Hydrophobically modified water-soluble polymers and polyelectrolytes as micellar promotors in the Rh(I) catalyzed hydrogenation of an amino acid precursor in water

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Hydrophobically modified water-soluble polymers (HMWSP's) and hydrophobically modified polyelectrolytes (HMPE's,''polysoaps'') of various compositions and different molecular weights have been prepared and used in the micellar promoted enantioselective hydrogenation of methyl (*Z*)-α-acetamidocinnamate with a chiral Rh(I) catalyst in aqueous medium. The efficiency of the micellar polymers in the catalytic reaction is greatly determined by their solubility (dispersibility) behavior and solubilization capacity for catalyst and substrate. The latters depends on the compactness of the polyamphiphiles as revealed by transmission electron microscopy (TEM) and light microscopy images. The highest catalytic performance was obtained with polymer-surfactant complexes prepared by micellar copolymerization with neutral or anionic tensides, regardless of the electrical charge of the hydrophobically modified polymer. In most cases a synergism between rate and enantioselectivity has been observed.

The advantage of water as a solvent in organic reactions consists not only in that it is the cheapest, most environmentally friendly and ubiquitous solvent, but also that it is the base of all chemical and physical processes in living organisms. Therefore, water has been chosen as a solvent even where the reacting components are scarcely water-soluble. In such cases the reactivity can be dramatically enhanced when amphiphiles are present, which above a certain concentration (critical micelle concentration, CMC) may self-assemble into aggregates (micelles, vesicles) that are capable of solubilizing the reactants. The enhancement of reaction rates within micelles is designated as micellar catalysis.[1] Several attempts have been made to use polymerized micelles and micellar polymers as microreactors for catalytic reactions.[2–4] An important argument to chose polymer micelles for the encapsulation of the catalyst in place of micelles from monomer amphiphiles was the intention to use them in the future in a membrane reactor with the purpose to separate the micellar entrapped catalyst from the reaction medium. The aim of this work was to use hydrophobically modified water-soluble polymers (HMWSP's) and polymer-surfactant complexes (PSC's) as carriers for a chiral Rh(I) catalyst and see whether there is any relation between the chemical nature and structure of the polyamphiphiles and the catalytic activity and stereoselectivity examplified in the asymmetric hydrogenation of a prochiral amino acid precursor in water.

Experimental

General

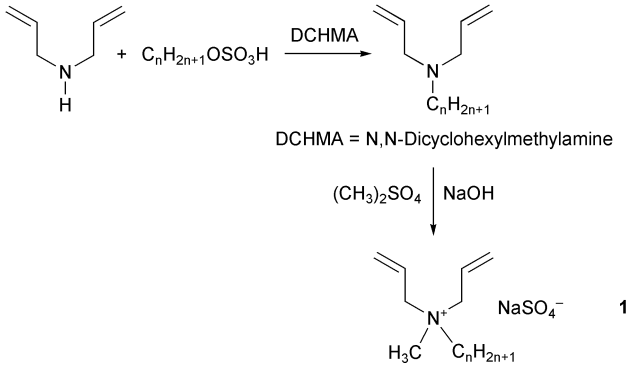
Synthesis and turnover control were performed by recording of ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.63 MHz) spectra (Bruker ARX-400), FTIR spectroscopy (Nicolet magna 550) and elemental analysis (Leco C, H, N, S automatic analyzer).

The separation and purification of the polymers was done by gel filtration on Sephadex G25 and dialysis (3 500 NMWL tubing from Spectra/Por). The molecular weights (MW's) were measured 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 3 000, 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 appropriate objective lens underfocus 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 Kamera.

The enantiomeric excess of the hydrogenation product methyl *N*-acetylphenylalaninate was determined by GLC on a 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. The hydrogenation educt methyl (*Z*)-α-acetamidocinnamate[5] and the hydrogenation precatalyst $[Rh(cod)_2]BF_4$[6] were prepared by known methods.



Scheme 1

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

Polymerization and copolymerization of amphiphiles

The photoinitiated free-radical polymerization of the monomers and comonomers in water was carried out in a quartz reactor mostly in the presence of 1–2 mol % of a radical initiator. For details see ref. 4*d*. The concentration of the monomers was 3–5 wt %. In all cases the polymerization experiments were conducted to completion as was judged by the disappearance of the ^{1}H NMR signals of the vinylic (6.3–5.5 ppm) protons. The polymerization conditions were chosen according to the reactivity of the components to be polymerized and are indicated in the next paragraph. To remove initiator residues and low molecular side products the polymerization products were dialyzed against water (72 h). In case of micellar polymerization in the presence of tensides the dialysis was continued until no tenside could be detected in the filtrate. Samples of the isolated or re-dispersed polymerized amphiphiles were taken for elemental analysis, molecular mass determination, structural characterization (particle size analysis, high-resolution light microscopy, TEM) and catalysis.

Syntheses

Sodium diallyldodecylmethylammonium sulfate **1** (Scheme 1) was prepared by reaction of the dodecyl monoester of sulfuric acid [from 1-dodecanol and $SO_3{\cdot}(CH_3)_3N$ in DMF] and diallylamine (1 : 1 in the presence of *N*,*N*-dicyclohexylmethylamine as the binding agent for the released sulfuric acid). In a further step the quaternization of the tertiary amine was effected by an excess of $(CH_3)_2SO_4$ in dilute NaOH (pH ~9). **1** was extracted from the reaction mixture with hot ethanol. After evaporation of both the solvent and excess amine the residue was dissolved in warm acetone from which **1** precipitated on cooling. **1** was recrystallized from acetone. Elemental analysis of **1**: calcd for $C_{19}H_{38}NO_4SNa$: C 57.14, H 9.52, N 3.51, S 8.02%. Found: C 56.71, H 9.70, N 3.39, S 7.38%.

1a was obtained after polymerization of **1** in water under the following conditions: UV light 185 nm, 60 °C, 6 h, 2 mol % $K_2S_2O_8/Na_2S_2O_5$ (Scheme 2). The copolymerization with acrylamide (20 mol %) at 60 °C, 4 h, 254 nm UV, 1 mol % α,α-diethoxyacetophenone (DEAP)/triethylamine as initiator gave **1b**. The copolymerization of **1** in a micellar medium of sodium dodecylsulfate (SDS) under the aforementioned conditions but with 70 mol % acrylamide resulted in a polymer-surfactant complex **1d** with a content of 8 mol % SDS.

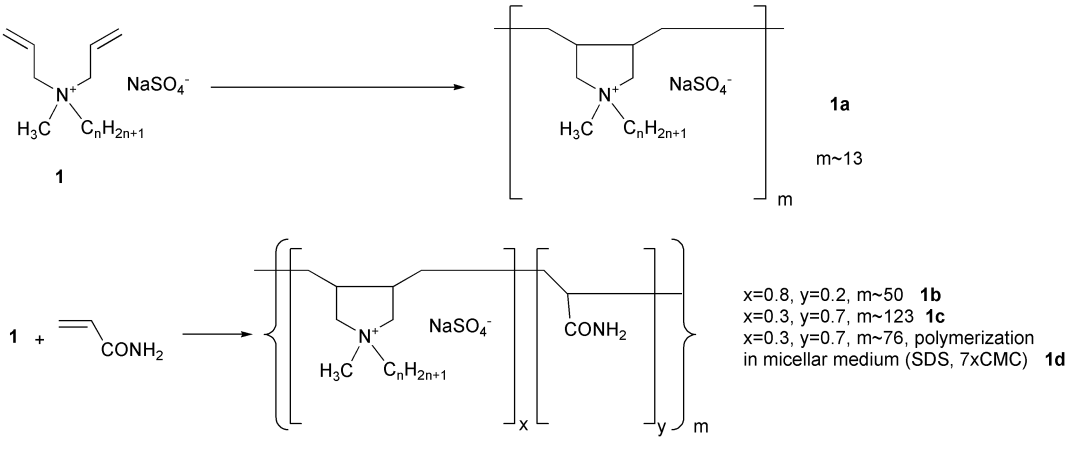
The copolymerization of dimethylacrylamide with 2 mol % of sodium methacryloyloxyundecyltrimethylammonium sulfate **2**, the synthesis of which was described in ref. 4*d*, afforded **2b**. Polymerization conditions were 254 nm UV, 30 °C, 4 h, 2 mol % 4,4′-azobis(4-cyanovaleric acid) (ACVS) as initiator (Scheme 3).

3 was obtained by copolymerization of *N*-vinyl-2-pyrrolidone with sodium *N*-dodecylmaleamate (prepared by reaction of maleic anhydride with dodecylamine in dioxane following neutralization with NaOH in a 1 : 1 molar ratio). Polymerization conditions were 254 nm UV, 60 °C, 6 h, 2 mol % azoisobutyronitrile (AIBN) (Scheme 4).

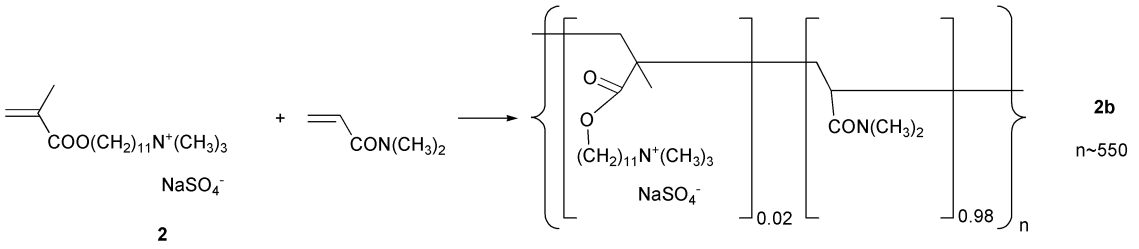
The copolymerization of acryloyloxyethyltrimethylammonium methyl sulfate (Aldrich) with 2 mol % **2** at 60 °C, 4 h, UV 254 nm, yielded a copolymer with amphiphilic properties (**4a**, Scheme 5). The same reaction in the presence of SDS at a concentration of about 7 times the CMC resulted in the polymer-surfactant complex **4b** containing after dialysis 6 mol % SDS as checked by sulfur analysis.

The copolymerization of acrylic acid (Fluka) with 1 mol % dodecylacrylate (Fluka) and the neutral amphiphile poly(oxyethylene)$_{23}$dodecylether methacrylate[4c] (5 mol %) resulted in **5a** (Scheme 6). The micellar copolymerization of acrylic acid with 1 mol % dodecylacrylate in an aqueous solution of SDS afforded **5b**. Polymerization conditions were 254 nm UV, 40 °C, 4 h, 1 mol % DEAP/Et_3N. The copolymer solutions of **5a** and **5b** were neutralized with NaOH. After dialysis **5b** contained 3 mol % SDS.

The polymer-surfactant complex **6** was prepared by mixing the quaternized and sulfated poly(ethylenimine), the synthesis of which was described in ref. 4*d*, with an exess of the surfactant Tween 20. The aqueous solution was stirred for 3 h. Thereafter the mixture was dialyzed until no surfactant could be detected in the filtrate. The amount of the entrapped surfactant was ~6 mol % (from elemental analysis) (Scheme 7).

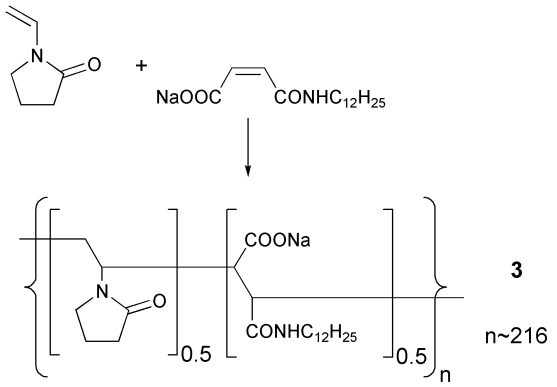


Scheme 2



the synthesis of **2** and its homopolymer **2a** are described in ref. 4d

Scheme 3



Scheme 4

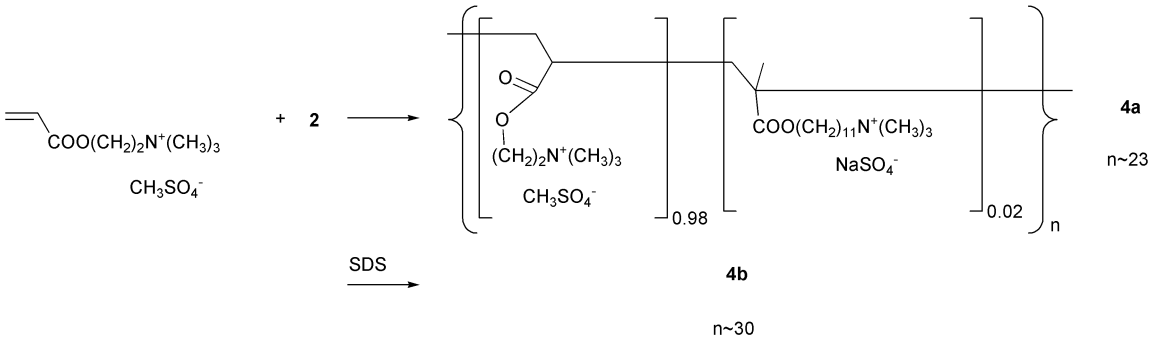
Asymmetric hydrogenation

The hydrogenation was performed by an isobaric method at 25 °C under air-free conditions in a thermostatted apparatus (Scheme 8).[4d] $[Rh(cod)_2]BF_4$ (0.01 mmol) and 0.01 mmol of the chiral, nonracemic ligand (2*S*,4*S*)-*N*-*tert*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine (BPPM) together with 0.1–0.2 mmol of the polymer amphiphile and 1 mmol of methyl (*Z*)-α-acetamidocinnamate were stirred in 15 mL water under argon. Thus, the molar ratio catalyst : amphiphile : substrate was 1 : 20 : 100. The amount of polymerized amphiphile was related to the molar percentage of amphiphile within the polymer. In the case of the polymer-surfactant complexes (micellar polymerization) the percentage of the entrapped tenside was estimated by comparison of the elemental analysis data of the amphiphilic polymers generated in the absence or presence of the tenside. Also, in these cases the polymerization was conducted quantitatively and the samples had been dialyzed as mentioned above. The time of stirring (equilibration time) of the dissolved polyamphiphile with the catalyst and the substrate varied between 1 h and 20 h, depending on the bulkiness of the polyamphiphile. The argon was replaced by hydrogen at ambient pressure and the reaction was started and followed volumetrically.

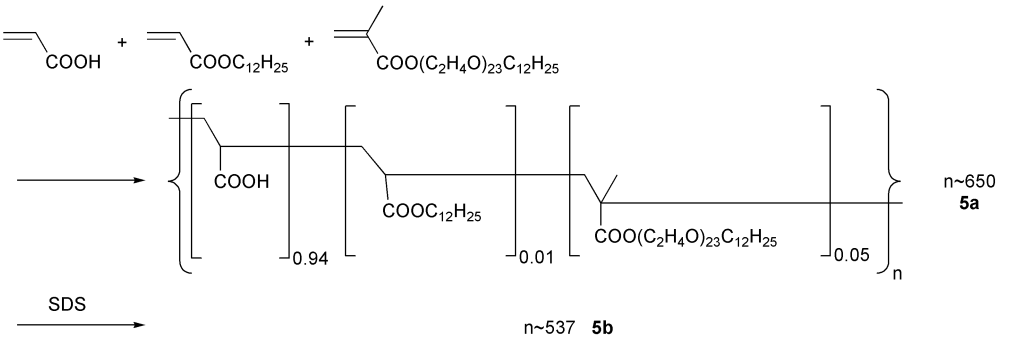
The time necessary to consume half of the theoretical amount of hydrogen ($t_{1/2}$) was taken as a measure of the activity. After finishing the experiment the mixture was extracted with 5 mL chloroform. The enantiomeric exess of the product was determined by GLC on a chiral column as mentioned above.

Results and discussion

In contrast to polymerized nonionic amphiphiles showing a high efficacy in the asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate with the $[Rh(bppm)(cod)]BF_4$ catalyst,[4c] ionic polyamphiphiles proved to be less efficient in many cases because of their poor water solubility and unfavorable solubilization properties.[4d] Therefore, to improve both properties, the polymerizable ionic amphiphiles were copolymerized with water-soluble monomers remaining dispersable also in the polymeric state. In general, most water-dispersable associating polymers are copolymers of a water-soluble monomer and a very hydrophobic comonomer at low mole fraction (usually between 0.1–2 mol %). In aqueous solution the hydrophobic moieties self-assemble intra- or intermolecularly. Intermolecular associations give rise to three-dimensional networks. Such systems are used as thickeners because of their high viscosity. A special case of associating polymers are the hydrophobically modified polyelectrolytes (HMPE's, "polysoaps") whose aqueous solutions have a rather low viscosity reflecting their compact conformation, which arises because the hydrophobic groups of the polyelectrolyte associate and form hydrophobic microdomains. This is obviously the case when the amphiphilic diallylammonium salt **1** is homopolymerized, giving a scarcely water-dispersable polymer which shows no catalytic effect (Table 1, **1a**). The free-radical-initiated polymerization, being a cyclopolymerization,[7] generates a rather hydrophobic main chain, which does not allow for sufficient water solubility. Therefore, the copolymerization with the



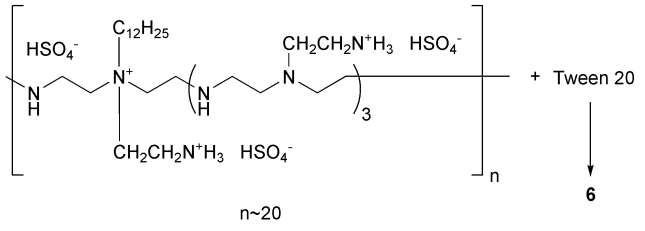
Scheme 5



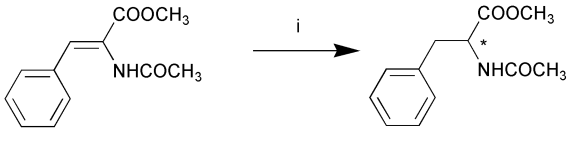
Scheme 6

water-soluble acrylamide was envisaged to obtain a water-soluble HMPE. The copolymer is presumed to be random.[3e] However, it may be possible that a blocky microstructure is formed due to the formation of micelles by the polymerizable surfactant **1**, providing a high concentration of the reactive allyl groups in the micelles.[8] Real block copolymers containing uncharged hydrophilic and cationic polysoap blocks were prepared for the first time by use of poly(ethylene oxide) based macroinitiators.[9] Contrary to what we expected, the catalytic effect of the amphiphilic copolymer **1b** was only moderate (Table 1, **1b**). Increasing the amount of acrylamide in the copolymer from 20 to 70 mol % (Table 1, **1b** and **1c**) led to a considerable increase of the hydrogenation rate, but practically did not affect the enantioselectivity. Obviously, the change of the hydrophilic/hydrophobic balance has improved the solubility behavior while leaving the stereoselectivity unchanged. But it was substantially increased when the copolymerization was run in micellar medium (Table 1, **1d**). This points to a favorable influence of the anionic surfactant SDS, which was embedded within the polyamphiphile at a level of 8 mol %. Micellar polymerization is characterized by a large excess of the surfactant in the polymerization solution. Surfactant/hydrophobe ratios of 20–100 are not uncommon in order to solubilize the hydrophobic monomer in the aqueous phase. Although we used an amphiphile as comonomer, its concentration was too low as to assure a continuous micellar phase during the polymerization. This is why the external surfactant SDS was used in excess. The role of the surfactant is two-fold: it ensures the solubilization of the hydrophobic/amphiphilic monomer in the aqueous medium and induces the formation of hydrophobic sequences whose length depends on the micellar concentration. In a micellar polymerization process one cannot *a priori* exclude compositional heterogeneity of full conversion samples because a greater incorporation of the hydrophobe at the beginning of the copolymerization may occur.[10] In general, micellar polymerization should favor a blocky structure of the copolymers,[11–13] although Hill *et al.*[14] demonstrated that the microstructure of hydrophobically associating polyacrylamides—random or blocky—is determined by the hydrophobe/micelle ratio. Unfortunately, a detailed analysis of the microstructure of our amphiphilic copolymers by NMR spectroscopy (determination of block sequences and block lengths) gave no reliable results on account of low signals resolution.

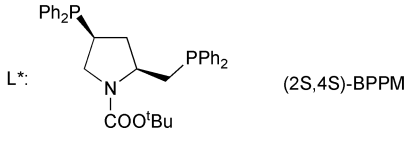
In Fig. 1 are shown TEM micrographs from a 0.1 wt % aqueous solution of the polymer-surfactant complex **1d** in the absence (a) and presence (b) of the solubilized catalytic system. Within a gel-like polymeric network consisting of cross-linked



Scheme 7



i = [Rh(cod)L*]BF_4, 25 °C, 1 bar H_2, H_2O, amphiphile
cod: 1,5-cyclooctadiene
catalyst : amphiphile : substrate = 1 : 20 : 100



Scheme 8

Table 1 Hydrogenation of methyl (*Z*)-α-acetamidocinnamate in water with the catalytic system [Rh(bppm)(cod)]BF_4 in the presence of polymeric amphiphiles. Molar ratio catalyst : amphiphil : substrate = 1 : 20 : 100

Polyamphiphile	Molecular weight/ g mol^{-1}	Equilibration time/h	Halftime of hydrogenation ($t_{1/2}$)/min	Excess of the R enantiomer (eeR) (%)
Without	–	1	90	78
1[a]	399	1	11	88
1a	5300	20	–	–
1b	16900	20	51	82
1c	21000	20	19	83
1d	12900	1	7	92
2[b]	395	1	480	80
2a[b]	2200	20	720	83
2b	58000	2	7	86
3	45000	1	110	89
3	45000	20	117	88
4a	6300	20	114	80
4b	8100	2	187	91
4b	8100	20	176	91
5a	86400	2	128	83
5b	71500	1	16	91
6	12700	1	6	94
6[c]	12700	1	10	93
6[d]	12700	1	13	92

[a] The monomer amphiphile, concentration 45 mmol L^{-1} (corresponding to two times the CMC). [b] The data from ref. 4*d* are shown for comparison. [c] Molar ratio amphiphile : catalyst = 10 : 1. [d] Molar ratio amphiphile : catalyst = 5 : 1.

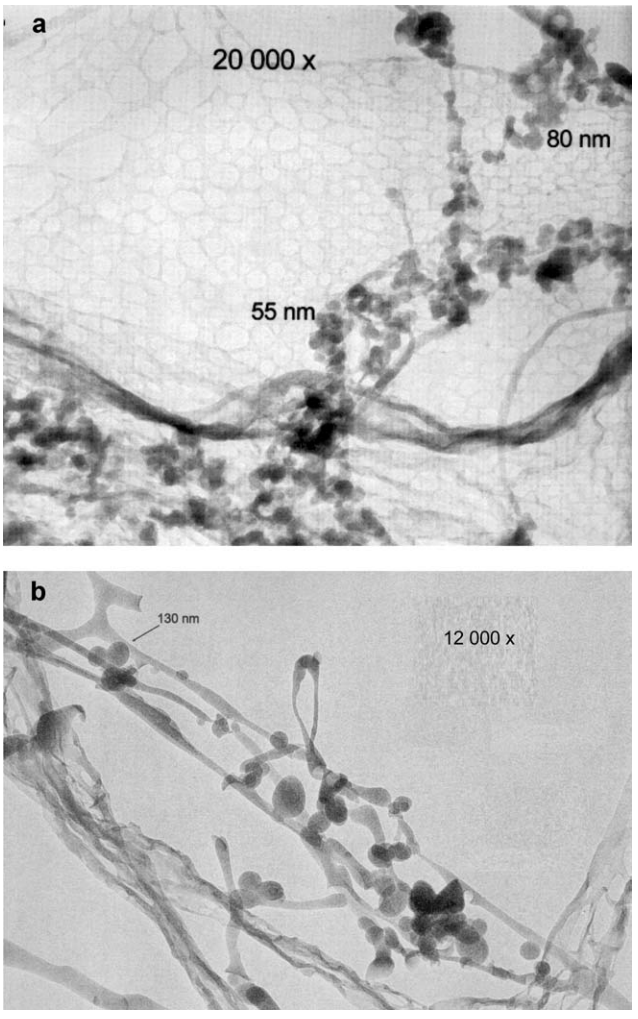


Fig. 1 TEM micrographs from a 0.1 wt % aqueous solution of the PSC **1d** after sublimation of the vitrified ice (a) before and (b) after solubilization of the catalytic system.

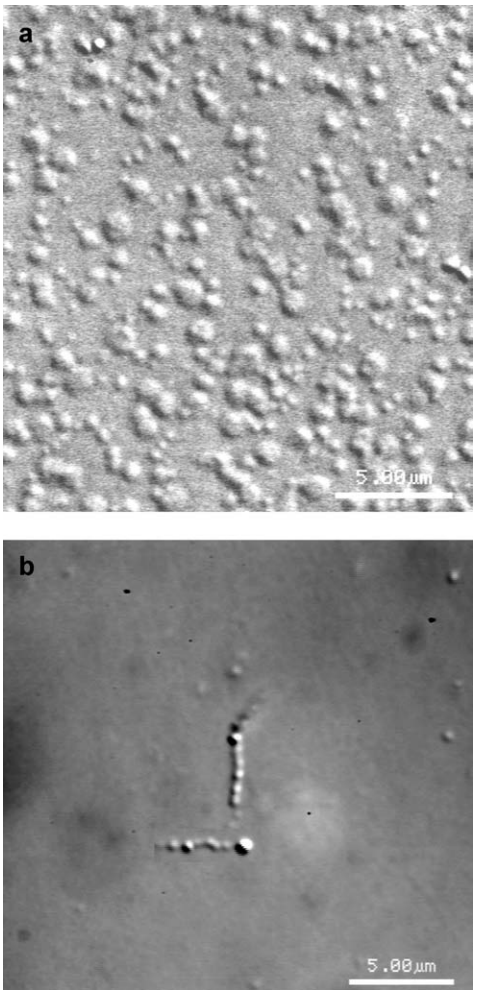


Fig. 2 Light microscope images of a 2 wt % aqueous solution of the PSC **1d**: (a) at the glass–solution interface before solubilization of the catalytic system, (b) in solution after solubilization of the catalytic system.

polymer strands individual spherical micelles are seen to be embedded into 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, which is not seen without solubilization. In the latter case only spheres with a diameter < 100 nm could be detected within the polymeric network. The polymer network that is seen in the TEM micrographs was not visible in the light microscope. The solution was optically void even at a 20-fold higher concentration (corresponding to the conditions of the catalytic reaction), although the detection limit of the used high-resolution light microscope was as low as 50 nm. This discrepancy can be explained by the fact that the contrast of the strings of the water-swollen hydrogel is too low to be perceptible. This is different for the TEM images of the 0.1 wt % solutions where after sublimation of the vitrified ice from the specimens in the high vacuum a xerogel remains, which is decorated with spheroidal micelles. This recalls the well-known ''beads-on-a-string structure'' or the ''necklace'' model for hydrophobically modified polymer-surfactant complexes.[15,16] However, light microscopy revealed composed structures at the polar glass–solution interface [Fig. 2(a)]. Possibly, these are floccules formed in a coagulation/precipitation process. At the moment when the reaction components (catalyst and substrate) were solubilized within the polyamphiphiles, the solution became milky. Mainly agglomerated particles of a diameter between 500 and 800 nm are seen in the light microscope [Fig. 2(b)]. The increase of particle size upon solubilization, which has also been manifested by TEM [Fig. 1(b)] was confirmed by photon correlation spectroscopy. Fig. 3 shows the particle size distribution of PSC **1d** before (a) and after (b) solubilization has occurred. In the latter case the shift of the average particle size is remarkable.

A good example for rate enhancement of the hydrogenation reaction by copolymerization of the amphiphile **2** with dimethylacrylamide is the HMWSP **2b** (Table 1). Due to the lack of hydrogen atoms in the amide group, polydimethylacrylamide cannot form inter- or intrachain hydrogen bonds and therefore it does not exhibit the time and stability drawbacks encountered with polyacrylamide.[17] While the monomer amphiphile as well as the homopolymer need very long reaction times for complete turnover, the copolymer works faster by two orders of magnitude. HMWSP **3**, a copolymer of sodium dodecylmaleamate with *N*-vinyl-2-pyrrolidone, showed an enhanced enantioselectivity but a rather low rate. As may be seen from Table 1, a prolonged equilibration time does not necessarily raise the activity. The same was observed for HMPE **4b**: an extension of the equilibration time from 2 h to 20 h did not alter considerably the catalytic result. The results with HMPE **4** suggest that the catalytic activity is mainly determined by the secondary structure of the polyamphiphile.

In contrast to the gel-like structure of the PSC **1d**, the TEM images of the salt-like PSC **4b** show an ordered and

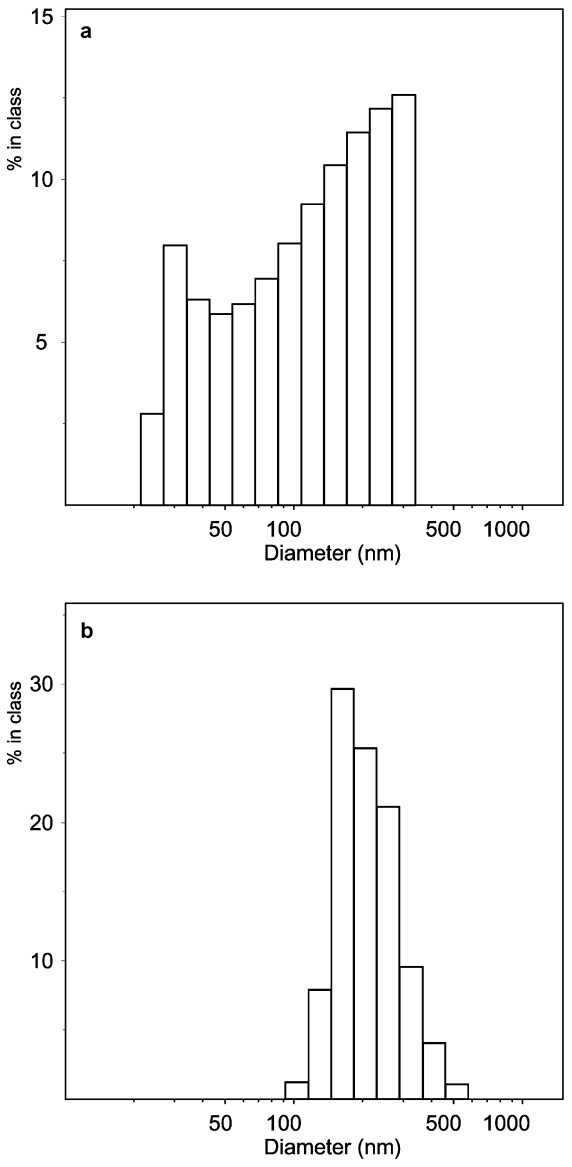


Fig. 3 Particle size distribution in a 2 wt % aqueous solution of the PSC **1d** measured by photon correlation spectroscopy: (a) before and (b) after solubilization of the catalytic system.

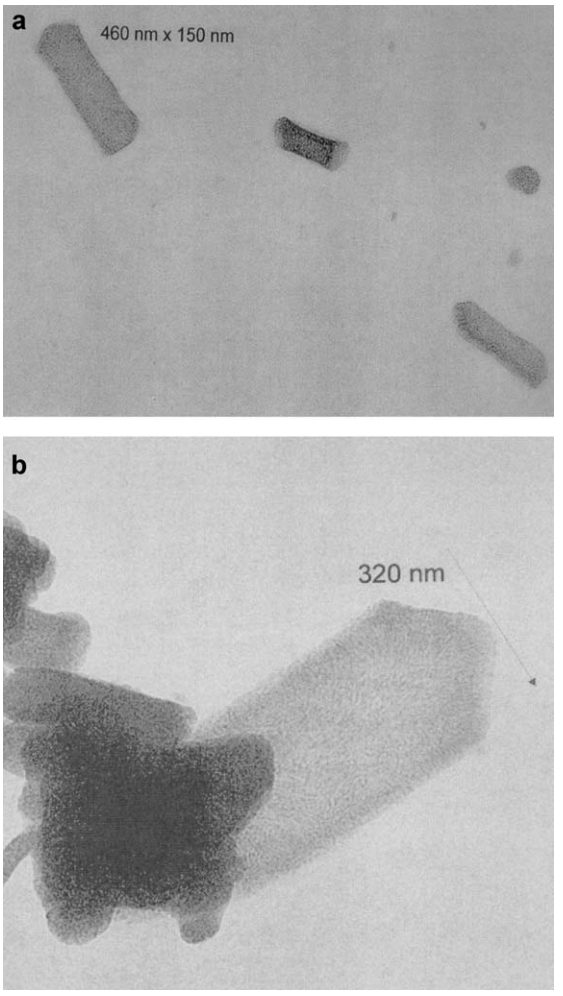


Fig. 4 TEM micrographs from a 0.1 wt % aqueous solution of the PSC **4b** after sublimation of the vitrified ice: (a) ordered tubular structures and (b) pseudo-crystalline aggregates are seen.

rather compact structure (Fig. 4). It is fair to assume that equilibration time and halftime of hydrogenation are increased because transport processes are retarded. The binding of the anionic SDS with the positively charged polyelectrolyte **4a** is a highly cooperative process where hydrophobic interactions between adjacently bond surfactant molecules stabilize the complex aggregate. When a large amount of surfactant is included, the polyelectrolyte gel collapses.[18] In an aqueous dispersion the charged surfactant chains associate inside the polyelectrolyte gel network even when the external solution concentration is significantly lower than the CMC.[19] The complex of the polyelectrolyte gel and the oppositely charged surfactant can form three-dimensional supramolecular structures in aqueous solutions due to a combination of hydrophobic and electrostatic interactions.[20] Moreover, the interaction of the polyelectrolyte gel with SDS can induce a sharp conformational transition, giving rise to sharp diffraction peaks.[21] The latter indicates that the structure in the gel must be in a highly ordered state, in agreement with the results of Okuzaki and Osada,[22] who have reported a polycrystalline structure formed in a cationic surfactant-anionic polymer network complex. The degree of supramolecular order in the PSC increases with increasing amount of SDS. There is no doubt, crystalline structures could not be formed without charges in the polymer network. Neutral polyacrylamide gel does not show any ordered structure.[21] Comparing the enantioselectivities of **4a** and **4b** it seems reasonable to assume that they are influenced by the charge of the micelles: micelles from neutral or anionic amphiphiles afford higher enantioselectivities of the positively charged chiral Rh(I) phosphine complex than cationic micelles do.

The PSC's **5b** and **6** show a similar catalytic behavior as the PSC **1c**, although they have another charge combination. In the PSC **5b** the HMPE **5a** and the surfactant SDS are both negatively charged: the quantity of SDS that is left after dialysis within the polymer network depends on the chemical nature and the number of hydrophobic sites or microdomains.[23] It has been shown for like-charged complexes[24,25] that a strong hydrophobic interaction may overcome the electrostatic repulsion. Additionally, the observed favorable results (Table 1, **5b**) might be traced to a facilitated diffusion due to an extended hydrogel structure of the PSC. It is known that PSC chains can form a cross-linked network upon UV-initiated polymerization.[26]

A similar structure may be considered in the case of the highly branched amphiphilic polyethylene imine **6** complexed with the neutral surfactant Tween 20. Here the best catalytic result in our study was obtained (Table 1, **6**). Obviously, the solubilization capacity of this PSC is high enough as to reduce the molar ratio amphiphile : catalyst from 20 : 1 to 5 : 1 (Table 1, $\mathbf{6}^{c}$ and $\mathbf{6}^{d}$) without changing substantially the hydrogenation activity and stereoselectivity.

Conclusions

It was shown that polymerizable amphiphiles, when copolymerized with water-soluble monomers, afford polyamphiphiles that self-assemble in water and may serve as microreactors for catalytic reactions. Exemplified by the asymmetric hydrogenation of a prochiral amino acid precursor, it was demonstrated that the catalytic performance is greatly determined by the microstructure of the polyamphiphile. Visualization of the associates by TEM and light microscopy supported the view that a loose gel structure with embedded micelles is most favorable for the solubilization of catalyst and substrate. The compactness of oppositely charged polymer-surfactant complexes proved to be a hindrance for the micellar catalysis. As will be shown in a further report, polymer-surfactant complexes are suitable as recyclable micellar catalysts.

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References

1 (*a*) J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975; (*b*) T. Kunitake and S. Shinkai, *Adv. Phys. Org. Chem.*, 1980, **17**, 435; (*c*) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 1968, **22**, 213.
2 (*a*) B. André, B. Boyer, G. Lamaty and J.-P. Roque, *Tetrahedron Lett.*, 1991, **32**, 1881; (*b*) B. Boyer, G. Lamaty, A. Leydet, J.-P. Roque and P. Sama, *New J. Chem.*, 1992, **16**, 883.
3 (*a*) Y. J. Yang and J. B. F. N. Engberts, *J. Org. Chem.*, 1991, **56**, 4300; (*b*) G. J. Wang and J. B. F. N. Engberts, *J. Org. Chem.*, 1994, **59**, 4076; (*c*) G. J. Wang and J. B. F. N. Engberts, *Eur. Polym. J.*, 1995, **31**, 409; (*d*) G. J. Wang and J. B. F. N. Engberts, *J. Org. Chem.*, 1995, **60**, 4030; (*e*) G. J. Wang and J. B. F. N. Engberts, *Langmuir*, 1995, **11**, 3856.
4 (*a*) H. N. Flach, I. Grassert and G. Oehme, *Macromol. Chem. Phys.*, 1994, **195**, 3289; (*b*) A. Kumar, G. Oehme, J.-P. Roque, M. Schwarze and R. Selke, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2197; (*c*) G. Oehme, I. Grassert, E. Paetzold, R. Meisel, K. Drexler and H. Fuhrmann, *Coord. Chem. Rev.*, 1999, **185–186**, 585; (*d*) H. Fuhrmann, I. Grassert, T. Schareina, G. Holzhüter and G. Oehme, *Macromol. Chem. Phys.*, 2001, **202**, 426.
5 A. H. Cook, G. Harris and J. Heilbron, *J. Chem. Soc.*, 1948, 1060.
6 M. Green, T. A. Kuc and S. H. Taylor, *J. Chem. Soc. A*, 1971, 2334.
7 (*a*) J. E. Lancaster, L. Baccei and H. P. Pancer, *Polym. Lett.*, 1976, **14**, 549; (*b*) G. B. Butler, *Acc. Chem. Res.*, 1982, **15**, 370.
8 Y. Chang and C. L. Mc Cormick, *Macromolecules*, 1993, **26**, 6121.
9 W. Jaeger, U. Wendler, A. Lieske and J. Bohrisch, *Langmuir*, 1999, **15**, 4026.
10 S. Biggs, A. Hill, J. Selb and F. Candau, *J. Phys. Chem.*, 1992, **96**, 1505.
11 W. J. Peer, *Polym. Mater. Sci. Eng.*, 1987, **57**, 492.
12 K. C. Dowling and J. K. Thomas, *Macromolecules*, 1990, **23**, 1059.
13 (*a*) S. A. Ezzell and C. L. Mc Cormick, *Macromolecules*, 1992, **25**, 1881; (*b*) S. A. Ezzell, C. E. Hoyle, D. Creed and C. L. Mc Cormick, *Macromolecules*, 1992, **25**, 1887.
14 A. Hill, F. Candau and J. Selb, *Macromolecules*, 1993, **26**, 4521.
15 K. Shirahama, K. Tsujii and T. Takagi, *J. Biochem.*, 1974, **75**, 309.
16 B. Cabane and R. Duplessix, *Colloids Surf.*, 1985, **13**, 19.
17 L. Guillaumont, G. Bokias and I. Iliopoulos, *Macromol. Chem. Phys.*, 2000, **201**, 251.
18 S. G. Starodubtzev, E. E. Makhaeva, E. Y. Kramarenko and A. R. Khokhlov, *Macromolecules*, 1992, **25**, 4779.
19 O. E. Philippova and S. G. Starodubtzev, *J. Polym. Sci., Part B: Polym. Phys.*, 1993, **31**, 1477.
20 A. R. Khokhlov, E. Y. Kramarenko, E. E. Makhaeva and S. G. Starodubtzev, *Macromol. Theory Simul.*, 1992, **1**, 105.
21 F. Yeh, E. L. Sokolov, A. R. Khokhlov and B. Chu, *J. Am. Chem. Soc.*, 1996, **118**, 6615.
22 H. Okuzaki and Y. Osada, *Macromolecules*, 1995, **28**, 380.
23 I. Iliopoulos, *Curr. Opin. Colloid. Interface Sci.*, 1998, **3**, 493.
24 I. Iliopoulos, T. K. Wang and R. Audebert, *Langmuir*, 1991, **7**, 617.
25 O. E. Philippova, D. Hourdet, R. Audebert and A. R. Khokhlov, *Macromolecules*, 1996, **29**, 2822.
26 C. B. Tsvetanov, R. Stamenova, D. Dotcheva, M. Doytcheva, N. Belcheva and J. Smid, *Macromol. Symp.*, 1998, **128**, 165.