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Hydrophilic gels with new superstructures and their hybrids by nanocasting technologies

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SUMMARY: The polymerization of hydrophilic monomers, such as acrylamide, in the nanoscale confinement of lyotropic surfactant phases or microemulsions produces gels with variable pore architecture in the hundreds of nanometers to micrometers size range. The porous gels are characterized by scanning electron microscopy after critical-point drying. The structure of the gels is not a direct copy of the structure and symmetry of the parental surfactant assemblies, but depends on the type of monomer, cross-linking density and both the monomer and surfactant concentration. Nevertheless, a controlled structure set-up is obtained, where different pore morphologies and different pore sizes can be systematically adjusted. In such a way it is possible to build the polymer network structure on a mesoscopic length scale, optimizing different network properties which are otherwise coupled in an opposite fashion, e. g. polymer networks with very large pore size and high mechanical stability can be made. Such porous gels are interesting for modern gel-monolith separation techniques, such as gel electrophoresis for protein and DNA separation where micron sized pores are required. Implementation of a further "nanocasting"-procedure within the pore channel system of these gels allows generation of polymer/inorganic hybrid materials with a similar degree of mesoscale organization and exciting combinations of material properties. The value of such a multiple replica procedure is demonstrated by making superparamagnetic rubbers ("elastic magnets") and highly porous, continuous TiO_2-networks for photocatalytic applications.

Synthesis of mesostructured gels by templating surfactant assemblies

Hydrophilic polymer gels, such as polyacrylamide gels, are important for modern water-based protein and gene separation processes. In spite of this fact, optimisation of the gel structure is somewhat neglected by the scientific community: these gels are still made by in-situ radical polymerization in water inside the separation devices$^{1)}$. From the viewpoint of supramolecular polymer science, it is a challenge to meet the demands of biotechnology by constructing polymer networks with a mesoscale architecture. Here, nanometer to micron size pores are separated by highly cross-linked polymer regions which provide sufficient

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mechanical stability. This strategy is well known for the generation of the so-called macroreticular gel beads for GPC or HPLC, which are however restricted to diameters in the micron range[2)]. Recently, Frechet et al. extended a similar technique to produce solid monolithic gels and column fillings of macroscopic dimensions, using classical low molecular weight porogens such as hydrophobic alcohols[3)].

A more sophisticated structure control is given by application of self organizing surfactant media as porogens: here, one might in principle expect to copy the symmetry and connectivity of ordered lyotropic phases into a pore structure. Polymerization in the continuous aqueous phase of a lyotropic liquid crystal has been examined by a number of research groups[4-9)]. In those studies, the monomer mixture is dissolved in the water phase surrounding surfactant assemblies, ordered in a hexagonal, bicontinuous cubic or lamellar fashion. Polymerization is performed to stabilize the ordered structure, and the second subphase, formed by the surfactant assemblies and other non-polymerizable components, displace the polymer growth.

The key problem with this approach is the preservation of the originally well ordered phase structure, since the growing polymer chains influence the thermodynamic stability of the microemulsion or the lyotropic phase. Specific interactions, as well as the entropy loss of a polymeric chain in a confined geometry, usually result in destruction of the nanometer-scale order. Nevertheless, differently ordered products with interesting properties are obtained. Some of these problems have been recently reviewed in context with polymerization in microemulsions[10,11)]. The loss of the mesomorphous order and the appearance of new structure patterns in the micrometer range were demonstrated for polymerization in bicontinuous microemulsions containing hydrophobic as well as hydrophilic monomers by a variety of techniques[12-16)].

In a recent paper, the polymerization of hydrophilic standard monomers (such as acrylamide and 2-hydroxyethyl methacrylate) was performed in the aqueous domains of lyotropic liquid crystalline phases of nonionic amphiphiles, and parameters like amount and type of monomer, amount and type of surfactant or cross-linking density were varied in a systematic fashion[17)]. In addition, more stable and slower relaxing surfactants as couterion coupled gemini surfactants[18, 19)] or glass-forming block copolymers[20)] were employed as templates, preserving a higher degree of the original order.

Diversity of gel structures

White or slightly opaque gels with good mechanical performance, which are easily handled in the solid state, were obtained in most experiments. Prior to polymerization all mixtures are transparent, and become opaque or turbid-white shortly after start of the reaction. Lyotropic order prior to polymerization is easily observed by polarized-light optical microscopy. The addition of monomer usually blurs the optical textures, indicating a decrease of order. The textures are, however, re-established during polymerization. Systems with lower surfactant concentration start the polymerization reaction as a solution of globular micelles (L_I) but end up as strongly birefringent phases, corresponding to an increase of the surfactant concentration in a surfactant-rich phase during polymerization. In selected cases, small-angle X-ray scattering (SAXS) experiments were performed, indicating that the surfactants preserve some type of order throughout the polymerization, although the peaks shift to higher scattering vectors and the related lower Bragg spacings[17)]. All these facts, as well as the strong increase in turbidity, suggest that the surfactant remains in a lyotropically ordered state, but expels the polymer from this phase. Both the coexisting polymer and surfactant-rich phases compete for the water, which does (or does not) lead to a change of the lyotropic phase structure. The polymer gel is generated by cross-linking the phase which is low in surfactant. Therefore the gel architecture is a result of demixing, not of the lyotropically ordered assemblies themselves acting as a template.

To confirm these observations, we examined the morphologies of the final polymer gels using scanning electron microscopy following purification and preparation by the critical-point drying method (involving a gradual exchange of the solvent from water to ethanol, then acetone and finally supercritical CO_2). It was shown that this technique allows an artifact-poor visualization of the gel architecture[21)]. The dried and freeze-fractured samples were sputter-coated using a Pd/Ir target.

The series of micrographs in Fig. 1 depicts a variety of the different gel morphologies in the final, purified state (complete conversion, surfactant removed) obtained by monomer and surfactant variation. In the absence of surfactant, gels with glass-like fracture surfaces but without pronounced mesostructure are observed, proving the absence of major artifacts by the gel preparation technique as well as the fact that the porosity is really due to the presence of the surfactant assemblies.

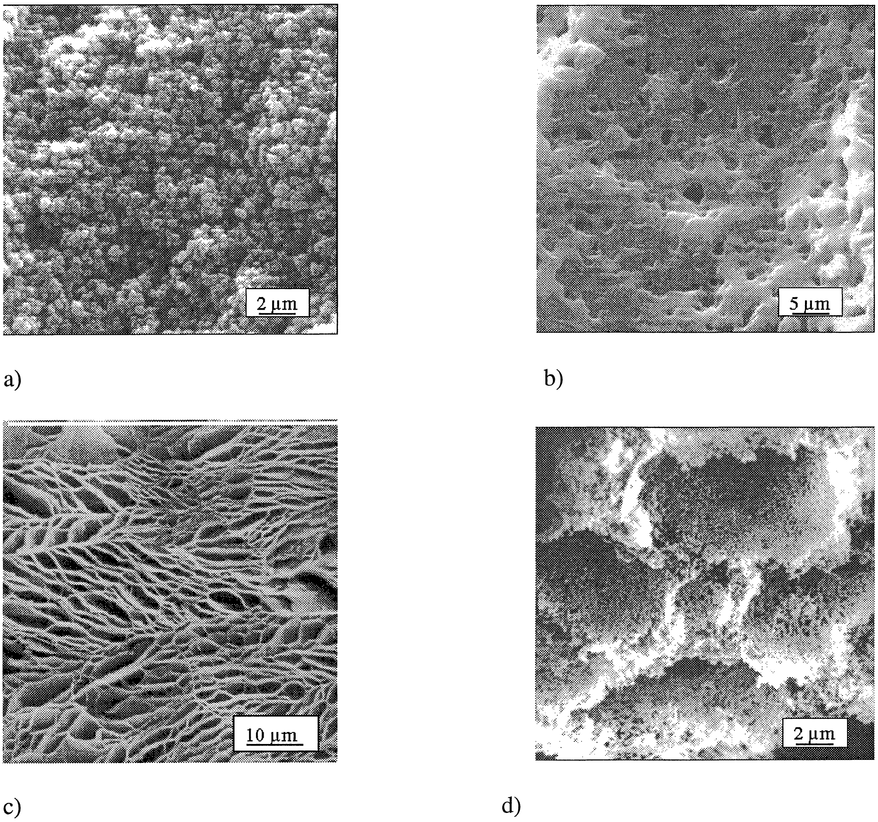


Fig. 1: Scanning electron microscopy images show the different gel morphologies obtained by polymerization in continuous microemulsion and lyotropic phases of different monomer/surfactant combinations

A frequently occurring morphology, found for poly(acrylamide), other acrylamides, and a number of monomer combinations, is given by a structure consisting primarily of small polymer spheres. These spheres are mutually cross-linked to form a rather continuous, mesoporous network (Fig. 1a). Poly(hydroxyethylmethacrylate) (PHEMA), polymerized both in microemulsions and in lyotropic phases, adopts a gel morphology which is constructed of porous sheets or platelet-like objects (Fig. 1b). The mesophases of the cocogem system, bis(cetyltrimethylammonium)tartrate, are stable enough to preserve some anisometry within the gel structure, and layered gels with grain boundaries and typical liquid crystal defects are obtained (Fig. 1c).

A remarkably interesting morphology for chromatographic applications is achieved from the combination of Tween 60 as the surfactant and the polymer poly(acrylic acid-co-glycidylmethacrylate) (Fig. 1d). This pore system consists of interconnected, large spherical pores (ca. 10 μm in diameter), the cast of demixed, and subsequently removed, surfactant phase droplets. Additionally, the polymer-rich phase itself is porous and shows continuous channel systems on a length scale of ca. 200 - 400 nm. This second ”tier” of pores is formed presumably during a second demixing step at a later stage of the reaction. The smallest building units of the gel observed using SEM are ca. 60 nm thick polymer rods scaffolding the gel. Hierarchical pore structures have the advantage of both excellent flow transport and a high interface area for exchange due to the large and small pores, respectively. Since this gel structure is also highly functionalized (carboxylic acids and hydroxy groups from the opened epoxy-rings), its structure is most attractive and was therefore used for the generation of hybrids detailed below.

Explaining the different morphologies produced by varying the monomer is complex, since the choice of monomer influences the interface energy between the demixing phases, the distribution of water between the two phases, the rheology of the two-phase system, as well as the polymerization kinetics and the time to reach gel transition. The gel architecture is therefore the product of a complicated balance. Although the found structures can be reproduced, predicting the structure of a new polymer gel derived from an analog microphase-separated medium is not possible. We can only summarize that the gel structure is obtained kinetically and not according to thermodynamic laws.

Formation of organic/inorganic hybrids based on mesostructured gels

By using ordered surfactant assemblies as templates to generate ordered gels, we have transferred a relaxing, ordered, complex fluid into a more permanent polymer structure. There have been many trials to use such surfactant based "copying" or "casting" procedures for inorganic matter or ceramic materials, but these usually fail because the interfacing between a crystalline solid and surfactants of a completely different chemistry is even harder to obtain.

A very promising solution for this problem in materials chemistry is opened by a "double-casting" procedure involving mesostructured polymer gels: a surfactant structure is used initially to organize a functional polymer gel, which secondly is replicated into the inorganic structure. Hereby, one makes use of both the variable functionalization chemistry of polymers, as well as the non-structure relaxing nature of gels. Leaving the polymer matrix intact, one directly obtains a hybrid or compound material with interesting and unconventional property combinations. Removal of the polymer, for instance by calcination, results in the pure mesostructured inorganic material. Both approaches are illustrated below.

Generation of a magnetic polymer/inorganic hybrid material is conventionally performed in a liquid based two-step procedure22). Here, the purified, mesostructured polymer gel containing carboxylic acid functionalities is submersed in an aqueous solution of Fe^{2+}. As in an ion exchange resin, the gel strongly binds all iron ions until its binding capacity (given by the number of carboxylic groups) is reached. This procedure is very fast, which is due to the excellent hydrodynamic accessibility of all surfaces in a hierarchical channel system. Precipitation of these surface bound iron ions under alkaline conditions directly result in monodisperse, well defined magnetite (Fe_3O_4) nanoparticles, which are strongly coupled to the gel (Fig. 2). The size of the particles is so small that just superparamagnetic behavior is obtained, i. e. the compound is strongly magnetic, but does not show remanescence.

Magnetite contents of 3.5 - 8 wt % can be achieved in one reaction cycle, higher loads and magnetization densities are also accessible by repetition of the loading cycle. Such materials combine the viscoelasticity of polymers with the magnetic properties of inorganic systems, e.g. elastic magnets (or superparamagnetic rubbers) or glassy, but shapable, magnets for diverse applications are accessible.

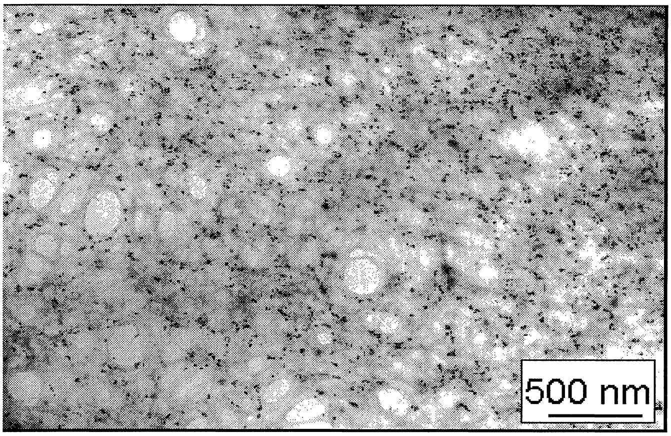
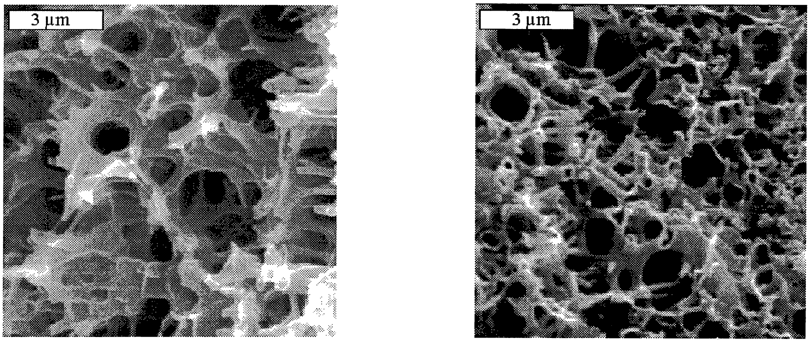


Fig. 2: TEM image of an ultramicrotomed elastic magnet. The hybrid consists of monodisperse magnetite particles attached to a mesostructured gel

Replication of the gel structure into a pure inorganic system was performed for instance with the sol-gel synthesis of TiO_2-networks[20,23)]. Here, a hydrophilic gel is placed in titanium isopropoxide and hydrolysis is performed, in an iso-propanol/water mixture, within the mesostructured cast. The precipitating amorphous TiO_2 is deposited onto the polymer gel, thus coating the structural details with a homogeneous layer. Heating such a hybrid to 450 - 900°C under oxygen results in both the complete removal of the polymer and the conversion of the amorphous TiO_2 layer into pure nanocrystalline anatase or rutile phases (depending on calcination temperature).

The perfection of the copying procedure as well as the preservation of the particular inorganic network is demonstrated in Figs. 3a & b, where the structure of the parental gel and the one of the TiO_2 replicas are presented:



a) b)

Fig. 3: Replica formation by gel coating: a) Parental mesostructured gel; b) Replica in nanocrystalline TiO_2

In combination with high resolution TEM, it is seen that the former gel rods are replicated as hollow inorganic rods being composed of TiO_2 nanocrystallites, ca. 50 nm in size). The porosity of the shown structure was calculated to be ca. 97 %, still preserving a macroscopic mechanically stable system. The similarity is also proof for the homogeneity of the titania deposition as well as the connectivity of the pore and channel system of the parental polymer gel. Such porous TiO_2 sponges, with a relatively wide mesh size of ca. 2 µm, are meaningful for contacting gaseous or liquid media, i. e. for photocatalysis or flow-through reactors and reactive membranes. The gel coating, or multiple replica technique, has also be employed for mesostructured polymer gels with finer structural details, thus resulting in a titania network with 50 nm pore size and effective surface areas of 60 - 100 m^2/g (as determined by BET measurements)$^{20)}$. These latter systems are better suited for photoelectric and solid state applications.

Conclusion

It has been shown that polymerization reactions in either the continuous water phase of lyotropic surfactant phases or in both subphases of continuous microemulsions allow the controlled generation of highly ordered polymer hydrogels. The gel structure is not a cast of the original mesophase architecture, but exhibits structural elements two or three orders of magnitude larger than those addressed by the lyotropic assembly structure. This underlines previous observations that the structure is not directly generated by templating the surfactant aggregates but occurs due to demixing into a surfactant-rich and a polymer-rich subphase.

The gel structure depends on the choice of monomer and, for more developed systems, also on the type of surfactant. In this article we presented a number of globular and sheet-like morphologies, but the accessible range of structures is wider and far from completely explored. The size of the gel structures can be - within a certain range - adjusted by the monomer concentration: the higher the monomer content, the smaller the pores. This is explained by crossing the gel transition in an earlier stage of the demixing, thereby fixing finer structures.

Using the purified gels as nanostructured reaction environments, for instance for inorganic precipitation reactions or inorganic polyreactions, results in nanostructured compounds and hybrid materials. By adjusting the surface functionality of the polymer gel and appropriately choosing the secondary reaction conditions, one can generate both disperse, filled systems as well as bicontinuous structures. The former can be directly employed as hybrid systems, where an interesting combination of polymer and inorganic properties, such as thermoprocessability and elasticity with magnetism, coloration or scratch resistance, are obtained. For the bicontinuous systems, it is very attractive to remove the polymer, thus giving access to mesostructured porous inorganics with well defined structure.

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