor. The polymer complex should, however, not be too stable since this could prevent the formation of the desired colloid in the subsequent chemical reaction (CT). Chemical reactions typically involve reduction to obtain noble-metal colloids or the preparation of sulfides or oxides to obtain semiconductor colloids.

The precursor salts can be loaded onto the monomer, onto the polymer, into micelles, or into ordered bulk structures as schematically shown in Figure 5.

5.1.1. Binding to Monomers

In certain cases it is possible to bind transition-metal ions to monomers that can subsequently be polymerized via a living mechanism to form the desired block copolymer. Cohen and coworkers coupled Pd^{2+} and Pt^{2+} to norbornene monomers containing cyclopentadienyl groups, which form stable coordination complexes with the transition-metal ions.[171] These monomers undergo ROMP, with MTD as the monomer forming the second block.

5.1.2. Binding to Block Copolymers

Since only a few transition metal coordinated monomers undergo living polymerization, it is more common to bind precursors to preformed block copolymers. It is possible to bind Zn^{2+} (as ZnO) to PS-PMAc (PMAc = poly (methacrylic acid)) block copolymers in THF, which is a

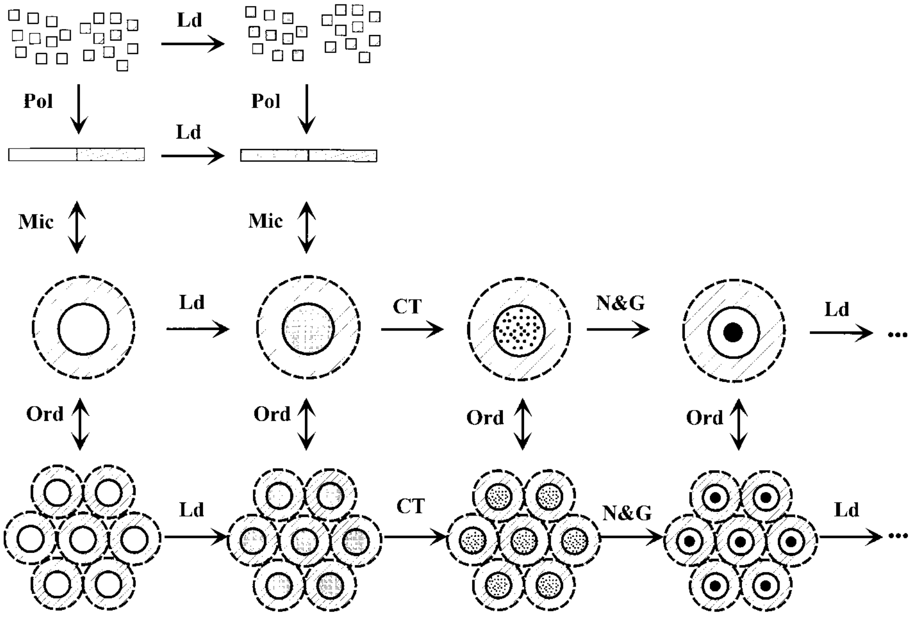

Fig. 5. Various schemes that have been used to prepare inorganic colloids in block-copolymer microdomains. The various steps include polymerization (Pol), micellization (Mic), loading of the precursor (Ld), ordering (Ord), chemical transformation (CT), and nucleation and growth (N&G). Domains may be reloaded to form binary inorganic colloids.

common solvent for both the PS and the PMAc block.[172] In most cases, the binding of the precursor will make the functional block insoluble and induce micellization. This seems to occur in a similar manner for the binding of Ca^{2+} to PMAc-PEO block copolymers in water, a preliminary step in the controlled biomineralization of $CaCO_3$.[173]

5.1.3. Loading into Micellar Cores

For a size-controlled synthesis of nanoparticles it is necessary to control the size of the microcompartment. As discussed in Section 2, it is possible to adjust the aggregation number and the size of block-copolymer micelle over a wide range. Since loading of an inorganic precursor can change aggregation numbers, it is advantageous to cross-link the micellar core and thereby fix the aggregation number. The precursor can subsequently be loaded into the micellar core, which is usually achieved by simply stirring the precursor salt in the micellar solution. Transition metals are either bound directly to the polymeric ligand in the micellar core (e.g. $Pd(AcO)_2$,[75] $Cd(ClO_4)_2$[172]) or indirectly as the counterion. For example, $HAuCl_4$ protonates the poly(vinylpyridine) in the micellar core, thereby binding $AuCl_4^-$ as the counterion.[174,175] Even if the precursor salt is soluble in the solvent, e.g., for the PS-P4VP/THF system, the equilibrium distribution of metal ions is strongly shifted to the micellar cores (>98 %[174]) because of the much better coordination to the soft base P4VP compared to the hard base THF.

The loading of precursor salts into preformed block-copolymer micelles has become the most common method for the incorporation of precursors into block-copolymer microcompartments. It combines the control of precursor loading with tolerable loading times. It is quite versatile and can be used for a large number of precursor/block copolymer/solvent systems.[75] Figure 6a shows PS-P4VP micelles that have been loaded with $HAuCl_4$. The precursor is homogeneously distributed within the micellar core.

5.1.4. Loading into Bulk Block Copolymer Microphases

Precursors have also been loaded into bulk block copolymer samples. Various metal salts (Ag^+, Au^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Pd^{2+}, Pt^{2+}) have been solubilized by immersion of pieces of the solid polymer (microtomed sections for 20–50 h, bulk films for 2 weeks) in aqueous metal-salt solutions.[176] Similarly, Cd^{2+} and Pb^{2+} have been loaded into thin block-copolymer films for the preparation of semiconductor colloids.[177,178] Metal alkyl compounds ($ZnEt_2$, $CdMe_2$) delivered from the gas phase have also been loaded into bulk block copolymers. The time required for uptake of precursors is clearly much longer compared to all-solution processes and strongly depends on the thickness of the samples.

5.2. Chemical Transformation

5.2.1. Reduction to Form Noble-Metal Colloids

Reduction of noble-metal salts requires adjustment of the reactivity of the reducing agent to the redox potential of the metal. The redox potential of a given transition metal can depend strongly on the coordinated ligand. Complexes of soft-base ligands with many transition metals (Ag^+, Pt^{2+}, Au^{3+}, Cd^{2+}, Pd^{2+}) have low redox potentials because of partial charge transfer from the polarizable ligands to the positively charged metal. It is often surprisingly difficult to reduce noble-metal salts in such polymeric ligand matrices. For example, $AuCl_4^-$ is a strong oxidizing agent with a standard potential of +1.00 V in contrast to $Au(CN)_2^-$, which has a standard potential of –0.6 V. It is thus not possible to reduce $Au(CN)_2^-$ with hydrogen even under high pressure, usually a standard method for the preparation of noble-metal colloids. Common reducing agents are $LiAlH_4$, $NaBH_4$, $LiBEt_3H$, alkylsilanes, hydrazine, and hydrogen.

5.2.2. Preparation of Semiconductor Colloids

Most colloidal semiconductors preparations involve the addition of H_2S to the metal precursors to form the corresponding metal sulfides.[177–182] The chemical reactions can be performed in micellar solutions as well as in bulk samples, leading to the formation of quantum-size particles. An interesting route to ZnF_2 quantum dots has been described by Cohen and coworkers.[179] ZnF_2 was generated from the Zn^{2+}-containing polymer by treatment with a hydrogen fluoride–pyridine (HF-Py) complex at room temperature. Treatment with H_2S at elevated temperatures led to the formation of the more stable ZnS. At room temperature the ZnF_2 could be regenerated. ZnO quantum-size particles can be prepared by addition of an organic base (tetrabutylammonium hydroxide) to Zn^{2+}-loaded block-copolymer micelles.[172]

5.3. Nucleation and Growth

The chemical reaction (CT) initially leads to the formation of primary metal atoms or semiconductor particles, $(X)_1$. These particles subsequently aggregate to form larger particles by nucleation and growth processes. For some applications (e.g., electro-optics) one is interested in obtaining one single colloid per microdomain, for others (e.g., catalysis) it is of advantage to prepare a large number of small colloids within a microdomain. The number of colloids that are formed within one microcompartment depends on the degree of supersaturation c/c_0 with primary particles, the interfacial tension γ of the particle/polymer interface, and the diffusivity D of the particles.

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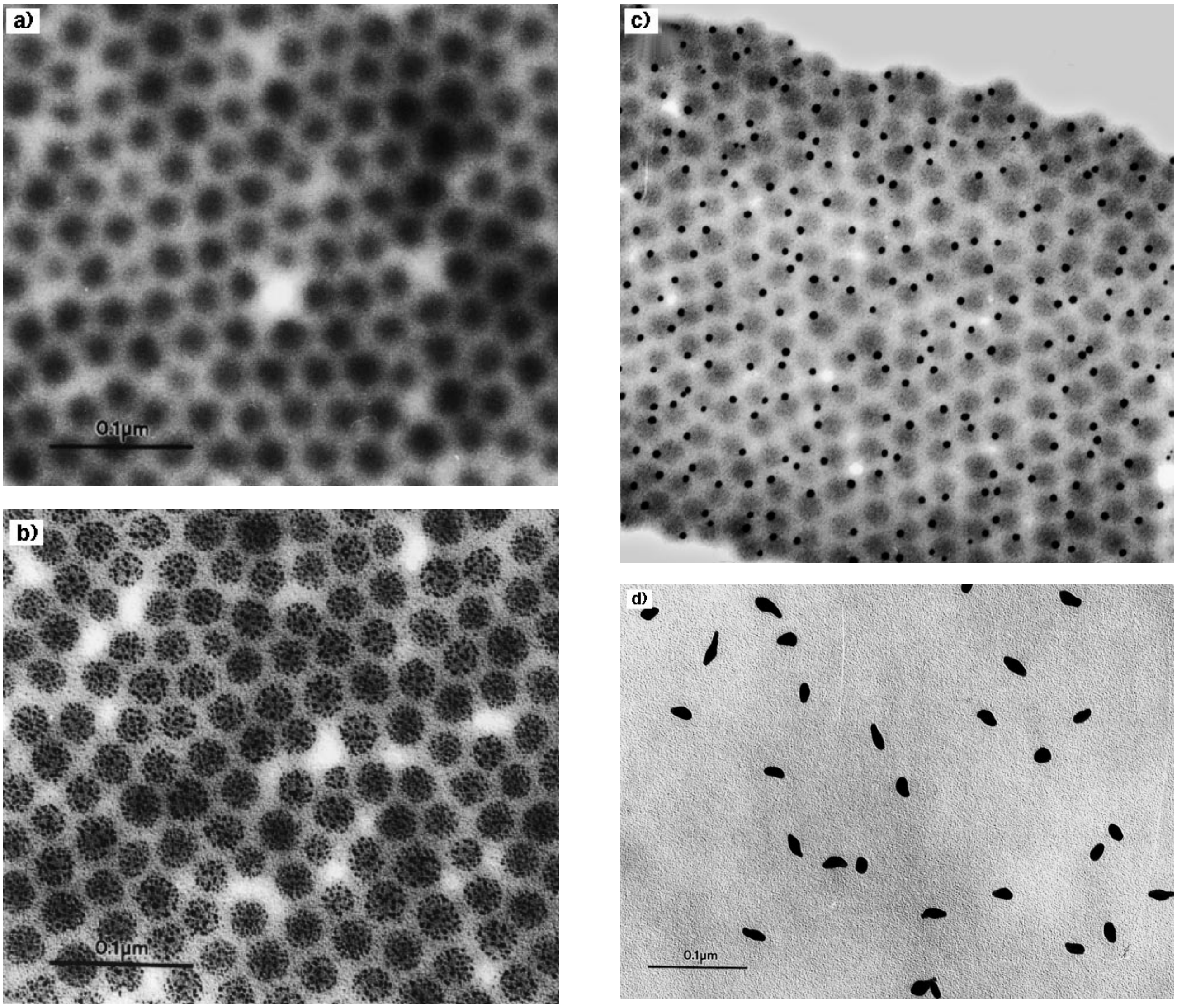

Fig. 6. Transmission electron micrographs of poly(styrene-*b*-4-vinylpyridine) block-copolymer micelles containing: a) the solubilized precursor ($HAuCl_4$), b) small Au colloids after fast reduction with $LiAlH_4$ (high supersaturation), c) one single Au colloid after slow reduction with Et_3SiH (low supersaturation), and d) anisometric ("aubergine") Au colloids after reduction with aqueous hydrazine (intermicellar aggregation). The mean diameter of the colloids in (c) is in good agreement with the calculated diameter from Equation 5. The scale bars represent 100 nm.

The crucial step in nucleation is the formation of aggregates $(X)_{N_c}$ with a critical radius R_c, which is proportional to the interfacial tension γ and c/c_0 (Eq. 4).

$$R_c \propto \frac{\gamma}{\ln(c/c_0)} \quad (4)$$

A small γ and large c/c_0 will lead to the formation of a large number of small colloids within a microdomain. These colloids can subsequently grow into larger colloids by an Ostwald-ripening process. This requires the solubility and diffusivity of the primary particles to be high enough to sustain a diffusional flow from the small to the large colloids. Both requirements need to be fulfilled; if not, and this is mostly the case, small colloids will be stable even at high temperatures.[183,184] If such an Ostwald-ripening process occurs, it eventually leads to the formation of one colloid per microdomain. The same result can alternatively be obtained under conditions of low supersaturation and high interfacial tension, which leads to large values of the critical radius R_c. Under favorable conditions, after some time (critical nucleation time) only one particle in a microdomain exceeds this value of R_c. Given a sufficient diffusional flow of primary particles, this results in the formation of one single colloid per microdomain before a second particle exceeds R_c.

Recent experimental studies by different research groups have demonstrated how to control the parameters that affect the nucleation and growth processes in polymeric microdomains. The degree of supersaturation depends on the

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rate of the chemical reaction CT. Fast chemical reactions lead to high supersaturation and vice versa. The interfacial tension γ depends on the stabilization of the polymer/inorganic interface. By using appropriate functional blocks that stabilize the polymer/inorganic interface, the value of γ can be made small. Small values of γ also leads to good solubility of the primary particles. Besides the use of functional blocks, the addition of or swelling with solvents that are good ligands for the inorganic particles will also stabilize the particle surface. The diffusivity in polymeric matrices is generally small. It can be increased by swelling with solvents or by heating above the glass transition temperature of the polymer.

5.3.1. Limit of High Supersaturation

In this limit initially a large number of small particles form within a microcompartment. An example is shown in Figure 6b, where small Au colloids were prepared in micelles of a PS-P4VP block copolymer by reduction with $LiAlH_4$. The morphology in Figure 6b has been named "raspberry" morphology. Due to the large specific surface area of up to 1000 m^2/cm^3, this morphology is of advantage for catalytic applications. The colloids are generally quite stable. Precipitation, redispersion, or heating (below the glass transition temperature, T_g) does not affect the size distribution of the nanocolloids.[178,180,183]

Cohen and coworkers noted the possibility of increasing the size of the nanocolloids by addition of solvents such as pyridine or picoline, which act as coordinating ligands to the inorganic particles.[183] A similar effect was recently observed by Wozniak et al.[185] in their attempts to synthesize CdS clusters within homopolymers of PVP. These ligands swell the polymer matrix and increase the solubility of the primary particles. The increase in solubility and diffusivity eventually leads to an Ostwald-ripening process yielding one colloid per microdomain. This was shown by Möller and coworkers who obtained one single particle per microdomain ("cherry" morphology) by heating thin films of PS-PEO block copolymers containing Au colloids[186] and by reducing $HAuCl_4$ with hydrazine, which simultaneously swells the micellar core and stabilizes the colloid surface.[187] An example, a thin monolayer of micelles containing gold colloids, is shown in Figure 10.

The "cherry" morphology is of advantage in the size-controlled preparation of nanocolloids. For a given loading ratio $f = [M]/[A]$ of metal precursor (M) and monomer A, the diameter d of the colloid can be calculated according to Equation 5, where m is the molar mass and ρ the density of the metal, and N_L is Avogradro's number.

$$d = \left(\frac{6fmZ}{\pi\rho N_L}\right)^{1/3} \qquad (5)$$

As the aggregation number Z is determined by the degree of polymerization according to Equation 1, and the degrees of polymerization N are determined by the monomer/initiator ratio, this basically represents the transformation of the control of the mechanism of living polymerization to the control of the growth of inorganic colloid.

5.3.2. Limit of Low Supersaturation

This limit can be realized with weak reducing agents such as alkylsilanes. In Figure 6c the formation of one colloid per micelle by reduction of $HAuCl_4$ in PS-P4VP micelles using Et_3SiH can be recognized. The Au colloids are located at the edge of the micellar core, where the reducing agent, which is incompatible with the core, nucleated the first critical particle.

One aim of using microcompartments to synthesize nanocolloids is to prevent aggregation of particles into neighboring compartments. Such an aggregation can in many cases be prevented, but in cases where it occurs the formation of interesting colloidal structures can be observed. For example, the use of heterogeneous reagents, i.e., reagents that are immiscible with the block copolymer/solvent system, can induce aggregation or even Ostwald ripening of neighboring particles. At intermediate stages of such aggregation one often observes the formation of anisometric particles, as shown in Figure 6d, where $HAuCl_4$ loaded in PS-P4VP block-copolymer micelles was reduced with aqueous hydrazine. The anisometry of the particles leads to characteristic double plasmon resonances in the UV-vis spectrum.[188] Anisometric PbS[189] and CdS[172] quantum-size particles can be prepared in PS-P4VP block-copolymer micelles at very low loading ratios.

5.4. Repeated Loading

After preparation of the desired colloid, the microdomains can be reloaded with precursor materials, which can subsequently be reacted to obtain intermetallic nanocolloids, sometimes in the form of onion-type clusters. Eisenberg and coworkers used this method to increase the size of CdS colloids.[178] Yue and Cohen prepared $(ZnCd)S_2$ colloids by multiple loading experiments.[180]

The carboxylic acid coordination sites are regenerated and can be reused to make onion-type binary clusters. This technique allows for the possibility of cluster-size control and the synthesis of core-shell clusters through multiple metal-loading and reduction cycles. Recharging leads to ZnCdS colloids. In a similar fashion, bimetallic Au/Pd nanocolloids have been synthesized as catalysts for hydrogenation of dienes.[190]

A summary of the inorganic precursors and colloids that have been prepared in block copolymers is presented in Table 4.

Table 4. Inorganic precursors and colloids that have been prepared in block copolymers. bTAN = 2,3-*trans*-bis((*tert*-butylamido)methyl)norborn-5-ene, PA = η^3-1-phenylallyl.

Precursor	Colloid	References
$FeCl_2/FeCl_3$	Fe_2O_3	[190]
$Cd(ClO_4)_2$, $CdMe_2$	CdS	[175,176]
$Pb(ClO_4)_2$, $PbEt_4$, $PbCl_2$	PbS	[179,192]
$ZnEt_2$, bTAN$(ZnPh)_2$	ZnS	[177,192]
$Cu(OAc)_2$	CuS	[179]
$CoCl_2$	CoS	[179]
$FeCl_2$	FeS	[179]
$ZnEt_2$, bTAN$(ZnPh)_2$	ZnF_2	[177]
H_2PtCl_6, $Pt(Cp)Me_3$	Pt	[197,203]
$PbCl_2$	Pb	[175]
bTAN$(ZnPh)_2$, $ZnCl_2$	Zn	[74,193]
$HAuCl_4$, $LiAuCl_4$, $AuCl_3$, $Au(PMe_3)Me$	Au	[74,174,187,194–197]
$Cu(OAc)_2$, $Cu(ClO_4)_2$	Cu	[74,175]
Na_2PdCl_4, Pd(Cp)PA, $Pd(OAc)_2$	Pd	[74,189,198,199,203]
$Rh(OAc)_2$	Rh	[74]
$CoCl_2$, $Co_2(CO)_8$	Co	[200]
$NiCl_2$	Ni	[175]
AgOAc, $AgClO_4$, $AgNO_3$	Ag	[74,191,193]

6. Properties of ABC/Nanoparticle Hybrids

The products of the reactions described above are hybrid materials with a combination of properties both from the inorganic and the polymer side, for example, the mechanical behavior, solubility, and the processability of the polymer, and the magnetic, catalytic, electronic, and spectroscopic features of the embedded colloids. Interference effects arise primarily from the surface modification of the inorganic colloid by the binding polymer (F-block) matrix, which can lead to changes in the optical[191] or magnetic properties of the colloids. [192] There are also synergistic effects that can lead to a surprisingly high effectivity of such materials as catalysts, as described below.

For practical applications these materials can be viewed as polymer-coated inorganic particles. In the case of solutions, the solvent can be completely removed, resulting in solvent-cast polymeric films having the additional properties of the inorganic colloids. This process is completely reversible: the solid films can be redissolved in all solvents for the outer block (S-block) without any significant change to the colloidal characteristics. This illustrates the effective stabilization of inorganic colloids by the block copolymer shells and the "quasi-molecular" nature of the resulting colloidal hybrids.

The exploitation of the properties of these hybrids is just beginning, but some first experiments have recently been published which visualize application concepts and possibilities.

The control of magnetic properties via particle morphology and size was successfully shown through the control of the morphology of Co colloids within block-copolymer micelles.[193] Here the whole transition from paramagnetic to superparamagnetic to ferromagnetic behavior was obtained, depending on the type of block copolymer and the reaction conditions. At the same time, the so-constructed magnetic fluids exhibited high magnetization densities.

The control and installation of special optical properties was achieved by means of the synthesis of CdS colloids in ordered block-copolymer films. Eisenberg and coworkers were able to prepare CdS colloids in the size range 3–5 nm by variation of the ionic block lengths. Figure 7 shows measured absorption spectra exhibiting a redshift in the absorption edge for larger CdS particles (quantum-size effect).

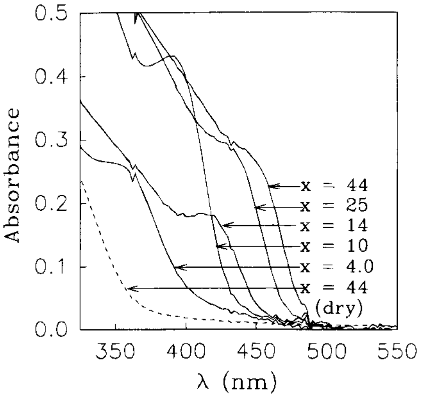

Fig. 7. Absorption spectra of CdS colloids prepared in PS-PAAc block copolymers at different PAAc-block lengths (after [177]). The observation of a redshift in the absorption edge with increasing core-block size is in qualitative agreement with Equation 5 and illustrates the possibility of controlling the electro-optical properties of the colloid by use of block-copolymer microcompartments.

ZnO colloids, which can similarly be prepared in block-copolymer micelles, have absorption edges in the UV region. In polymer films such nanocolloids can act as UV-absorbers, cutting the complete frequency range of $\lambda < 350$ nm.[172] The modular hybrid can replace the standard organic UV-absorbers with their known disadvantages.

The catalytic properties of micellar-stabilized Pd or Pt colloids have been investigated in case of hydrogenation[194] and the Heck reaction.[184] Experiments in the catalytic hydrogenation of 1,3-cyclohexadiene indicated good stability and selectivity at a level of reactivity roughly comparable to optimized industrial reference systems.[175] A systematic study on a variety of cyclic olefins demonstrated that Pd or bimetallic Au/Pd catalysts with "raspberry" morphology exhibit the highest catalytic activities owing to their large specific surface area.[190]

Micellar-stabilized Pd colloids also catalyze the Heck reaction, an important method for the carbon–carbon coupling of arylhalides with alkenes.[184] These Pd catalysts exhibit similar reactivities to standard low molecular weight Pd complexes, but show a much higher stability. In most reactions, the hybrid systems remain catalytically active even after more than 50 000 turn-over cycles. In addition, the Heck reaction could be performed in environmentally less hazardous solvents such as THF or toluene.

The hybrid Pd catalysts combine the advantages of homogeneous and heterogeneous catalysis. Owing to the polymeric shell, the Pd colloids can be dissolved in organic solvents very much like low molecular weight homogeneous catalysts. However, the regeneration of hybrid catalysts can be performed simply either by ultrafiltration using membranes that are impermeable to the micelles, or by precipitation from fluids in which the polymeric shell is insoluble. An interesting case is the catalysis in Θ-solvents for the solvating blocks. The switch between a stable colloidal solution at elevated temperatures and a colloidal gel phase at low T is fully reversible and allows a very simple separation of reaction products and the polymer-supported colloidal catalyst, which can be reused in the next reaction cycle in the same reaction vessel without any loss of materials and long-winded isolation procedures. This is a clear advantage brought into the system from the polymer side, and which is not known of classical colloids.

7. Ordered Arrays and Superstructures of ABC/Nanoparticle Hybrids

In the last two sections we briefly reviewed the synthesis and properties of ABC/nanoparticle hybrids. The magnetic, electro-optical, and catalytic properties arise primarily from single inorganic colloids. A major challenge has been the assembly of these materials into three-dimensional structures. The first tentative steps in self-assembly into new materials and devices were recently made with conventionally stabilized nanocolloids. Examples involved the construction of an opal-like crystal of CdSe nanocrystals,[195] the preparation of porous silica thin films,[196] and liquid-junction porous TiO_2 solar cells (Grätzel cell).[196]

If using polymer/hybrid materials, full advantage can be taken of the self-organizing properties of the block copolymers. This may allow the construction of samples with macroscopically well-ordered cylindrical or lamellar morphology containing metal nanoparticles, which can lead to interesting anisotropic, optical, and electronic materials properties. In addition, using the synthesis and aggregation processes in non-spherical microphases may allow the preparation of similarly shaped colloids, i.e., thin rods, tubes, or sheets. The preparation of nanowires in block-copolymer cylindrical micelles was recently described by Möller and coworkers.[197]

The self-organization of block copolymers includes several hierarchies spanning several orders of magnitude in length scales. This is schematically illustrated in Figure 8. Five different levels of self-assembly may be distinguished. Similar schemes are found in "supramolecular" chemistry.[198,199] One aspect of the present article is "supramolecular" physics, which can help chemists to assemble complicated structures without the need of specially tailored multistep synthesis.

The first step is purely chemical and involves the polymerization of monomers (typical length scale: 1 nm) into block copolymers (typical length scale: 10–100 nm). Parameters that control this step are the monomer A/monomer B/initiator ratio, which determines the degree of polymerization, N_A and N_B, of the block copolymer. The incompatibility of the two blocks, characterized by the interaction parameter χ, is the driving force for the self-assembly into block-copolymer micelles. The aggregation number Z can be controlled by N_A and N_B at a given value of χ as discussed in Section 3 (Eq. 1). Typical length scales of block-copolymer micelles are of the order of 10–100 nm. Within the micellar cores one can prepare nanocolloids, the diameter of which depends on the loading ratio and the aggregation number as given in Equation 5. Upon evaporation of the solvent, the system undergoes a disorder/order transition into lyotropic and bulk liquid-crystalline phases. The kind of topology (LAM, HEX, BCC, etc.) is determined by the volume fraction f and the segregation parameter χN as shown in the phase diagram in Figure 3. The ma-

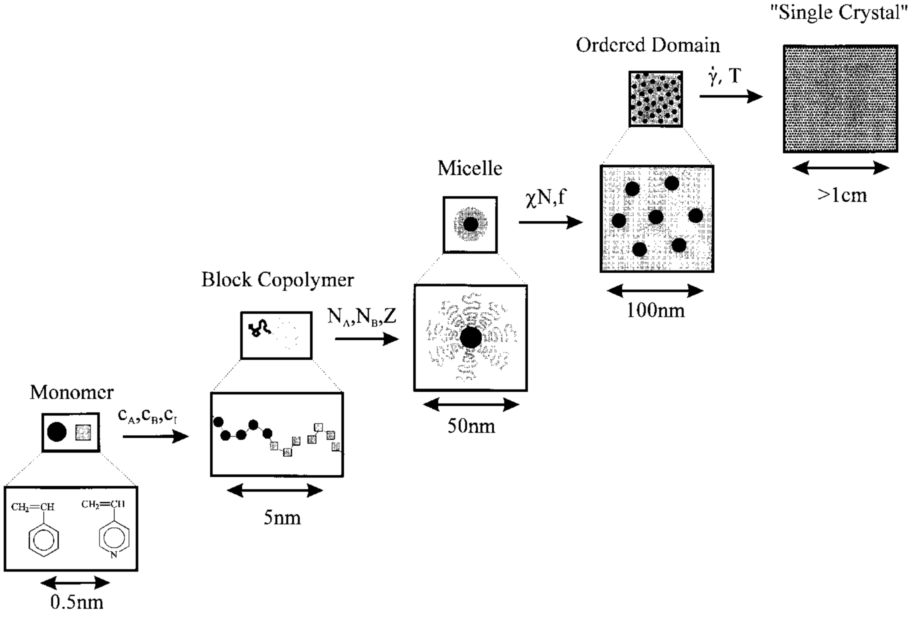

Fig. 8. Hierarchy of structures formed by block copolymers. The monomers determine the solubility, functionality, and interaction parameter χ. Living polymerization techniques allow the control of the degree of polymerization N_A, N_B, and $N = N_A + N_B$, of the block copolymer through the concentration of monomers, c_A and c_B, and initiator, c_I. If dissolved in a solvent selective for the B-block, the polymers form micelles with an aggregation number Z that is determined by N_A, N_B, and the packing parameter Z_0. Upon evaporation of the solvent the system undergoes a disorder–order transition into ordered continuous domains. Their size and topology depend primarily on the parameter χN and the relative block length $f = N_A/N$, as shown in the phase diagram in Figure 3. The size of the ordered domains can be increased by large amplitude shearing at given shear rates γ and temperatures T. This allows the preparation of macroscopic (>1 cm) "single crystals".

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terials exhibit a domain size of several hundred nanometers. Domain sizes can be increased to macroscopic dimension by the application of a large amplitude oscillatory shear. Shear conditions such as shear rate and temperature enable different macroscopic orientations of LAM,[200,201] HEX,[202] or BCC[203] samples to be obtained. This enables the preparation of macroscopic "single" crystals with anisotropic properties. An example of an ordered multidomain array is shown in Figure 9. The cylinders, arranged in a HEX structure, contain Au precursors.[204]

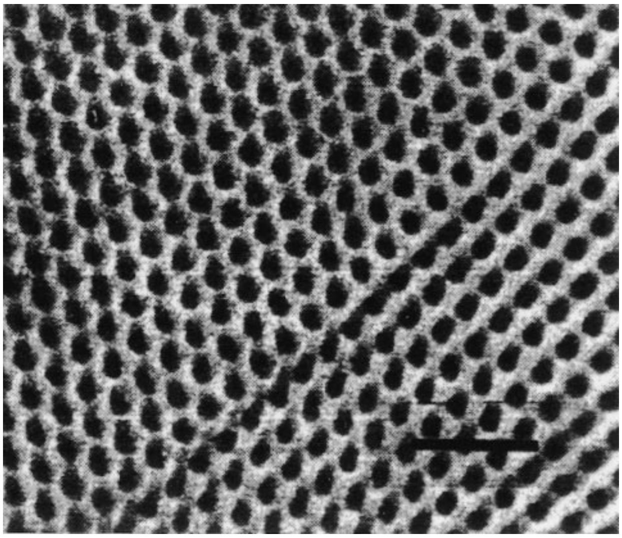

Fig. 9. Electron micrograph of ordered block-copolymer domains (HEX) containing an Au precursor. The samples were prepared by solvent-casting from benzene (after [202]).

Recently there has been a lot of interest in the self-assembly of block-copolymer monolayers.[205] Highly ordered "ultra-monomolecular" films with spherical microdomains were prepared simply by spin-coating a dilute block-copolymer solution onto a surface and heating the copolymer above its glass transition temperature.[206] With micellar block-copolymer solutions it is possible to form monolayers with hexagonally arranged spherical domains containing Au particles as shown in Figure 10.

In contrast to the micelles in Figure 6, the block copolymers in Figure 10 form a continuous film. The micelles in Figure 6 have a fixed shape (due to crosslinking of the micellar core) with a well-defined outer boundary. In Figure 10 the block copolymers are free to rearrange under annealing, thereby forming highly ordered lateral structures. Micelles thereby "lose their identity" and become part of the ordered microdomain.

The self-assembly of micelles into such highly ordered structures can also proceed in the direction normal to the surface. An example is shown in Figure 11, where micelles spontaneously self-assembled into "stripes" and "dots", arising from cylindrical and lamellar domains grown normal to the surface.

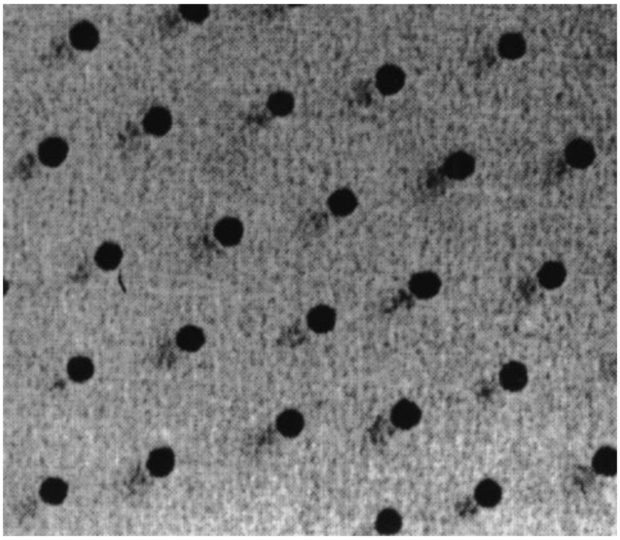

Fig. 10. Ordered thin film of a block copolymer (PS-P2VP) containing an Au precursor salt (after [187]).

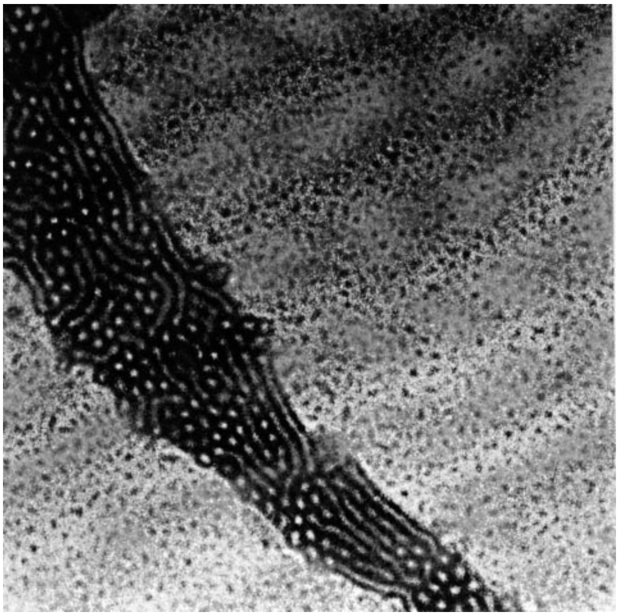

Fig. 11. Thin ordered continuous domain obtained by self-assembly of block-copolymer micelles. The domain shows the "stripe-out" instability typical for thin, ordered films. The height of the thin films comprises several micellar layers.

Such an assembly reaches the height of several monolayers, giving rise to sufficient contrast in transmission electron microscopy to avoid the necessity of staining the sample. The morphology seen in Figure 11 resembles the "stripe-out" instability, in which spherical domains transform into stripe domains. Such instabilities are well-known for magnetic[207] and organic thin films.[208] The thin film in Figure 11 represents an example of self-assembly comprised of three hierarchies, i.e., block copolymer → micelle → ordered, continuous structure.

In the studies described so far, the inorganic material was the discontinuous phase embedded in a polymer matrix. It is, however, also possible to prepare polymer/inorganic hybrid materials with an inorganic continuous phase.

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Figure 12 shows a mesoporous silicate that was prepared by templating a lyotropic liquid-crystalline phase of an amphiphilic block copolymer (PB-P2VP·HCl).[209] The templating procedure is completely analogous to that for low molecular weight lyotropic phases.[210] Tetramethyl orthosilicate (TMOS) is hydrolyzed in the aqueous microphase, thereby forming a continuous silicate structure. Pyrolysis of the polymer leaves a mesoporous structure that represents a cast of the lyotropic phase. By using block copolymers, larger pore sizes are accessible. Such materials have great potential as catalyst supports and as sorption media.[211]

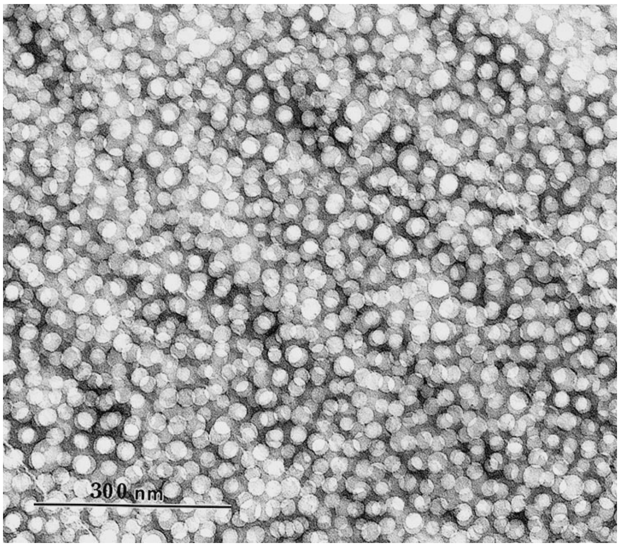

Fig. 12. Mesoporous silicate structure obtained by templating a lyotropic solution of an amphiphilic block copolymer (PB-P2VP·HCl) [209].

8. Conclusion and Outlook

Amphiphilic block copolymers represent a class of polymers important in technology for a variety of problems of interface and particle stabilization. The chemical structure of the block copolymers can easily be adapted to the energetic nature of the dispersion problem. This adaptation includes a "chemical" layout that determines the respective cohesion-energy densities of the two blocks as well as the consideration of special chemical interactions between the polymer and the solvent. The "physical" layout involves the variation of absolute length, the relative block sizes, and the architecture, which predetermine the size of the self-assemblies as well as the phase structure, which can adopt a broad range of topologies.

The controlled preparation of hybrid materials with tailored properties, e.g., superparamagnetism, UV-cut-off, or catalytic activity seems to be only the beginning of this recently developed field in polymer and materials science. Future prospects include the preparation of nanowires (in HEX phases) or nanocapacitors (in LAM phases). Further work will include the modular modification of such polymers to prepare bio-hybrid materials with biocompatible interfaces and more complex "stickers" such as proteins and oligosaccharides. The next few years should also see further progress in the development of high-quality chemical synthesis routes to nanocrystals composed of colloids, and efforts to markedly improve photovoltaic and electroluminescent devices by incorporation of nanocrystals. Liquid electrochemical junctions in nanocrystal materials involve new science and offer distinct advantages, and their use in practical devices should be considered carefully.

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