# Nanostructured Amphiphilic Conetworks and Gels as Nanoreactors for the Synthesis of Novel Nanohybrids

**Project Number: K112094**

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## 1. Introduction

Polymer conetworks, especially amphiphilic conetworks (APCNs) composed of two or more, otherwise incompatible hydrophilic and hydrophobic polymer chains connected to each other by chemical bonds belong to a new class of crosslinked macromolecular assemblies, and there are intensive fundamental scientific and applied investigations with these unique macromolecular materials worldwide nowadays (see e.g. Refs. 1-26 and references therein). APCNs possess two major characteristics. One is related to their amphiphilic nature, i.e. these materials are able to swell in and to interact with both hydrophilic and hydrophobic solvents and material constructs, respectively. Due to the chemical bonds between the immiscible polymer components, macroscopic phase separation is prevented in these materials, and the existing results indicate nanophase separation in APCNs. However, systematic investigations on the details of the nanophasic morphologies are still lacking, although this is one of the major characteristics from the point of view of their application possibilities. The major directions of current research in the field of APCNs aim at finding new and reproducible synthetic methods for constructing amphiphilic conetworks of the immiscible hydrophilic and hydrophobic components, revealing the fundamental properties and structural arrangements of the polymer chains with different philicities of the resulting APCNs, and utilization of their unique structure and properties for various applications. The application possibilities reported so far include, for instance, biomaterials, such as contact lenses, artificial organs, antibacterial materials and wound healing promoters, controlled drug release matrices, antibiofouling coatings, intelligent (responsive) materials, energy storage materials (Li-ion conducting membranes for batteries), sensors, templates for nanoporous materials, membranes for environmental protection etc. (see e.g. Ref. 1 and references therein).

On the basis of the status of this highly challenging research field at the beginning of this project, we aimed at to explore not only the synthetic pathways and the unique properties of these new kinds of materials, but also to carry out systematic investigations on the most principal structural features, that is, on the dependence of the nanophasic morphologies in conetworks as a function of composition, and to carry out experimental research on the possibilities for creating novel, so far non-existing nanohybrid materials, especially with noble metal nanoparticles, such as silver and gold, by utilizing the nanophasic morphologies as nanoreactors in such attempts. As previous research indicates, the immiscible but chemically coupled polymer chains form a network, in which phase separation is prevented at the macroscopic scale. As a result, nanophase separated morphologies are formed as the results of investigations by scattering techniques (SAXS and SANS) [19,22,27-32] and solid state spin diffusion NMR studies [33] indicate. Imaging techniques, such as sporadic transmission electron microscopy (TEM) and atomic force microscopy (AFM), showed indeed the nanophase separated structures [27,34]. However, systematic investigations on the relation between the composition and the nanophase separated morphology have not been carried out in the past. This knowledge is crucial to utilize the separated nanophases as nanoreactors to construct completely new nanohybrids which have not existed before.

On the basis of the backgrounds outlined above, the challenging research task of obtaining inorganic-organic nanohybrids based on nanophase separated APCNs was planned in this project. In addition and at the same time, systematic, laborious and time-consuming experimental works were planned for exploring new ways of conetwork syntheses, due to the miscibility limits for the preparation of many desired APCN structures, on the one hand. On the other hand, a series of APCN syntheses in broad composition ranges with different molecular weight of the macromolecular crosslinkers were also planned in order to investigate the composition-morphology relationships in

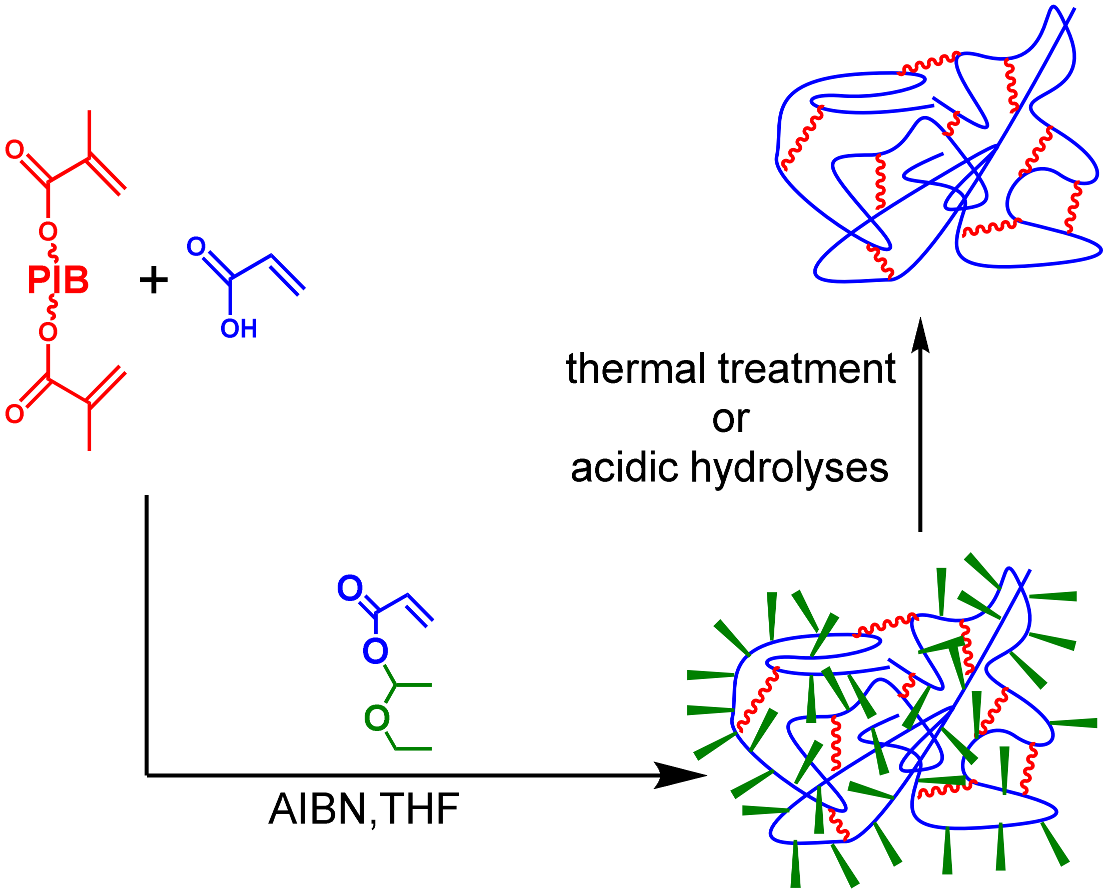
APCNs. In addition, some unexplored properties APCNs, especially with intelligent (responsive) components, were also investigated together with their application possibilities.

## 2. New routes of APCN syntheses

APCNs are mainly prepared by the so called macromonomer method, which means copolymerization of a telechelic or multifunctional macromonomer as crosslinker with a small molecule monomer. In order to obtain APCNs, three major requirements should be fulfilled: (1) the macromonomer should be able to copolymerize with the low molecular weight (MW) monomer, which is mainly based on the suitable copolymerization ratios; (2) the polymer chain formed from the low MW monomer should be long enough in order to incorporate at least two macromonomer crosslinker, otherwise gelation does not occur; (3) phase separation of all the components should be avoided, otherwise sufficient copolymerization reaction does not take place. This later requirement is the most critical in the large majority of desired APCN structures.

### 2.1. Synthesis of poly(acrylic acid)-*l*-polyisobutylene conetworks with a suitable hydrophobic protecting group for acrylic acid

One of the most desired component in APCN is poly(acrylic acid) (PAA), due to its polyelectrolyte nature and biocompatibility. However, there is no condition by which the strongly hydrophobic and also biocompatible polyisobutylene (PIB) form a homogeneous solution with acrylic acid. Therefore, a protected acrylic acid was synthesized and copolymerized with methacrylate-telechelic PIB macromonomer with narrow molecular mass distribution ($M_n$ = 5000 Da, D = 1.01) and functionality of 2. This macromonomer was prepared via quasiliving carbocationic polymerization of isobutylene followed by subsequent quantitative chain end derivatizations [32,35,36]. A hydrophobically protected monomer, 1-ethoxyethyl acrylate (EEA) was synthesized by reacting acrylic acid with ethyl vinyl ether according to literature procedure [37-39]. The radical copolymerization and the deprotection reaction are displayed in Scheme 1. Either thermal or acidic cleavage of the acetal can be envisioned. However, according to our experimental findings, the acidic deprotection is more feasible than the thermal treatment. In this way, a series of poly(acrylic acid)-*l*-polyisobutylene (PAA-*l*-PIB; *"l"* stands for *"linked by"*) conetworks with 47-73% PAA, possessing pH-responsive intelligent behavior were successfully synthesized [40]. As shown in Figure 1, these novel conetworks are able to swell in both hydrophilic (water) and hydrophobic (hexane) solvents, that is, they possess amphiphilic character, on the one hand. On the other hand, due to the polyacid component, the swelling degree of the PAA-*l*-PIB conetworks shows strong pH-dependence and composition dependent, very high swelling capacities at high pH, as displayed in Figure 2. Additional investigations with this novel polyelectrolyte APCNs are in progress in our laboratories.



Scheme 1. Synthesis of poly(acrylic acid)-*l*-polyisobutylene conetworks using ethoxy-ethyl protected acrylic acid monomer.

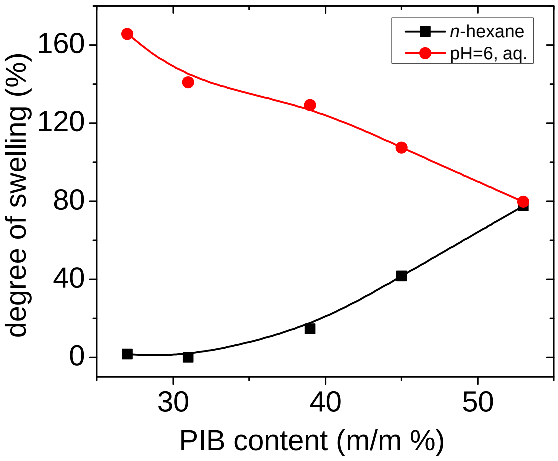


Figure 1. The amphiphilic swelling behavior of the PAA-*l*-PIB conetwork series: the equilibrium swelling degree in water and hexane as a function of the PIB content.

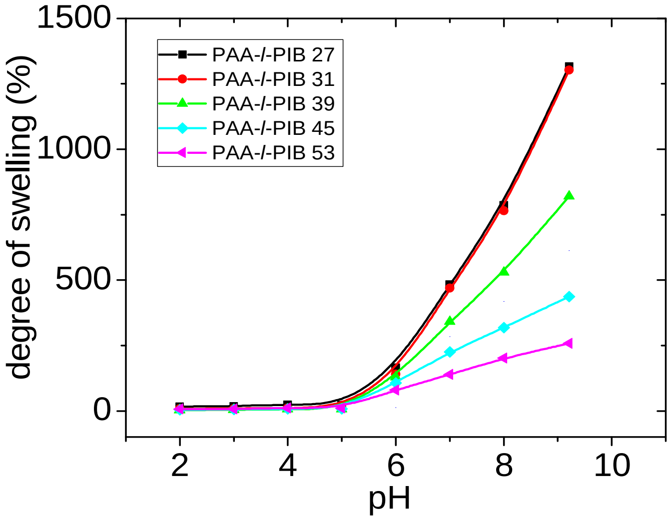
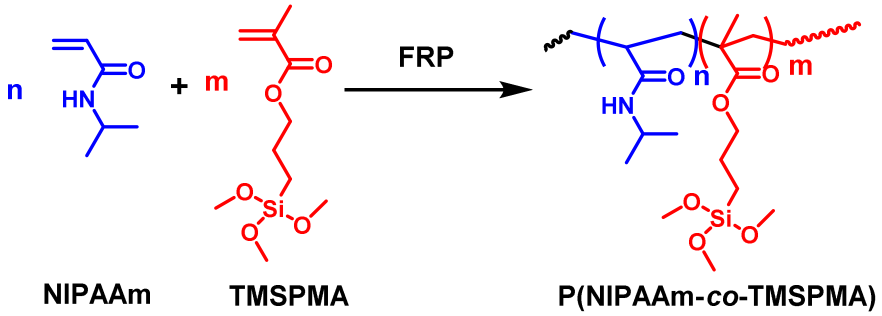


Figure 2. The equilibrium swelling degree of PAA-*l*-PIB conetworks with different compositions as a function of pH. The numbers in the legend correspond to the PIB content of the conetworks.

### 2.2. Inorganic-organic hybrid conetworks by sol-gel reaction of trialkoxysilyl containing copolymers of N-isopropylacrylamide

Responsive (smart, intelligent, adaptive, self-healing) polymers with well-defined functionalities are of great interest from both scientific and industrial point of views, and as a consequence, such macromolecular materials are intensively explored nowadays. Among these polymers, the thermally responsive poly(N-isopropylacrylamide) (PNIPAAm), its copolymers, gels, and hybrids have been undoubtedly the most investigated intelligent materials. This is mainly due to its lower critical solution temperature (LCST) near to the body temperature of ~32-35°C, and especially to its biocompatibility (see e.g. Refs. 41-44 and references therein).

Previously, we have attempted the synthesis of poly(N-isopropylacrylamide)-*l*-polyisobutylene which showed composition dependent thermoresponsive behavior with broad transition temperature range [45]. In order to overcome this problem, we thought that PNIPAAm-based conetworks with inorganic silica as crosslinker might lead to thermoresponsive gels with much narrower thermal transition periods. Due to the advantageous properties of silica, especially its biofriendly characteristics, several attempts have been already made to combine PNIPAAm with silica in one network structure. The usual way applied broadly is the preparation and then functionalization of silica particles with various sizes obtained by sol-gel chemistry, functionalization of the silica surfaces and attachment of the PNIPAAm chains to these particles. A more convenient way came to our minds which involves the synthesis NIPAAm copolymers containing trialkoxysilyl groups, capable of sol-gel reactions and thus obtaining silica-PNIPAAm hybrid conetworks, in which the resulting hydrophobic silica particles are the crosslinkers of the PNIPAAm chains. The copolymerization of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) with NIPAAm seemed to be the best choice as the first step to obtain NIPAAm copolymers capable of subsequent sol-gel reaction. However, a closer look into the existing literature indicated either unsuccessful copolymer syntheses or gelation during copolymerization (see e.g. Refs. 46,47). Therefore, first a reliable and reproducible copolymerization process was developed by us. Because we thought that even very mild protic conditions, that is the use of alcohol or not dry enough solvent, might be the catalytic impurities for gelation, free radical copolymerizations (FRP) were carried out by us in dry dioxane as displayed in Scheme 2. This polymerization process resulted in soluble copolymers of poly(N-isopropylacrylamide-*co*-3-(trimethoxysilyl)propyl methacrylate), P(PNIPAAm-*co*-TMSPMA), with well-defined TMSPMA content up to more than 10 mol% [48].



Scheme 2. The synthesis of P(NIPAAm-*co*-TMSPMA) copolymers by free radical copolymerization.

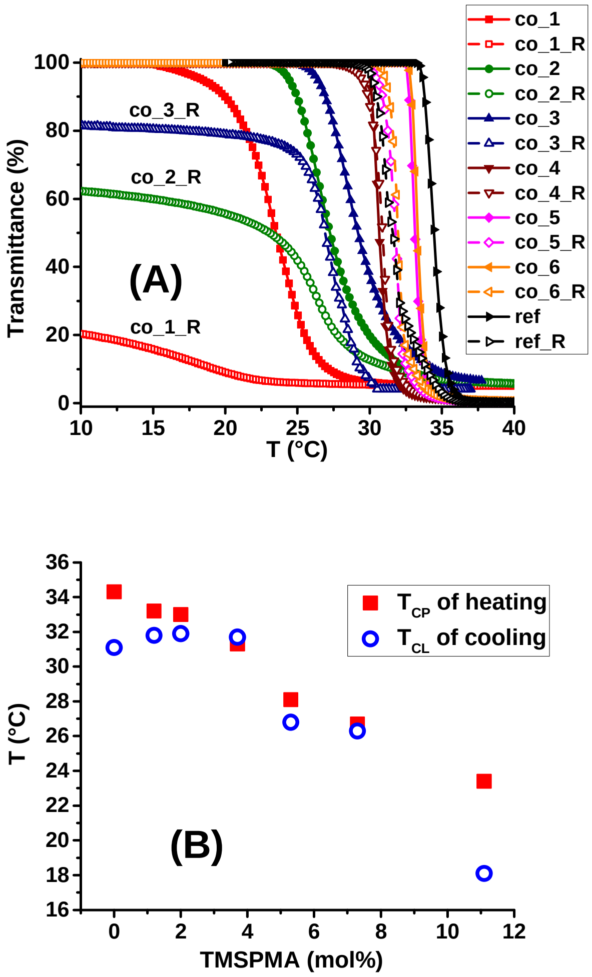


Figure 3. Transmittance-temperature curves (A) and the cloud point and clearing point (B) during heating (solid lines) and cooling (dashed lines) of the P(NIPAAm-*co*-TMSPMA) solutions as a function of copolymer composition (TMSPMA contents of copolymers in mol%: 1-11.1, 2-7.3, 3-5.3, 4-3.7, 5-2.0, 6-1.2; conditions: 0.1 wt%, 0.2 °C/min heating rate with 5 min equilibration, 488 nm).

As shown in Figure 3, the resulting copolymers show composition dependent thermoresponsive behavior. An unexpected interesting phenomenon was observed by us during these experiments. The solutions of the copolymers by cooling become opaque indicating that by heating above the critical solution temperature, the copolymers with higher TMSPMA contents are partially crosslinked in the collapsed state, and full recovery of the transparency does not occur [48]. This finding will be further explored by us in the near future.

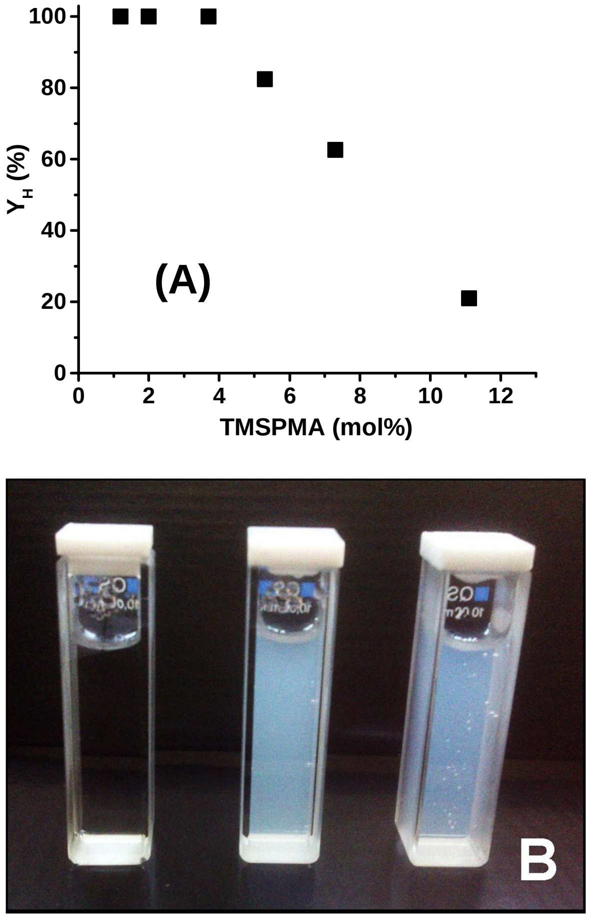
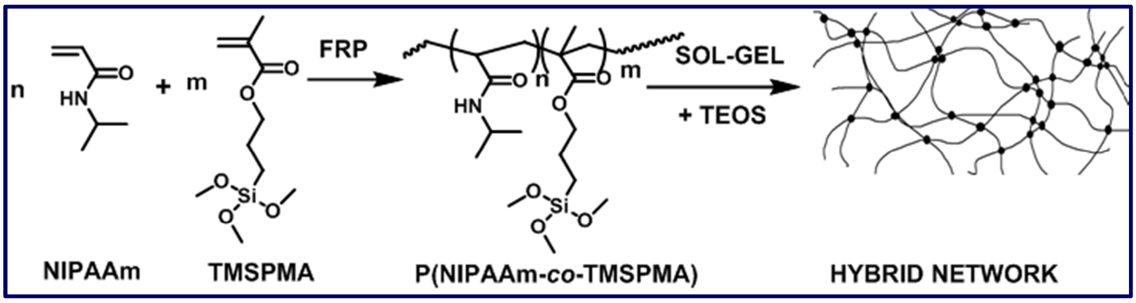


Figure 4. The extent of transmittance recovery ($Y_H$) as a function of TMSPMA content in the P(NIPAAm-*co*-TMSPMA) copolymers (A) and photographs of the copolymer (sample co_1) solutions before the first heating, and after the first and second cooling cycles (left to right) (B) (conditions: 0.1 wt% P(NIPAAm-*co*-TMSPMA), 0.2 °C/min heating rate with 5 min equilibration, 488 nm).

With the compositionally well-defined and water soluble P(NIPAAm-*co*-TMSPMA) copolymers, we attempted the synthesis of PNIPAAm conetworks crosslinked by silica particles formed by the sol-gel reaction of the trimethylsilyloxy group in the TMSPMA comonomers [49]. As shown in Scheme 3, the conetwork syntheses were carried out by either direct sol-gel reaction of the copolymers or by the addition of tertaethoxysilane (TEOS), the most widely used silane compound for silica particle preparation via a sol-gel reaction. It was found by us that both methods led to conetwork formation, in which the silica particles formed are chemically bound to the PNIPAAm chains and provide the crosslinking points in the conetworks. These novel hybrid materials were characterized by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). In contrast to expectations, there are no detectable larger silica domains in these inorganic-organic hybrid materials, but small silica particles with dimensions in the nanometer range are practically molecularly distributed along the PNIPAAm chains.



Scheme 3. The synthetic procedure of the PNIPAAm-l-silica temperature responsive conetwork hydrogels.

These new unique PNIPAAm-*l*-silica conetwork hydrogels show gel collapse at somewhat lower temperatures than that of the corresponding water soluble linear chains [49]. The degree of swelling at temperatures lower than the gel collapse temperature (GCT) depends on composition. The higher the silica crosslinker content, the lower the swelling degrees at temperatures lower than that of the GCT. In other words, a completely new kind of hybrid conetworks composed of thermoresponsive PNIPPAAm and inorganic silica as crosslinker were synthesized by us. The hydrogels of these novel conetworks possess intelligent (thermoresponsive) behavior, on the one hand. On the other hand, in contrast to ususal PNIPAAm hydrogels with organic molecules as crosslinkers, the PNIPAAm-*l*-silica conetwork hydrogels do not collapse completely but retain certain amounts of water in the collapsed state as well.

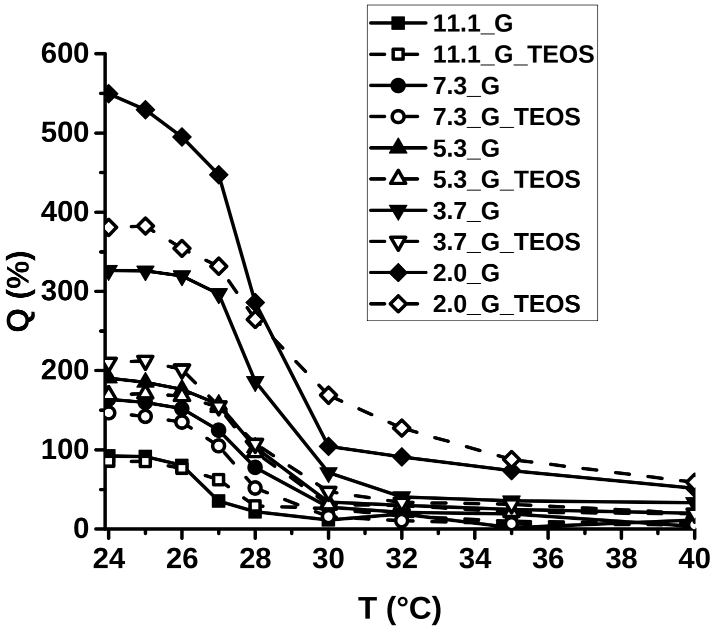


Figure 5. Equilibrium swelling ratios of the temperature responsive PNIPAAm-*l*-silica hybrid conetwork gels with and without added TEOS crosslinking agent as a function of temperature.

The incomplete gel collapse above GCT led to the assumption by us that this property might be utilized for sustained drug release even above the GCT, i.e. at the body temperature. It was found with theophylline, as model drug, that the PNIPAAm-*l*-silica conetwork hydrogels are able to encapsulate efficiently the drug molecules. The drug release was investigated at temperatures both lower and higher than that of the body temperature. As shown in Figure 6, controlled drug release takes place even at temperatures higher than that of the GCT. The rate of drug release is lower above GCT than that at lower temperatures at which the conetwork have higher swelling degrees. These findings allow to conclude that the PNIPAAm-*l*-silica conetwork hydrogels are capable to encapsulate drug molecules and release them with long release times at body temperature. In other words, a novel intelligent nanostructured hybrid inorganic-organic conetwork gels with controlled release property were developed in the course of our studies [49].

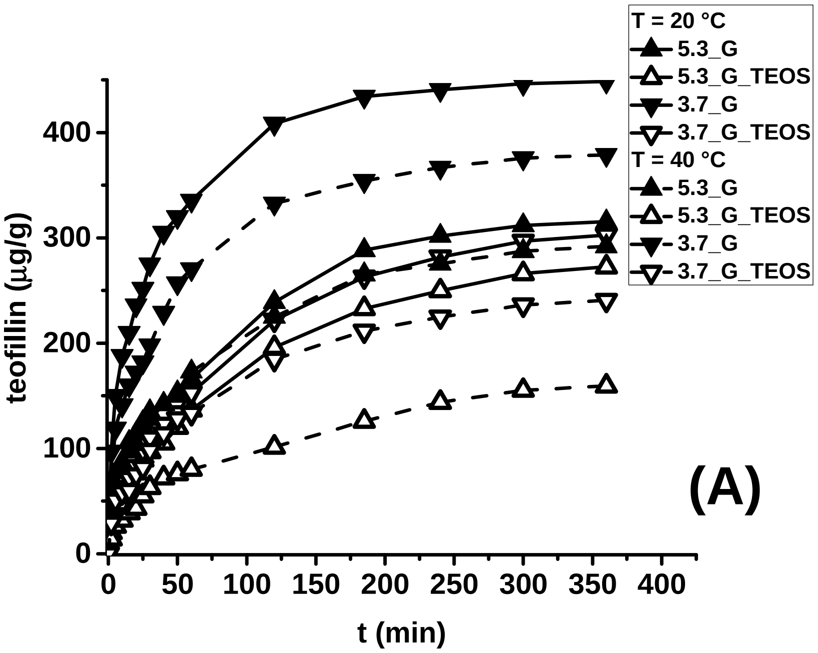


Figure 6. Extent of drug release from the PNIPAAm-*l*-silica hybrid gels with and without added TEOS crosslinking agent at 20 °C and 40 °C as a function of time.

## 3. Non-collapsing polyelectrolyte amphiphilic conetwork hydrogels in the presence of calcium ions

It is well-known that negatively charged polyelectrolytes of weak acids, such as the biocompatible hydrogels of (meth)acrylic acid based polymers, undergo gel collapse in the presence of certain amounts of multivalent cations [50,51], such as calcium ions which is an essential ion in the living organisms. Because poly(methacrylic acid) (PMAA) and its gels are widely used in biomedicine and sustained drug release formulations, and in certain nanostructures as well, detailed investigations were performed by us on the calcium ion responsive behavior of a series of poly(methacrylic acid-*l*-polyisobutylene (PMAA-*l*-PIB) amphiphilic conetworks with a broad composition range. To our surprise, gel collapse does not occur with the PMAA-*l*-PIB conetworks under physiological conditions or even in the presence of high calcium ion concentrations as shown in Figure 7. These new unexpected results indicate that such conetworks can be utilized as either novel biomaterials or components of a variety of nanohybrid materials without gel collapse in the presence of bivalent cations. It is also noteworthy, that the swelling process is reversible, i.e. after removal of the calcium ions by ion exchange with sodium ion, the swelling degrees of the conetwork gels increase to the starting states of zero calcium ion concentration [52]. Our unique, unprecedented findings on these unique unexpected characteristics of polyelectrolyte amphiphilic conetworks is planned to be further investigated especially in the direction of biomedicine in the future.

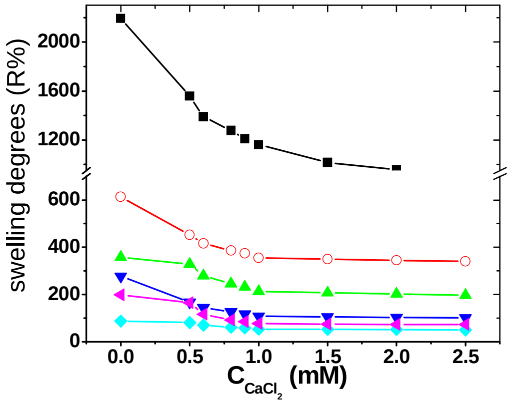
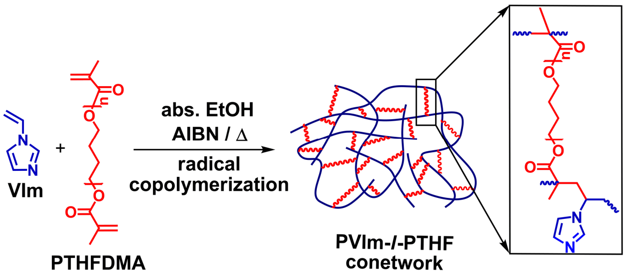


Figure 7. The equilibrium swelling degree as a function of $CaCl_2$ salt concentration for APCNs with (■) 15 wt.% (○) 22 wt.% (▲) 29 wt.% (▼) 39 wt.% (◀) 47 wt.% and (◊) 55 wt.% PIB contents.

## 4. Nanostructured morphology investigations of amphiphilic conetworks

The amphiphilic conetworks (APCNs) composed of covalently bonded, otherwise immiscible hydrophilic and hydrophobic polymer chains possess nanophase separated domain structures with low domain sizes in the nanometer scale, because macroscopic phase separation is prevented by the covalent bonds between the composing hydrophilic and hydrophobic chain segments, as previous scattering techniques, such as small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) measurements indicated [27-34]. Thus, revealing the spatial arrangements of the immiscible components at the nanoscale, that is the morphologies of APCNs is crucial not only for a variety of fundamental research purposes, i.e. for revealing the relationship of the nanoscale morphologies and structure and composition of the conetworks, but for application possibilities as well. Therefore, we have made significant experimental efforts in order to explore the dependence of the nanophasic morphologies of APCNs on their structural characteristics. In the framework of this fundamental research task, we have prepared various conetworks with broad composition ranges. Subsequently, in collaboration with the Freiburg Materials Research Center and Institute for Macromolecular Chemistry of the University of Freiburg (Germany), systematic morphological investigations were carried out by differential scanning calorimetry (DSC) and atomic force microscopy (AFM) accompanied with selective swelling measurements on a series of amphiphilic conetworks in which two structural parameters were varied: the composition and the average molecular weights of the macromolecular cross-linker. Specifically, phase mode atomic force microscopy (AFM) on cryo-microtomed surfaces was used for the morphology investigations. As far as we are concerned, our investigations provide the first comprehensive studies on the effect of these structural parameters on the dependence of morphology and average domain sizes in polymer conetworks [53].



Scheme 4. Schematic representation of the synthesis and structure of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks. The colors in the conetwork structure represent hydrophobic PTHF (red) and hydrophilic PVIm (blue).

For these investigations, as displayed in Scheme 4, a series of poly(N-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetworks were synthetized *via* free radical copolymerization of N-vinylimidazole (VIm) and methacrylate telechelic poly(terahydrofuran (PTHFDMA) macromonomer as crosslinkers with various molecular weights ($M_n$ = 2170, 6850 and 10030 g·mol$^{-1}$). As a result, PVIm-*l*-PTHF conetworks were obtained in a broad composition range, from 25 to 91 wt% PTHF content.

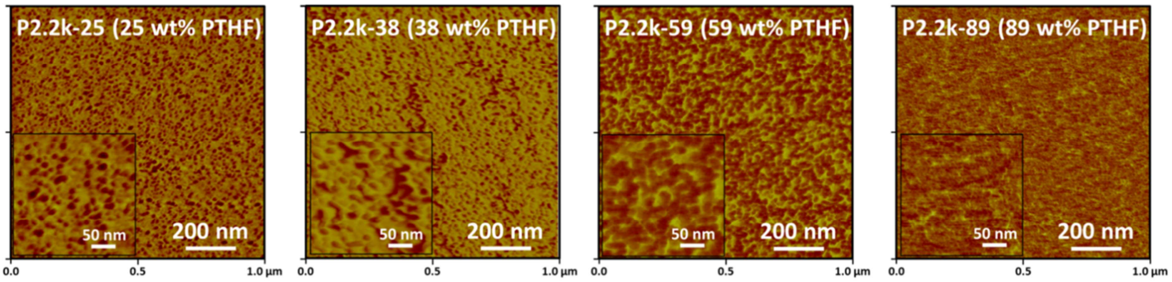


Figure 8. Representative phase mode AFM images of cross sections of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) conetwork samples with different compositions. Inset: AFM image of conetwork samples (the softer PTHF phase appears dark and the harder PVIm is bright).

As our published results on these investigations indicate, it has been found that these conetworks possess compositionally asymmetric phase separated structure [53]. A representative series of AFM images of nanophase separated PVIm-*l*-PTHF conetworks with various PTHF contents are shown in Figure 8. The contrast, that is the tone difference between the phases in the phase mode AFM images can be used to map directly the morphology. In the AFM phase images the two distinct polymer nanophases in the conetworks, specifically the glassy, hydrophilic PVIm and the elastic, soft PTHF phases appear with different colors, light and dark brown, respectively. These AFM images indicate nanophase separation of the two polymers with different philicities, but the domains do not organize in a regular lattice over the whole composition range due to the randomly crosslinked structure of the conetworks in all cases. At relatively low PTHF contents, the hydrophobic PTHF domains are dispersed in the continuous hydrophilic PVIm matrix as spherical domains (P2.2k-25 and P6.8k-52; in these sample codes, the first number means the molecular weight of PTHF, the second stands for the PTHF content as w/w%). At increased hydrophobic ratio (P2.2k-38 and P10k-46) elongated structures arise. From 47 wt%, 61 wt% and 66 wt% PTHF crosslinker content, depending on the molecular weight of the macromonomer the elongated PTHF phases interconnect to form continuous, more precisely cocontinuous (bicontinuous) phase next to the interconnected PVIm phases. In other words, the AFM micrographs of the PVIm-*l*-PTHF conetworks clearly indicate the two incompatible hydrophilic and hydrophobic polymers exist in mutually continuous phases next to each other. This cocontinuous (bicontinuous) nanophase morphology appears in a broad composition range, from 47 to

86 wt% PTHF contents. At high PTHF contents, the PVIm phases are interconnected with a certain extent and appear as individual domains in the disordered continuous hydrophobic PTHF matrix. It was also found that the average domain sizes fall in the range of ~7-20 nm while the interdomain distances are in the ~15-30 nm range, and these can be controlled by the molecular weight of the PTHF crosslinker and composition. Increasing the PTHF content decreases the domain sizes, while increasing the PTHF molecular weight increases the domain sizes as depicted in Figure 9, which is in a good correlation also with the average molecular weights of the PVIm chain segments between two crosslinking points ($M_c$) which vary between 134 and 5870 g/mol in the investigated conetworks [54].

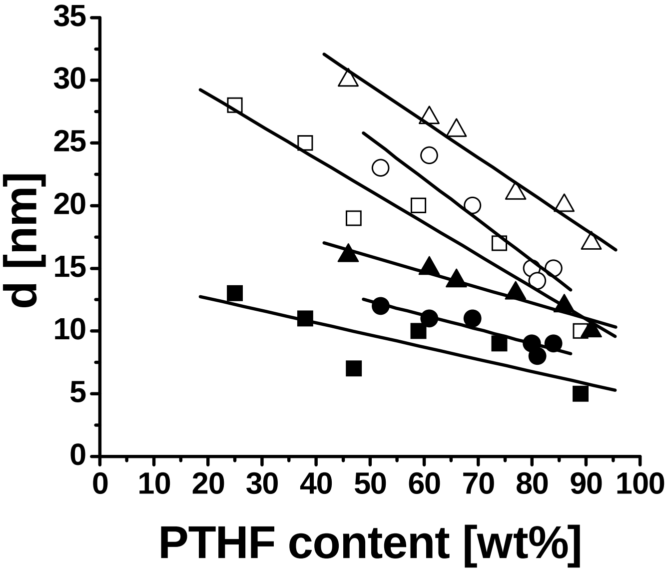


Figure 9. The average PTHF domain size (filled symbols) and average PTHF interdomain distance (open symbols) determined by phase mode AFM of the PVIm-*l*-PTHF conetwork series: PTHF domain size (■) and PTHF interdomain distance (□) for PVIm-*l*-PTHF(2.2k), PTHF domain size (●) and PTHF interdomain distance (○) for PVIm-*l*-PTHF(6.8k) and PTHF domain size (▲) and PTHF interdomain distance (Δ) for PVIm-*l*-PTHF(10k) APCNs.

Comparing our new findings related to the disordered nanophase separation morphologies of amphiphilic conetworks to the widely explored well-defined ordered phase separated morphologies of block copolymers with immiscible polymer chains, fundamental differences can be concluded. One of the main reasons of this comparison lies in the fact that very intensive research has been going on the preparation of bicontinuous block copolymer morphologies. As well established, in order to minimize the evolving incompatibility of the blocks, the copolymers self-assemble into various phase structures, as shown in Figure 10 [53,58-60]. According to the phase diagrams of block copolymers, the separate phases of block copolymers assemble into the following ordered geometries symmetrically with composition: spheres, cylinders, gyroid and lamellar with increasing volume fraction of one of the polymer blocks. In contrast, the bicomponent polymer conetworks, possess compositionally asymmetrical disordered morphologies with analogous phase structures from spherical to stable bicontinuous (cocontinuous) phase morphology. This bicontinuous phase separation appears in a broad composition range in conetworks, which is also in sharp contrast with the block copolymers in which thermally and mechanically instable biocontinuous double gyroid phase structures exist only in a very small, limited composition range (Figure 10). The physically stable bicontinuous nanophasic morphological arrangements in a wide composition window in amphiphilic conetworks provide unprecedented new opportunities to synthesize a large variety of novel bi- and multicomponent nanohybrid materials with structures and properties never existed before.

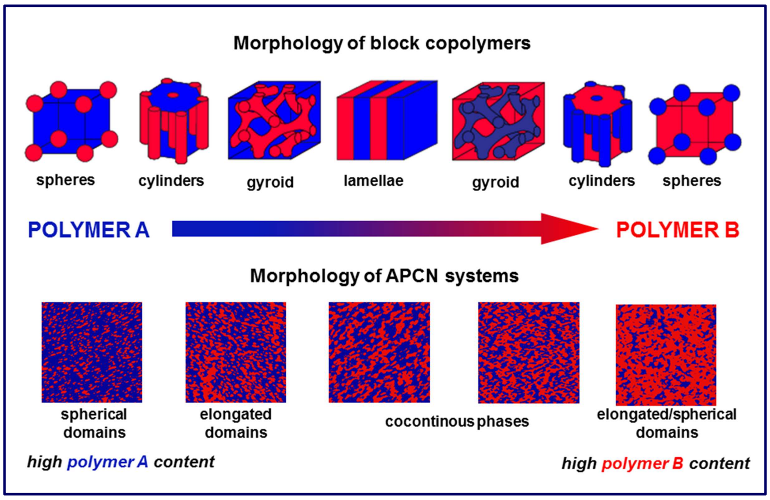


Figure 10. Comparison of the morphological arrangements of the immiscible components of A-B diblock copolymers with the compositionally asymmetrical nanophasic morphology of amphiphilic polymer conetworks.

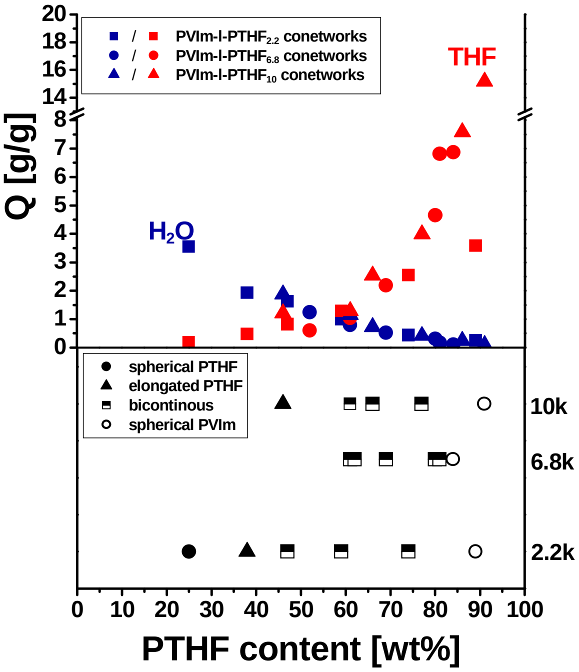


Figure 11. Correlation between morphological features and swelling of the PVIm-*l*-PTHF conetwork series: equilibrium swelling ratios (Q) in nonpolar (THF) and polar ($H_2O$) solvents and the morphology of the PVIm-*l*-PTHF conetworks as a function of the PTHF content.

Correlation between the morphological arrangements of the nanopahses and the swelling behaviour of PVIm-*l*-PTHF conetworks was also investigated. For this purpose, swelling measurements were performed in water (hydrophilic solvent) and the hydrophobic tetrahydrofuran (THF). The data in Figure 11 show the equilibrium swelling degrees (*Q*) as a function of composition of the conetworks (PTHF content). Below the swelling degrees graph, the morphological arrangements in the conetworks are also depicted. As shown in Figure 11, the equilibrium swelling degrees change with the composition in both solvents. The higher the PVIm/PTHF ratio in the conetworks, the higher the swelling degree in aqueous solutions, on the one hand. On the other hand, the swelling in the nonpolar THF follows opposite tendency, confirming that the increased hydrophobic content in the conetworks subserves the nonpolar swelling. In other words, the PVIm-*l*-PTHF conetworks behave as hydrogels in polar and as hydrophobic gels in nonpolar solvents, that is these conetworks indeed possess amphiphilic character. On the basis of the AFM measurements, it is revealed that mostly isolated spherical PTHF domains are present in the continuous PVIm phase at low PTHF contents. This means that the swelling of the conetworks in nonpolar solvents is restricted by the non-swollen, rigid hydrophilic matrix in this range of compositions. Increasing the PTHF content, the hydrophobic swelling becomes more pronounced, due to the diminished integrity of the glassy phase by the coalesced PTHF domains. In this case, the swelling capacity of the PTHF domains becomes larger in the coherent non-swollen PVIm phase, thus the swelling in THF is more feasible. In a relatively broad composition range, where the bicontinuous phase morphology emerges, both nonpolar and polar swelling occurs with nearly the same ratio. The coexistence of the separately continuous nanophases allows the interaction of the corresponding phases with either kind of solvents with different polarity. With increasing the hydrophobic content in the conetworks, the swelling tendency reverses. The predominant hydrophobic phase facilitates the swelling in nonpolar solvents, while the smaller and isolated hydrophilic PVIm phases in the coherent PTHF matrix are not able to force the whole conetwork to swell to high degrees. For conetworks with high crosslinker contents and distinct elongated/spherical PVIm domains, the aqueous swelling is negligible, while the hydrophobic swelling reaches high degrees of swelling (up to ~1500%) [53,58].

These fundamental new results of our systematic investigations is expected to serve as the basis of future investigations on the utilization of the unique bicontinuous (cocontinuous) morphologies and special amphiphilic swelling behaviour of amphiphilic conetworks.

## 5. Nanohybrids based on nanophasic amphiphilic conetworks as nanoreactors

As presented and discussed in the previous section of this report, bicontinuous nanophasic morphology and the selective swellability of amphiphilic nonetworks is a special feature of these materials. On the basis of these unique structural and property characteristics, we came to the idea to utilize one of the nanophases, preferentially the hydrophilic phases, as nanoreactors for targeting to synthesize novel organic-inorganic nanohybrids which have not existed before. The schematic arrangement of the nanophases for nanoreactor applications is depicted in Figure 12. Swelling the hydrophilic nanophases with metal salt solutions and carrying out reduction reactions in these swollen nanophases expected to result in metal nanoparticles with diameters not larger than the size of the nanophase. This means that the nonswollen other phase act as the "reactor wall" of the corresponding nanophase swollen with the solvent of the reactant.

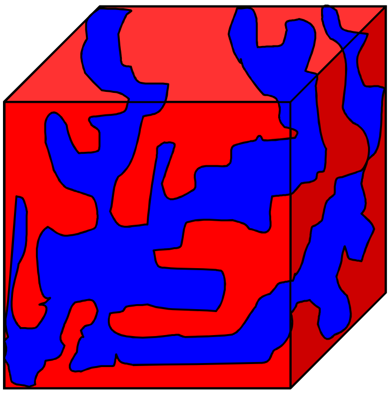


Figure 12. A schematic representation of the mutually bicontinuous (cocontinuous) morphology of amphiphilic polymer conetworks capable of acting as nanoreactors in which one of the phases serves as reactor while the other provides the wall of the nanoconfined reaction medium.

Figure 13 shows that silver nitrate solutions are able to swell poly(N,N-dimethylacrylamide)-*l*-polyisobutylene (PDMAAm-*l*-PIB) conetworks. Reduction of the silver ions to elemental silver by dimethylformamide (DMF) transferred the fully transparent conetwork hydrogels to a yellowish-brown film (Figure 14). Due to the yellow-brown color caused by the surface plasmon resonance effect of silver nanoparticles, this is a direct indication of the formation of silver nanoparticles in the conetworks. This was directly proved by transmission electron microscopy measurements (TEM) as displayed in Figure 14. The TEM investigations indicate that silver nanoparticles with diameter of ~7-20 nm are formed by the applied reduction process in the hydrophilic nanophases of the conetworks. This set of experiments has really proved that the nanoreactor concept for amphiphilic conetworks is a feasible way to obtain completely new nanohybrid materials.

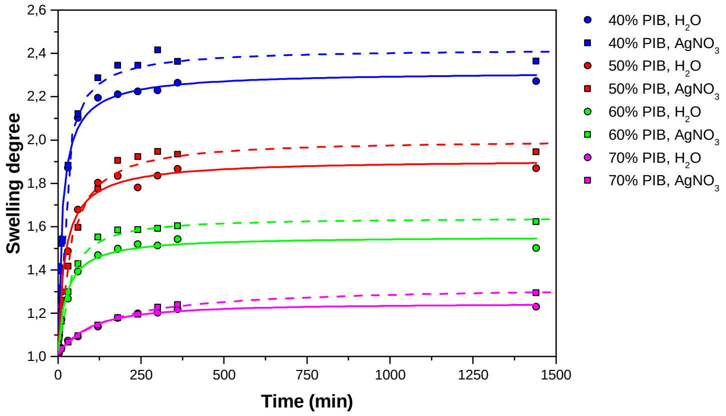


Figure 13. The swelling degree as a function of time during swelling of PDMAAm-*l*-PIB conetworks with water and silver nitrate solution.

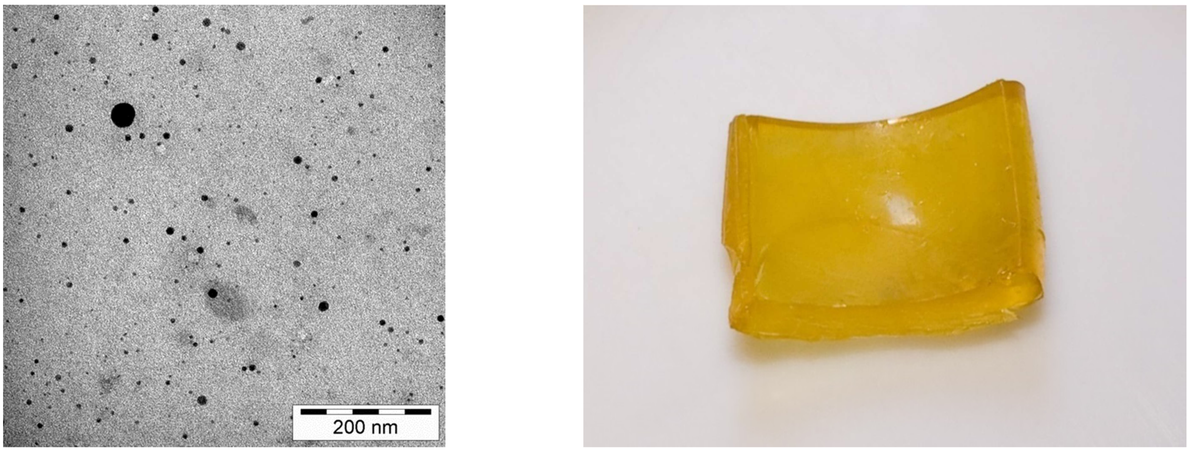


Figure 14. Transmission electron microscopic (TEM) image (left) and a photograph (right) on a silver nanoparticle containing PDMAAm-*l*-PIB conetwork.

It is known that noble metal nanoparticles, such as silver and gold, are able to catalyze a large variety of chemical reactions [55-57]. Thus, the conetwork based nanohybrids with silver nanoparticles have been tested as nanocatalyst in the reduction reaction of 4-nitrophenol (4NP), an environmentally dangerous compound, by sodium borohydride to the less hazardous 4-aminophenol (4AP). As shown in Figure 15, our novel silver nanoparticle containing nanohybrids are able to catalyze this reaction very efficiently, on the one hand. On the other hand, it was found by us with inductively coupled plasma optical emission spectrometry (ICP-OES) measurements that there is no any leaching of the silver catalyst particle from the nanohybrids in this reaction. It is well known that inorganic support for catalyst particles suffer from the problem of catalyst leaching and detachment, thus contaminating the products. The purification of products from especially toxic catalysts is laborious, material, time and energy consuming process. Therefore, catalyst supports with non-leaching capability is of high demand nowadays. The results obtained by us so far are very promising in this direction, because silver leaching under proper conditions has not been observed by us in the case of our investigations so far. As a consequence, further systematic investigations are planned in these directions in the future.

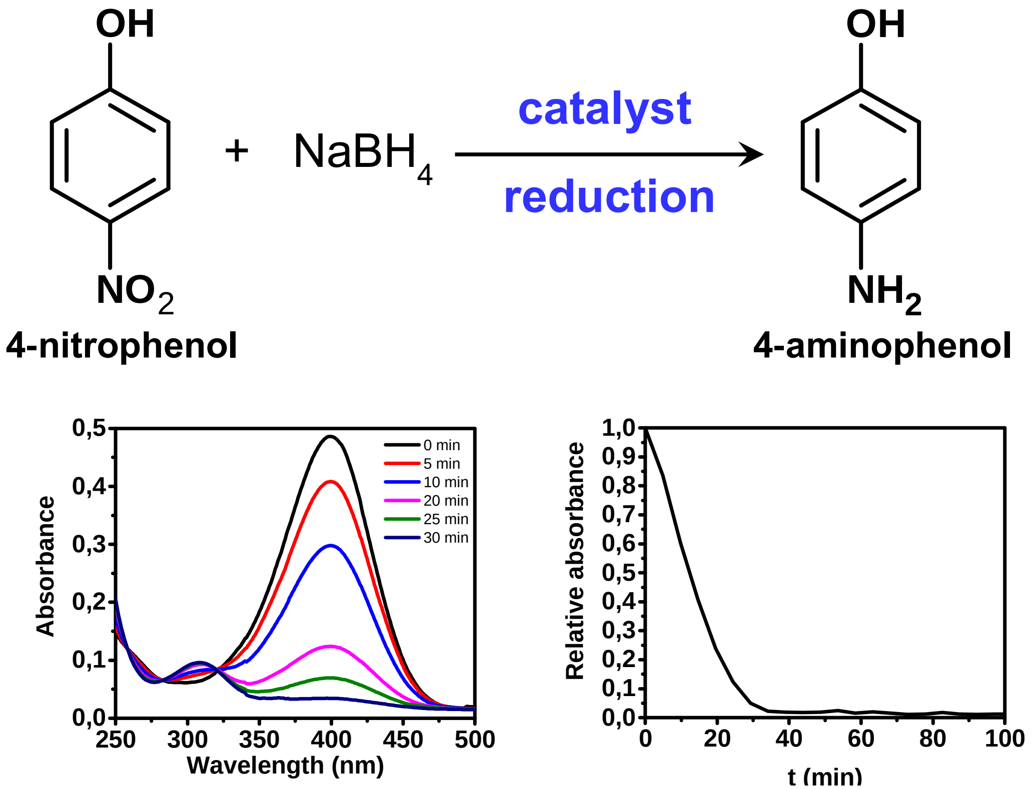


Figure 15. The catalytic reduction of 4-nitrophenol by sodium borohydride in the presence of silver nanoparticle containing PDMAAm-*l*-PIB nanohybrid as shown by the change in the UV-visible spectrum (left) and the relative absorbance of this process as a function of reaction time.

## 7. Summary

In the framework of this highly challenging project, we have carried out systematic experimental research in order to find new ways for the synthesis of nanostructured amphiphilic conetworks, to reveal their structure-property relationships and to prepare new, conetwork-based nanohybrid materials which have not existed so far. We have synthesized conetwork series with broad composition ranges, and first in the world, we experimentally revealed the relationship between the morphology of the nanostructured conetworks and their composition. We have unequivocally proved that the incompatible polymer chains are in a nanophasic cocontinuous (bicontinuous) arrangement in a broad composition window. This provides unprecedented possibilities to utilize one of the nanophases as nanoreactors for the preparation of completely new nanohybrid materials. On the basis of these findings, we have successfully attempted the synthesis of silver, and very recently gold nanoparticle containing conetwork-based nanohybrids. We have experimentally proved that these nanohybrids can be utilized as high-efficiency nanocatalysts in some reactions without catalyst leaching. This is a very promising finding which we are planning to further investigate in details in the future.

We have developed new synthetic routes for the preparation of intelligent (thermoresponsive) copolymers which were applied for the synthesis of nanostructured hydrogels and inorganic-organic thermoresponsive hybrid conetworks. It was demonstrated by us that these new materials are able to encapsulate drugs and to provide controlled, thermoresponsive drug release. A series of pH-responsive conetworks were also prepared by us successfully, and surprisingly it was found that poly(methacrylic acid) containing polyelectrolyte conetwork gels do not collapse in the presence of calcium ions which is in absolute contrast to the behavior of similar, but homopolymer-based polyelectrolyte gels. These findings are expected to open new possibilities for the applications of amphiphilic polyelectrolyte conetwork gels, especially in the medical and nanotechnology fields.

It has to be noted that publications on such approaches cannot be found in the literature yet, so we can assume that we are among the firsts for carrying out such kind of new fundamental research, on the one hand. On the other hand, our publications appeared in the leading international journals of this scientific field, and we were invited to write a chapter for a new book on amphiphilic conetworks [58]. Our new research results were also presented at several international conferences, mainly as invited presentations.

It has to be also mentioned that on the basis of our new and very promising fundamental scientific results, we are planning to carry out further systematic research in the field of amphiphilic conetworks based novel nanohybrids.

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