Catalyst Encapsulation and Substrate Solubilization in Polymer-Surfactant Complexes and Their Use in a Membrane Reactor

Hans Fuhrmann,[a] Torsten Dwars,[a] Dirk Michalik,[a] Gerd Holzhüter,[b] Cordula Grüttner,[c] Udo Kragl,[d] Günther Oehme[a,*]

[a] Institut für Organische Katalyseforschung e.V. an der Universität Rostock, Buchbinderstr. 5–6, 18055 Rostock, Germany
Fax: (+49)-381-4669324, e-mail: guenther.oehme@ifok.uni-rostock.de
[b] Fachbereich Physik der Universität Rostock, Universitätsplatz 3, 18051 Rostock, Germany
[c] micromod GmbH, Friedrich-Barnewitz-Str. 4, 18119 Rostock, Germany
[d] Fachbereich Chemie der Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany
Fax: (+49)-381-4986452, e-mail: udo.kragl@chemie.uni-rostock.de

Received: May 15, 2002; Accepted: July 18, 2002

Abstract: A chiral non-racemic Rh complex was entrapped in a number of charged polymer-surfactant complexes (PSCs) and used as micellar-enlarged catalyst for the enantioselective hydrogenation of an α-amino acid precursor in a membrane reactor. The retention behavior of different ultrafiltration membranes in dependence on the chemical nature and the molar mass of the PSCs as well as the loading behavior of the system were investigated. The chiral hydrogenation product was obtained with good enantioselectivity and space-time yield. A lowering of the activity of the multiply used catalyst was caused mainly by a blockage of the PSC and not by the decomposition and leaching of the encapsulated catalyst. TEM images before and after the solubilization of the catalytic system support the view that a PSC with a loose, gel-like structure and incorporated micelles yields the best results in the repetitive batch process.

Keywords: asymmetric hydrogenation; membranes; micelles; microreactors; polymer-surfactant complexes

Introduction

For many years several attempts have been made to recover homogeneously soluble catalysts by the aid of membranes.[1] Especially for chiral ligands, which are often more expensive than the metals which they coordinate, a facile recovery and repeated use are highly desirable in order to increase the total turnover number.[2] However, attempts to couple these ligands to insoluble polymers often resulted in a decrease of the enantiomeric excess (ee) of the product. Bayer and Schurig[3] described the first soluble polymer-bound catalysts and demonstrated that macromolecular phosphine ligands from non-cross-linked polystyrene are active in the rhodium-catalyzed hydrogenation of 1-pentene as well as in the hydroformylation of styrene. These complexes with macromolecular ligands could be separated by the membrane technique. Later the principle of polymer-enlarged homogeneously soluble catalysts with separation by nanofiltration and ultrafiltration membranes was efficiently verified in several cases.[4–7] Another concept developed and discussed in detail by Bahrmann et al.[8] consists of tailor-made, re-immobilized quaternary ammonium salts of functionalized tertiary phosphines which were successfully used as ligands in the hydroformylation with subsequent separation of the homogeneous catalyst by membranes. Also dendrimeric structures have been described as homogeneously soluble catalysts, which have been retained by ultrafiltration and nanofiltration membranes.[9,10] In contrast to these catalysts immobilized by chemical bonds, the retention by an ultrafiltration membrane of a rhodium hydrogenation catalyst solubilized and entrapped in a triblock copolymer was recently reported.[11] As was shown, the catalyst, embedded in micelles, was retained and reused several times without remarkable loss of activity and enantioselectivity. Only a minimal leaching of the catalyst components was observed.

We report herein on the design and synthesis of charged polymer-surfactant complexes (PSCs) and their structural characteristics by visualization methods before and after the solubilization of a chiral non-racemic Rh catalyst. Furthermore, we studied the retention behavior of the micellar-entrapped catalyst by different ultrafiltration membranes as well as the course of activity and enantioselectivity with the multiply reused

  1615-4150/03/3451+2-202–210 $ 17.50-.50/0

catalyst in the asymmetric hydrogenation of a prochiral amino acid precursor.

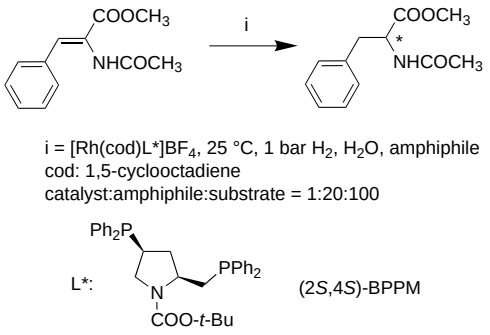
Results and Discussion

The polymerization of polymerizable amphiphiles in aqueous micellar media and the copolymerization of hydrophilic monomers with small amounts of hydrophobes (0.1 – 2 mol %) in the presence of tensides above their critical micelle concentration (CMC) affords polymer-surfactant complexes (PSCs). These water-soluble associative polymers with unique rheological characteristics have attracted growing interest in many applications during the past decade.[12] The formation of polymer-surfactant complexes is currently regarded as a depression of the critical association concentration (CAC) of the surfactant. According to this picture, superior solubilization in such systems can be anticipated over that provided by surfactants alone. Therefore, we considered it favorable to use the PSCs as a microenvironment for the asymmetric hydrogenation of the prochiral methyl (Z)-α-acetamidocinnamate with a chiral non-racemic Rh catalyst (Scheme 1).

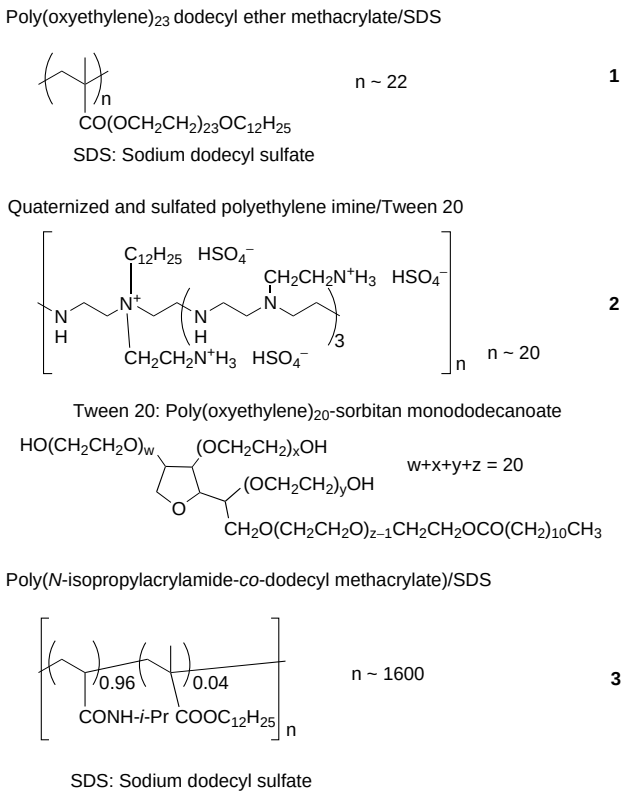
In comparison with polysoaps and hydrophobically modified water-soluble polymers the PSCs should offer a greater versatility considering their solubility and solubilization properties by variation of the hydrophile/hydrophobe ratio and the use of charged monomers or surfactants, respectively. Both, polyelectrolytes and non-ionic polymers have been proposed as precursors for the synthesis of PSCs. The advantage of polyelectrolytes is their good solubility in water even with a high level of hydrophobic units. In semidilute aqueous solutions they form interchain hydrophobic aggregates of micellar type which induce connectivity within the system resulting in a transient network.[13] The incorporation of hydrophobic groups into the polyelectrolyte chain promotes the association with non-ionic surfactants or even with surfactants having the same charge.[14,15] The hydrophobic interactions overcome the repulsive interactions between the polyelectrolyte backbone and the polar heads of the surfactants. In this case mixed micelles are formed in which the hydrophobic groups of the polyelectrolyte are involved.[16–18] We anticipated that PSCs of a suitable composition and microstructure could encapsulate the chiral Rh catalyst thus enabling its use in a membrane reactor repeatedly.

Scheme 2 shows the PSCs which have been used in the membrane reactor. Different membranes were tested at the beginning to find out the most suitable one for the hydrogenation reaction in water. The selectivity of porous membranes is based on the pore size and various properties of the membrane material such as hydrophilicity or hydrophobicity.

Exemplified by the PSC **1**, a complex of a neutral polyamphiphile and the anionic surfactant SDS with a



Scheme 1. Asymmetric hydrogenation of methyl (Z)-α-acetamidocinnamate.



Scheme 2. Polymer-surfactant complexes used in this study.

MW of 29,000 g mol^{-1}, the course of the hydrogenation reaction is illustrated in Figure 1. Depending on the density and the pore size of the membranes the outcome of the stereoselective hydrogenation differs in a characteristic manner. The membrane YC 05 with the smallest pore size and molecular weight cut-off (MWCO) of 500 D required filtration times of 120 minutes at the beginning and up to 200 minutes for the last reaction cycles. Obviously, the long filtration times are responsible for rather low turnover numbers and stereoselectivity values (Figure 1).

The situation has improved with the membrane YM 3 (MWCO 3,000). In this case the filtration time is reduced to 21 – 23 minutes per cycle. The best results

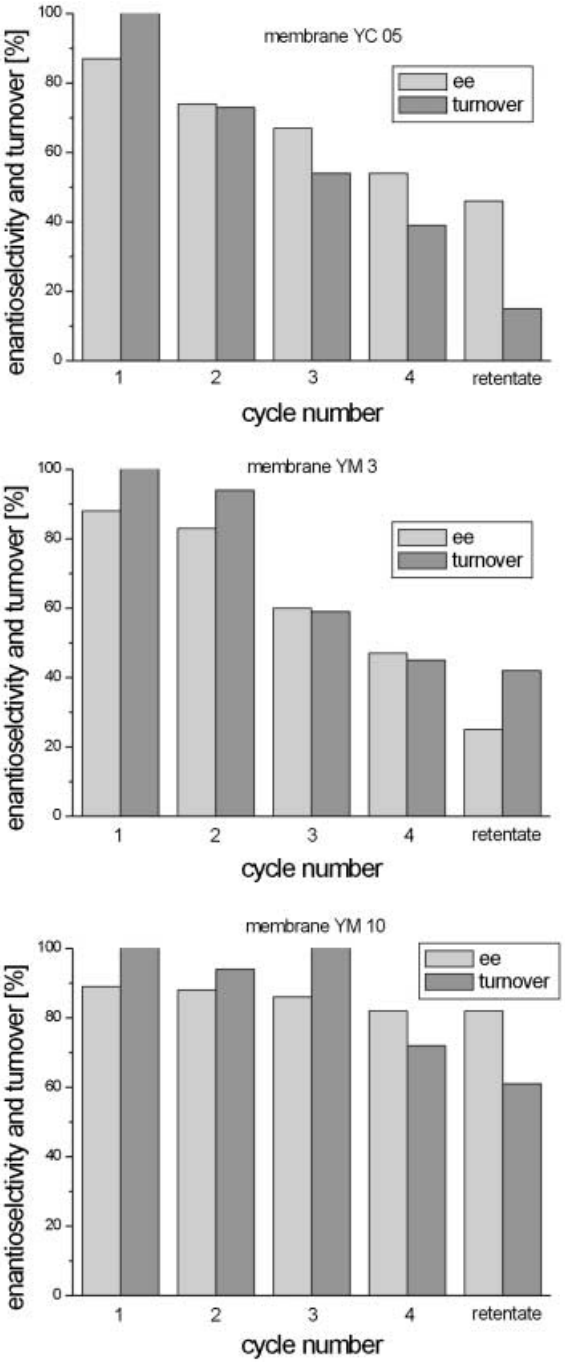


Figure 1. Turnover and enantioselectivity pattern of PSC **1** in the asymmetric hydrogenation for different membranes.

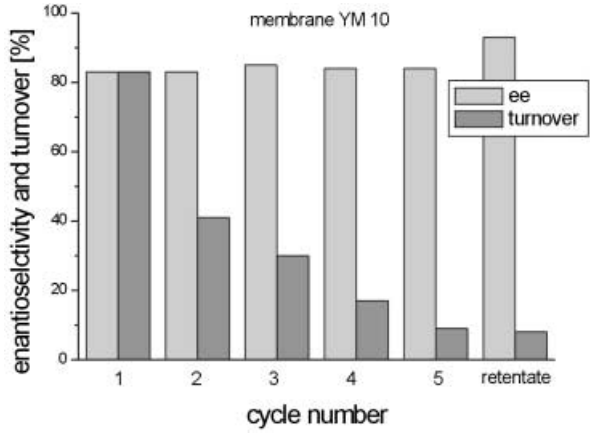


Figure 2. Turnover and enantioselectivity pattern of PSC **2** by use of membrane YM 10.

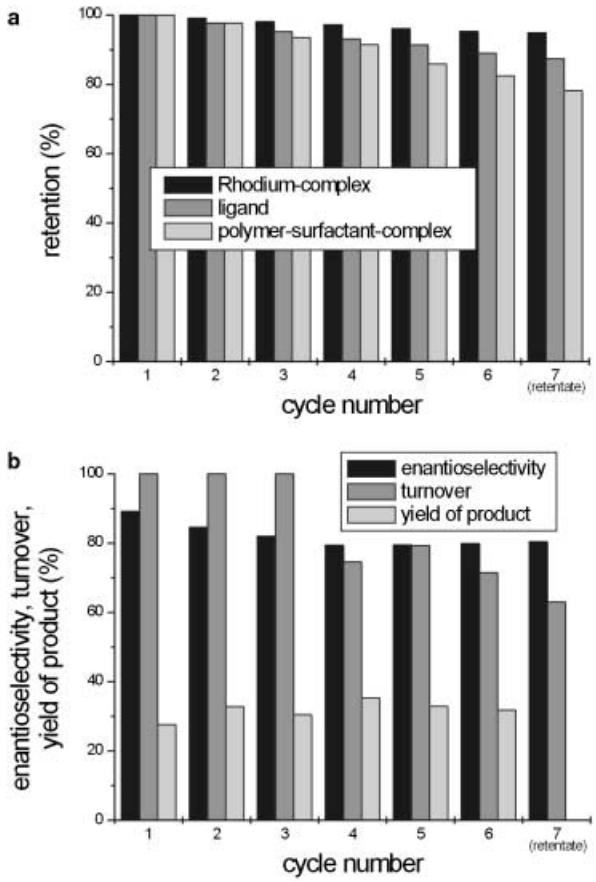


Figure 3. (**a**) Results of the asymmetric hydrogenation with PSC **3** using membrane YM 10; (**b**) retention of the Rh complex, the ligand and of PSC **3** for membrane YM 10.

were obtained with the membrane YM 10 (MWCO 10,000): after a filtration time of less than 8 minutes per cycle the reduction in both turnover and enantioselectivity was tolerable. That is why we chose the membrane YM 10 for further experiments. This was possible because the MW of the PSCs was high enough to expect that they are retained almost quantitatively.

In contrast to the PSC **1**, the quaternized and sulfated poly(ethyleneimine)/Tween 20 complex (PSC **2**) showed a quite different behavior (Figure 2): after a series of 6 cycles the turnover was reduced to a marginal value while the enantioselectivity did not change at all. On the contrary, it was raised in the retentate considerably. This means clearly that the catalyst cannot be decomposed, but seems to be blocked by the product.

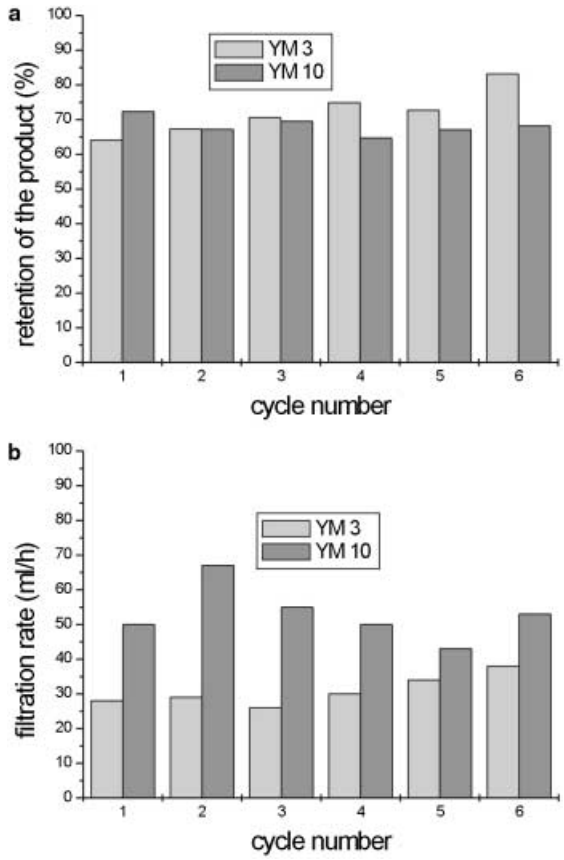


Figure 4. (**a**) Filtration rates of membranes YM 3 and YM 10 for the micellar-enlarged system with PSC **3**; (**b**) retention of the product by the membranes YM 3 and YM 10.

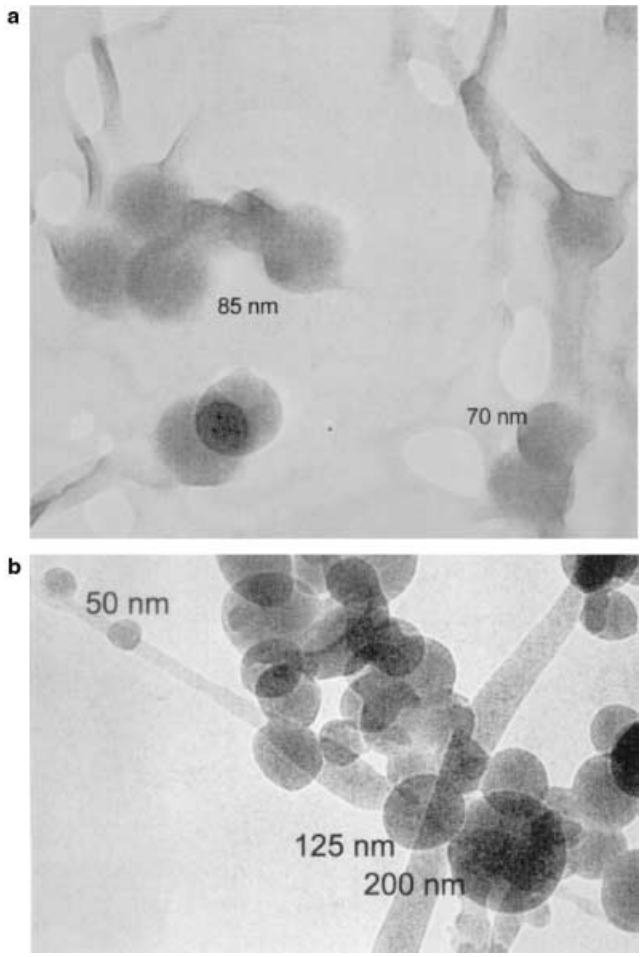


Figure 5. TEM micrographs from a 0.1 wt % aqueous solution of PSC **3** after sublimation of the vitrified water (**a**) before and (**b**) after solubilization of the catalytic system.

Apparently, the polyamphiphile has a rather compact structure, so that the hindrance of transport processes becomes evident. Moreover, the minor activity of PSC **2** in comparison to that of PSC **1** and PSC **3** can be explained by the different nature of the polyamphiphiles. PSC **2** is a positively charged ammonium polyamphiphile containing a neutral surfactant cooperatively bound to the hydrophobic domains. It seems reasonably that the positively charged Rh(I) complex is incorporated and immobilized by the PSC **2** to a lesser extent than by the other PSCs bearing a negative charge.

The slightly cross-linked PSC **3**, an amphiphilic diblock copolymer based on *N*-isopropylacrylamide which has been generated in a micellar dispersion of SDS, rendered the best catalytic results when applied in the membrane reactor (Figure 3a). The stereoselectivity remains on a rather high level (more than 80% ee) after 7 catalytic cycles. The turnover, however, drops continuously after being quantitative during the first 3 cycles. This can be rationalized by an increasing blockage of the encapsulated catalyst also in this case and a low exchange of the product by the educt within the PSC as is reflected by the low yield of product per cycle (about 30%). The reason for this is obviously the insufficient water solubility of the product. The decomposition and leaching of the catalyst is only of minor importance and not decisive as can be seen from Figure 3b. Also the leaching of the SDS from the PSC which has been determined by sulfur analyses after each cycle is practically not significant for the performance of the catalyst.

The retention behavior of the membranes YM 3 and YM 10 for the product is similar (Figure 4a), but the filtration rates are clearly different (Figure 4b).

To get more insight into the morphology of the polyamphiphiles, PSC **3** has been investigated by visualization methods. In Figure 5 are shown TEM micrographs from a 0.1 wt % aqueous solution of PSC **3** in the absence (**a**) and presence (**b**) of the solubilized catalytic system. Within a gel-like polymeric network consisting of cross-linked polymeric strands individual spherical micelles are seen embedded in the polymer structure: There is a significant difference in size between micellar assemblies before and after solubilization of the catalytic system. The solubilization entails an enlargement of the aggregates up to a diameter of 300 nm and leads partially to the formation of micellar clusters that are

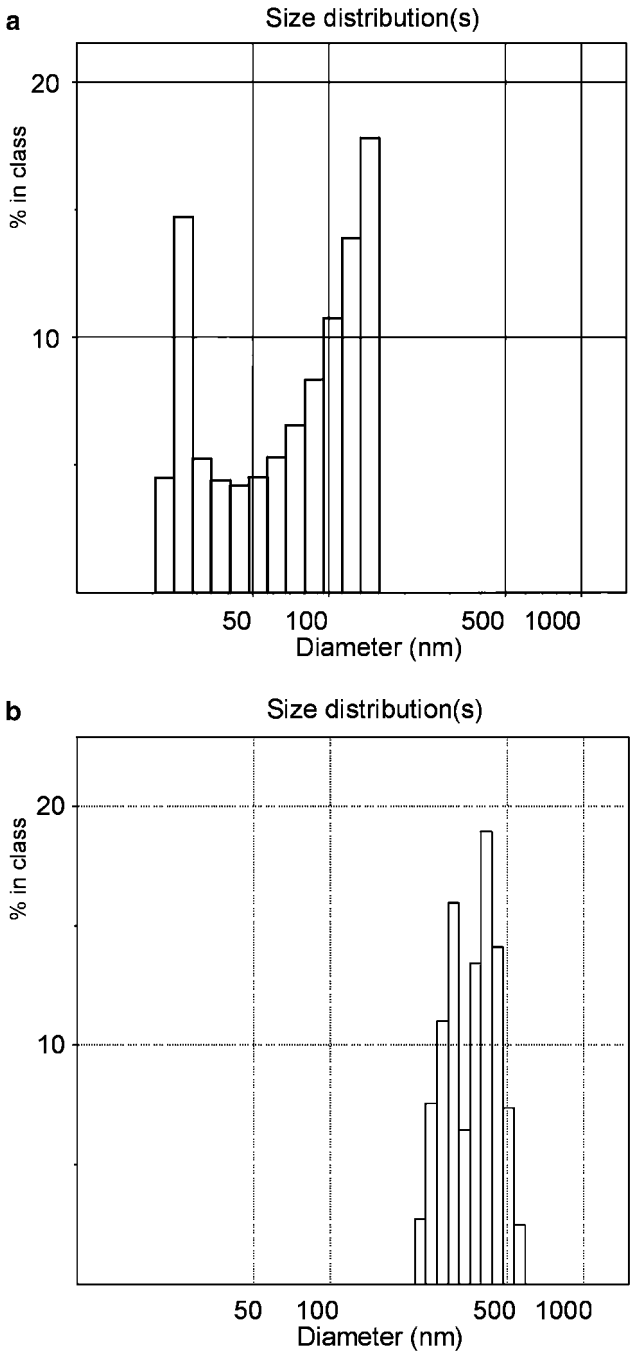


Figure 6. Particle size distribution in a 2 wt % aqueous solution of PSC **3** measured by photon correlation spectroscopy (**a**) before and (**b**) after solubilization of the catalytic system.

not seen before solubilization where only spheres with a diameter < 100 nm could be detected within the polymeric network. This finding was corroborated by particle size measurements.

Figure 6 shows particle size distributions measured by photon correlation spectroscopy. After solubilization of the catalytic system (catalyst and substrate) within PSC **3** a shift of the average particle size was clearly observed.

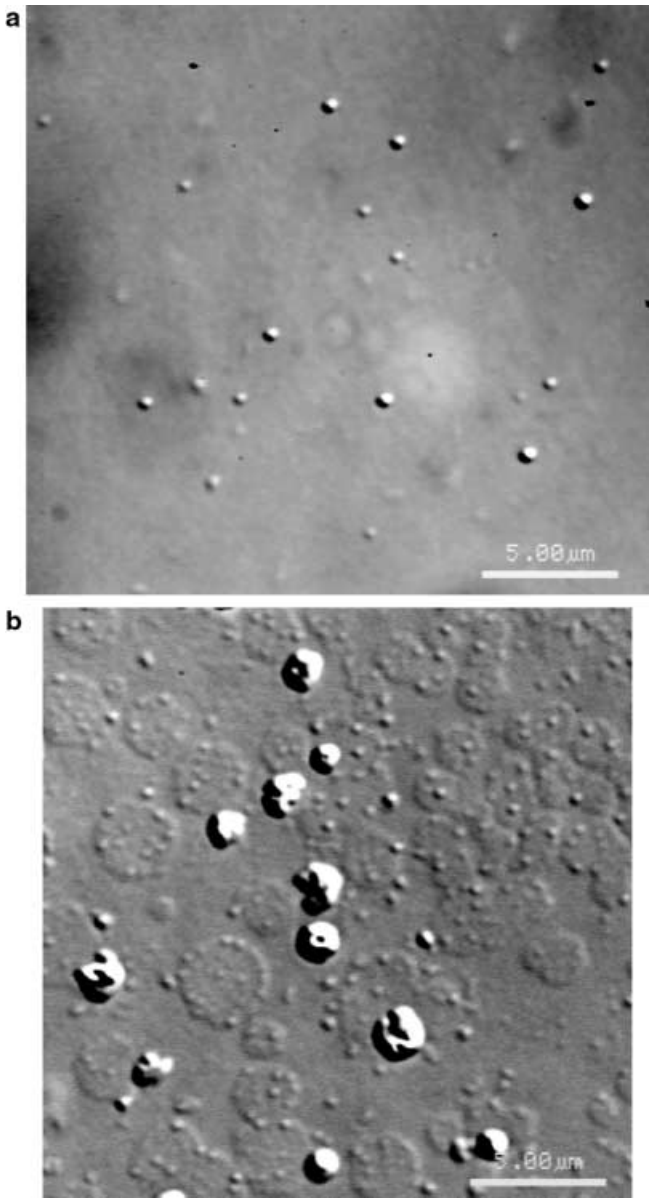


Figure 7. Light microscope images of a 2 wt % aqueous solution of PSC **3** (**a**) in solution after solubilization of the catalytic system; (**b**) near the glass-solution interface after solubilization of the catalytic system.

Additional information about the process that proceeds during solubilization was gained by high-resolution contrast light microscopy. Although the detection limit of this method is as low as 50 nm an aqueous solution of PSC **3** did not reveal any structures even though the concentration of the polyamphiphile was 2 wt % (the 20-fold concentration of the TEM solutions). However, upon solubilization of the catalyst and the substrate at the same concentration there emerged globular aggregates with a diameter in the range of 200 – 500 nm (Figure 7a). At the polar glass-solution interface characteristic circular-agglomerated structures composed of individual spheres became visible (Figure 7b)

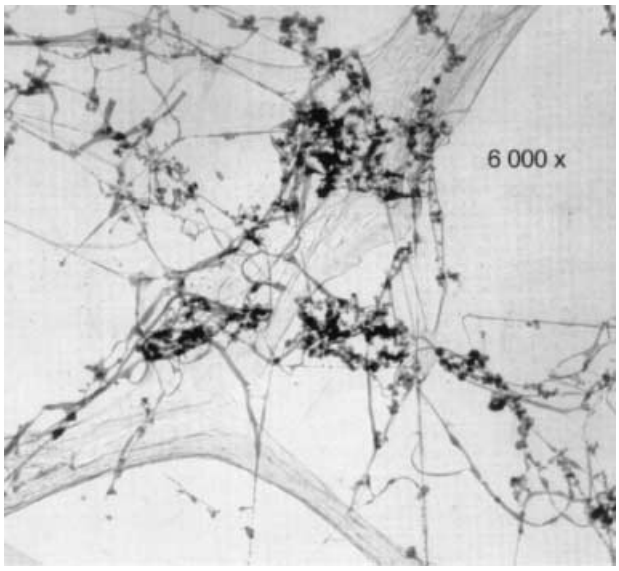


Figure 8. Gel structure with coordinated micelles of PSC **3** by TEM.

This might be an indication of a coagulation/precipitation process. Near the interface higher aggregated particles move within the solution being interpreted as floccules formed by secondary aggregation of polymeric micelles.

The polymer network which is seen in the TEM micrographs (Figure 8) could not be detected by light microscopy. This is due to the fact that the contrast of the strings of the water-swollen hydrogel is too low to be detected. This is different for the TEM images where, after sublimation of the vitrified water from the specimen in high vacuum, a xerogel remains decorated with spheroidal micelles (Figure 8). This is reminiscent of the well-known "beads-on-a-string"-structure or the "necklace" model for hydrophobically modified polymer-surfactant complexes[19,20].

Evaluating the TEM image of PSC **3** (Figure 8) one cannot exclude that shear forces contribute to the observed gel-like structure. It has been demonstrated by several authors[21–24] that shear-induced phase transitions can lead to supramolecular structures. Thereby three-dimensional networks are formed which behave like a gel. *N*-Isopropylacrylamide, the main component of PSC **3**, has some inherent hydrophobicity and interacts with surfactants like SDS under formation of intermolecular aggregates.[25–31] In general, when a non-ionic polymer acquires charges by binding an ionic surfactant, an increase in viscosity is to be expected on the basis of the "polyelectrolyte effect".[16] Micellar charge, whether positive or negative, definitely promotes micelle stabilization upon binding of polymers. The major effect comes from the influence of charged groups on the hydration sheath of the polymer.[32] It has been shown for a water-soluble non-ionic polymer[18] that increased interpolymer interactions lead to phase separations ("clouding") in the absence of an ionic surfactant. This indicates that an important consequence of the binding of surfactant is that it also counteracts the phase separation by increasing the osmotic pressure in the network and, hence, swelling the latter by strong hydration. Moreover, the polymer chains contribute to the formation of cross-linking micelles. Thereby, the gelling at the viscosity maximum corresponds to the highest cross-linking of the polymer chains, that is when approximately two intrachain aggregates merge into one cross-linking interchain aggregate.[33,34] To rationalize the good catalytic results of PSC **3** one can also speculate about a more open and water-penetrated structure of the polymer-bound micelles ("wet" micelles) as was postulated by Menger[35] and indicated by the results of several authors.[36–38]

Conclusion

It was shown that polymer-surfactant complexes of different composition and microstructure are suitable to encapsulate a homochiral Rh(I) catalyst and to use it repeatedly in the asymmetric hydrogenation of an prochiral amino acid precursor. The reaction pattern seems mainly be determined by the overall charge of the polyamphiphiles as well as their content of hydrophobic domains and, hence, their gel-like network structure in water. To reach acceptable times of filtration, the difference in the molecular weight of the polyamphiphiles and the MWCO of the membranes used should be as large as possible. It was shown in one case that the decomposition of the rhodium complex by gradual leaching of the chiral phosphine ligand is marginal. The main cause for activity depletion is an increased blockage of the PSCs by the product. Therefore, an important parameter is the hydrophilicity of the product, i.e., the more soluble in water it is, the more efficient is the separation process and the higher is the space-time yield. It has been demonstrated that amphiphilic gel-like structures with a high degree of coordinated micelles are preferable to more compact polyamphiphiles because they combine a high solubilization capacity with low diffusion constraints. Furthermore, it is apparent from this study that the stability and the enantioselectivity of the chiral catalyst are practically not affected by encapsulation.

Experimental Section

General

Synthesis and turnover control were performed by recording the ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.63 MHz) spectra (Bruker ARX-400) and by elemental analysis (Leco C, H, N, S automatic analyzer).

The separation and purification of the polymers was done by dialysis (3 500 NMWL tubing from Spectra/Por). The molecular weights (MWs) were determined by membrane osmometry (Knauer No. A 0330 with digital display, regenerated cellulose membrane 1 000 NMWL and cellulose acetate membrane 5 000 NMWL).

Size and size distribution of amphiphilic assemblies were determined by photon correlation spectroscopy (Zetasizer 3000, Malvern Instrument, analysis model: multimodal) and transmission electron microscopy (Zeiss EM 912 Omega, 120 kV). The micrographs were obtained after shock-frozen lamellas of the aqueous solution of the amphiphiles (0.1 – 0.2 wt %) had been carefully evaporated from a carbon-coated copper grid (200 mesh) under high vacuum at room temperature. Specimens were examined in a low-dose imaging mode to minimize electron-beam radiation damage. Images were recorded at an appropriate objective lens under focus conditions to enhance phase-contrast. High-resolution light microscopy was performed by differential interference contrast microscopy (AVEC-DIC) with a Nicon Diaphot 300 instrument and a Hamamatsu C 2 400-07 Newvicon camera.

The enantiomeric excess of the hydrogenation product methyl *N*-acetylphenylalaninate was determined by GLC on an HP chromatograph 5880A fitted with a 10 m capillary column coated with XE-60-1-*N*-*tert*-butylvalinamide (FID, split 1:60, 150 °C).

All chemicals were used as purchased from Aldrich or Fluka. Solvents were purified and dried following standard procedures. Methyl (Z)-α-acetamidocinnamate[39] and $[Rh(cod)_2]BF_4$[40] were prepared by known methods.

Water was purified and deionized by a TAK-LAB system. The measured conductivity value was as low as 0.056 μS cm^{-1}.

Asymmetric Hydrogenation

The hydrogenation reaction requiring a gas phase was run in a magnetically stirred filtration cell made from glass, teflon and stainless steel (model SR 75, Schleicher and Schuell, Einbeck, Germany). The filtration cell was fitted with ultrafiltration membranes of different MW cut-offs (MWCOs). The used membranes in a MWCO interval of 3,000 – 10,000 D were supplied by Amicon/Millipore, Eschborn, Germany. Before the start of the hydrogenation reaction the membranes were equilibrated by pumping deoxygenated water through the reactor for several hours under argon. Thereafter a catalyst dispersion containing 2 mg (0.005 mmol) $[Rh(cod)_2]BF_4$, 2.8 mg (0.005 mmol) of the chiral ligand (2*S*,4*S*)-*N*-*tert*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine (BPPM; Merck)[41] and 0.1 mmol of the polymer-surfactant complex in 15 mL deoxygenated water was introduced into the argon filled membrane reactor. The amount of the polymer-surfactant complex was calculated considering the molar percentage of amphiphile within the polymer and from the data of the elemental analysis of the amphiphilic polymers generated in the absence or presence of the surfactant. The prochiral substrate methyl (*Z*)-α-acetamidocinnamate (110 mg, 0.5 mmol) was added and the reactor was tightly closed. After two hours stirring under argon the latter was replaced by hydrogen at atmospheric pressure and the hydrogenation started by stirring. At intervals of two hours the hydrogenation reaction was stopped by flushing out the hydrogen by argon and removing 10 mL of the solution. Fresh substrate (110 mg, 0.5 mmol) and water (10 mL) were added and, after replacing the argon by hydrogen and starting the stirrer, a new reaction cycle was performed. Each collected sample was extracted with the same volume of chloroform. The organic phase was separated and the enantiomeric excess (ee) of the hydrogenation product methyl *N*-acetylphenylalaninate was determined by GLC on a chiral column as mentioned above. To determine the leaching rate of the catalyst and the ligand as well as of the surfactant, samples were analyzed for rhodium and phosphorus.

Poly(oxyethylene)$_{23}$ Dodecyl Ether Methacrylate/SDS (1)

Poly(oxyethylene)$_{23}$ dodecyl ether methacrylate[42] (2.6 g, 2.05 mmol) with 2 mol % of 2,2′-azobisisobutyronitrile (AIBN) as radical initiator were dissolved in 170 mL deoxygenated water containing sodium dodecyl sulfate (SDS) (2.62 g, 9.1 mmol) as surfactant. The concentration of SDS was seven-fold of the critical micelle concentration (CMC).[43] The micellar photopolymerization was conducted for 6 h at 60 °C with UV light (254 nm). The resulting clear solution was dialyzed with water until no SDS could be detected in the filtrate (72 h). The dialyzate was evaporated under vacuum and yielded 5.6 g of an almost colorless, waxy product which did not show methacrylic signals at 6.1 – 5.5 ppm in the ^{1}H NMR spectrum. Molecular weight: 29,000 g mol^{-1} (by membrane osmometry). Elemental analysis of the PSC (%): C 58.42, H 9.61, S 0.33. On the basis of the sulfur value a molar percentage of approximately 11% SDS was calculated.

Quaternized and Sulfated Poly(ethyleneimine)/Tween 20 (2)

2.0 g (1.57 mmol, related to one monomeric unit) of the quaternized and sulfated poly(ethyleneimine),[44] the structural formula of which is depicted in Scheme 1, were stirred with 3.0 g (2.45 mmol) of the surfactant Tween 20 (Fluka) in 150 mL deoxygenated water for 2 h at 60 °C. After that time the dispersion was dialyzed at 25 °C until no free surfactant could be found in the filtrate (96 h). The dialyzate was evaporated under vacuum and yielded 2.2 g of a hygroscopic, gel-like material (MW 11,500 g mol^{-1}). Elemental analysis (%): C 36.43, H 7.05, N 11.86, S 13.76. Considering the molecular weight of Tween 20 as 1226 g mol^{-1},[45] the content of the entrapped surfactant after dialysis was 8 mol %.

Cross-Linked Poly(*N*-Isopropylacrylamide-*co*-Dodecyl Methacrylate)/SDS (3)

N-Isopropylacrylamide (5.66 g, 50 mmol), dodecyl methacrylate (0.48 g, 2 mmol) and 1.2 mL of a 40% aqueous solution of the cross-linker acrylamide/*N,N*′-methylenebisacrylamide (37.5:1, Fluka) were dissolved in the micellar medium of SDS (3,5 g, 12.1 mmol) in 170 mL deoxygenated water. The mixture was polymerized by UV light (254 nm) for 4 h at 35 °C in the presence of 1 mol % α,α-diethoxyacetophenone/triethylamine as photoinitiator. This time was sufficient for a quanti-

tative polymerization as was judged by the disappearance of the ^{1}H NMR signals of the vinylic protons (6.3 – 5.5 ppm). The solution of the polyamphiphile was dialyzed with water until no SDS was in the filtrate (72 h). The residual dispersion of the polyamphiphile was evaporated under vacuum and yielded 9.4 g of a yellowish, waxy product. Elemental analysis (%): C 60.47, H 9.55, N 8.37, S 3.50. MW 226,000 g mol^{-1}. The content of SDS within the polyamphiphile was 15 mol %.

Acknowledgements

We are grateful to Mrs. R. Kross for the rhodium and phosphorus analyses and to T. Wöllert from the center of light microscopy, Fachbereich Biowissenschaften der Universität Rostock, for his assistance in making the micrographs. Funding of this work by the Bundesministerium für Bildung und Forschung (BMBF) is gratefully acknowledged.

References

[1] U. Kragl, C. Dreisbach, C. Wandrey, in *Applied Homogeneous Catalysis*, (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, pp. 832 – 843 and references cited therein.

[2] R. A. Sheldon, *Chirotechnology: Industrial Synthesis of Optically Active Compounds*, Marcel Dekker, New York, **1993**.

[3] E. Bayer, V. Schurig, *Angew. Chem*. **1975**, *87*, 484 – 485; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 388 – 390.

[4] E. Steckhan, S. Herrmann, R. Ruppert, J. Thömmes, C. Wandrey, *Angew. Chem*. **1990**, *102*, 445 – 447; *Angew. Chem. Int. Ed. Engl*. **1990**, *29,* 388 – 390.

[5] a) U. Kragl, C. Dreisbach, *Angew. Chem.* **1996**, *108*, 684 – 685; *Angew. Chem. Int. Ed. Engl*. **1996**, *35,* 642 – 644; b) G. Giffels, J. Beliczey, M. Felder, U. Kragl, *Tetrahedron Asymmetry* **1998**, *9*, 691 – 696.

[6] E. Schwab, S. Mecking, *Organometallics* **2001**, *20*, 5504 – 5506.

[7] J. Woltinger, A. S. Bommarius, K. Drauz, C. Wandrey, *Org. Process Res. Dev*. **2001**, 5, 241 – 248.

[8] a) H. Bahrmann, M. Haubs, Th. Müller, N. Schöpper, B. Cornils, *J. Organomet. Chem*. **1997**, *545-546*, 139 – 149; b) Th. Müller, H. Bahrmann, *J. Mol. Catal. A: Chem*. **1997**, *116*, 39 – 42.

[9] N. Brinkmann, D. Giebel, G. Lohmer, M. T. Reetz, U. Kragl, *J. Catal*. **1999**, *183*, 163 – 168.

[10] a) D. de Groot, J. C. de Wilde, R. J. van Haaren, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, E. B. Esseling, D. Vogt, H. Kooijman, A. L. Spek, A. W. van der Made, *Chem. Commun*. **1999**, 1623 – 1624; b) N. J. Hovestad, E. B. Eggeling, H. J. Heidbüchel, J. T. B. H. Jastrzebski, U. Kragl, W. Keim, D. Vogt, G. van Koten, *Angew. Chem*. **1999**, *111*, 1763 – 1765; *Angew. Chem. Int. Ed*. **1999**, *38*, 1655 – 1658; c) E. B. Eggeling, N. J. Hovestad, J. T. B. H. Jastrzebski, D. Vogt, G. van Koten, *J. Org Chem.* **2000**, *65*, 8857 – 8865.

[11] T. Dwars, J. Haberland, I. Grassert, G. Oehme, U. Kragl, *J. Mol. Catal. A: Chem*. **2001**, *168*, 81 – 86.

[12] F. Candau, J. Selb, *Adv. Colloid Interface Sci*. **1999**, *79*, 149 – 172 and references cited therein.

[13] I. Iliopoulos, *Curr. Opin. Colloid Interface Sci*. **1998**, *3*, 493 – 498.

[14] I. Iliopoulos, T. K. Wang, R. Audebert, *Langmuir* **1991**, *7*, 617 – 619.

[15] R. Zana, A. Kaplun, Y. Talmon, *Langmuir* **1993**, *9*, 1948 – 1950.

[16] E. D. Goddard, *J. Am. Oil Chem. Soc*. **1994**, *71*, 1 – 16.

[17] L. Piculell, F. Guillemet, K. Thuresson, V. Shubin, O. Ericsson, *Adv. Colloid Interface Sci*. **1996**, *63*, 1 – 21.

[18] P. Hansson, B. Lindman, *Curr. Opin. Colloid Interface Sci*. **1996**, *1*, 604 – 613.

[19] K. Shirahama, K. Tsujii, T. Takagi, *J. Biochem*. **1974**, *75*, 309 – 319.

[20] B. Cabane, R. Duplessix, *Colloids Surf*. **1985**, *13*, 19 – 33.

[21] a) I. Wunderlich, H. Hoffmann, H. Rehage, *Rheol. Acta* **1987**, *26*, 532 – 542; b) S. Hoffmann, A. Rauscher, H. Hoffmann, *Ber. Bunsenges. Phys. Chem*. **1991**, *95*, 153 – 164.

[22] S. Q. Wang, *J. Phys. Chem*. **1990**, *94*, 8381 – 8384.

[23] J. L. Jones, C. M. Marques, J.-F. Joanny, *Macromolecules* **1995**, *28*, 136 – 142.

[24] a) C. Liu, D. J. Pine, *Phys. Rev. Lett*. **1996**, *77*, 2121 – 2124; b) S. L. Keller, P. Boltenhagen, D. J. Pine, J. A. Zasadzinski, *Phys. Rev. Lett*. **1998**, *80*, 2725 – 2728.

[25] F. M. Winnik, H. Ringsdorf, J. Vencmer, *Langmuir* **1991**, *7*, 905-911; 912 – 917.

[26] H. G. Schild, D. A. Tirell, *Langmuir* **1991**, *7*, 665 – 671.

[27] E. Kokufuta, Y.-Q. Zhang, T. Tanaka, A. Mamada, *Macromolecules* **1993**, *26*, 1053 – 1059.

[28] G. Staikos, *Macromol. Rapid Commun*. **1995**, *16*, 913 – 917.

[29] G. Bokias, D. Hourdet, I. Iliopoulos, G. Staikos, R. Audebert, *Macromolecules* **1997**, *30*, 8293 – 8297.

[30] P. W. Zhu, D. H. Napper, *Macromol. Chem. Phys.* **1999** *200*, 783 – 790.

[31] D. Gan, L. A. Lyon, *J. Am. Chem. Soc*. **2001**, *123*, 7511 – 7517.

[32] J. C. Brackman, J. B. F. N. Engberts, *Chem. Soc. Rev.* **1993**, *22*, 85 – 92.

[33] A. Sarrazin-Cartalas, I. Iliopoulos, R. Audebert, U. Olsson, *Langmuir* **1994**, *10*, 1421 – 1426.

[34] B. Magny, I. Iliopoulos, R. Zana, R. Audebert, *Langmuir* **1994** *10*, 3180 – 3187.

[35] a) F. M. Menger, *Acc. Chem. Res.* **1979**, *12* 111 – 117; F. M. Menger, C. E. Mounier, *J. Am . Chem. Soc*. **1993**, *115*, 12222 – 12223.

[36] R. Zana, P. Lianos, J. Lang, *J. Phys. Chem*. **1985**, *89*, 41 – 44.

[37] R. Varadaraj, J. Bock, P. Valint, N. Brons, *Langmuir* **1990**, *6*, 1376 – 1378.

[38] N. Kamenka, I. Burgaud, C. Treiner, R. Zana, *Langmuir* **1994**, *10*, 3455 – 3460.

[39] A. H. Cook, G. Harris, J. Heilbron, *J. Chem. Soc*. **1948**, 1060 – 1065.

[40] M. Grenn, T. A. Kuc, S. H. Taylor, *J. Chem. Soc*. A **1971**, 2334 – 2337.

[41] K. J. Achiwa , *J. Am. Chem. Soc*. **1976**, *98*, 8265 – 8266.

[42] G. Oehme, I. Grassert, E. Paetzold, R. Meisel, K. Drexler, H. Fuhrmann, *Coord. Chem. Rev.* **1999**, *185*, 585 – 600.
[43] J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley-Interscience, New York, **1982**, p. 9.
[44] H. Fuhrmann, I. Grassert, Th. Schareina, G. Holzhüter, G. Oehme, *Macromol. Chem. Phys.* **2001**, *202*, 426 – 434.
[45] I. Grassert, E. Paetzold, G. Oehme, *Tetrahedron* **1993**, *49*, 6605 – 6612.