

The Effect of Assembled Amphiphiles on Catalytic Reactions in Aqueous Media^{1,2}

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Abstract—Micelle-forming amphiphiles can promote catalyzed reactions in aqueous media. An example is the asymmetric hydrogenation of amino acid precursors. In comparison to the most common solvent methanol, the hydrogenation in water leads to a decrease of activity and a decrease of enantioselectivity, but, by adding a small amount of a surfactant (20 mol %), the activity increased to a value similar to methanol and the enantioselectivity increased sometimes to values higher than in methanol. A disadvantageous consequence of the use of surfactants is the more difficult phase separation within the work up of the reaction mixture because of the detergent effect of the amphiphile. Another problem is the recycling of the catalyst. To solve both these problems, we developed two methods: (i) the use of polymerized and polymeric amphiphiles in a membrane reactor and (ii) an immobilization of amphiphiles on an inorganic support. The precondition for the realization of these concepts is a leaching-free embedding of the catalytic rhodium complex in the macromolecular amphiphilic layer. Advantages and disadvantages of these methods will be discussed.

INTRODUCTION

Water is the essential medium in living nature and a typical solvent in inorganic and analytical chemistry, but it is not characteristic in the development of organometallic chemistry because of the sensitivity of most organometallics to air and water and the low solubility in such an extremely polar solvent [1].

With the development of new homogeneously catalyzed processes arose the problem of the recycling of the catalyst resulting in a phase separation of the catalytic system within or after the reaction [2]. Three methods to change into a multiphase system warrant discussion:

(1) the immobilization of the catalytic complex on an inorganic or organic support;

(2) a liquid–liquid two-phase system formed by a polar (aqueous) and a nonpolar (organic) phase with or without a phase-transfer reagent; and

(3) a reaction in a bipolar (amphiphilic) microheterogeneous (colloidal) system, which can contain aqueous micelles or vesicles as a catalytic reaction medium.

Most important on an industrial scale is at present the second method and processes like SHOP [3] and the hydroformylation of propene developed by Ruhrchemie and Rhone-Poulenc [4].

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² This article was submitted by the authors in English.

The present paper contains some investigations for a practical application of the third method, the use of an aqueous micellar system in coordination catalysis.

Micelles and vesicles are formed by self-aggregation of amphiphilic molecules in an aqueous medium above a critical aggregation concentration (for micelles, critical micelle concentration (CMC)) [5]. The principle of aggregation is presented in Fig. 1.

Amphiphiles are compounds with a highly polar headgroup and at least one nonpolar chain. In water, amphiphiles form micelles with a hydrophobic core. Micelles are thermodynamically stable and kinetically labile. Association and dissociation occur in milliseconds and are faster than most chemical reactions. In nature, occurring amphiphiles are lipid molecules with two hydrophobic chains per hydrophilic headgroup forming bilayers and vesicles (or liposomes) with membranes, which surround a polar (aqueous) core. Vesicles are much larger than micelles and kinetically more stable.

The driving force of the formation of amphiphilic assemblies in water is the hydrophobic effect that means the increase of entropy owing to the dehydration of the hydrocarbon chain [6]. Subsequently, reactions in micelles will be discussed. The headgroup of the used amphiphiles can be anionic, cationic, zwitterionic, or nonionic. The acceleration of a chemical reaction in the presence of micelles is called “micellar catalysis.” Three types of micellar influences were summarized in an early review by Morawetz [7]. In the first type, the amphiphiles are the reagents themselves, e.g., in case of

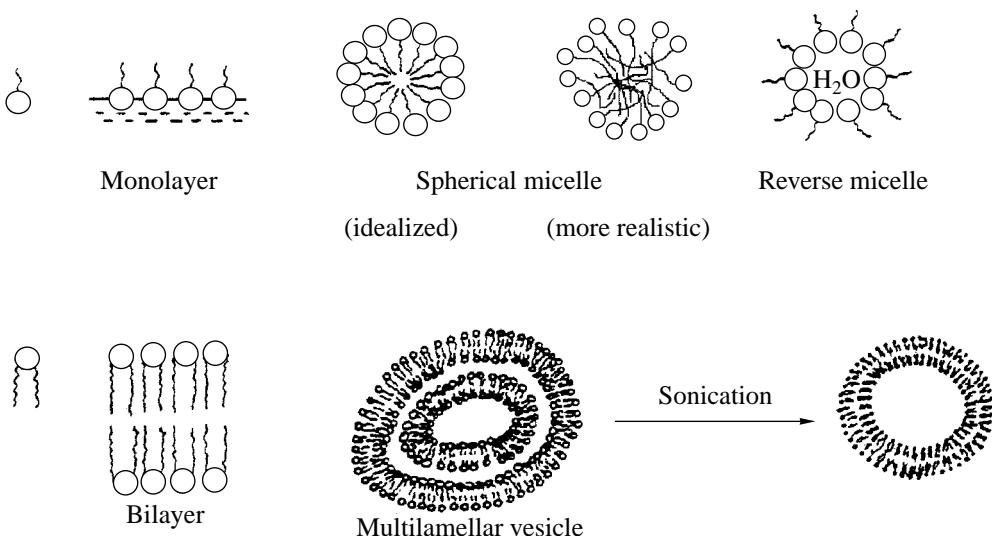


Fig. 1. Assembly of amphiphiles in water.

alkyl sulfates, the rate of hydrolysis increases above their CMC with the lengths of the chains. The second type is based on an influence of the ordered amphiphiles on the incorporated reagents, and the third type is characterized by a catalytic function of the head-group-modified amphiphile. Most reactions in a micellar medium correspond to the second type.

The reasoning behind the rate enhancement owing to aqueous micelles was summarized by Brown *et al.* [8].

First, there is an outstanding medium effect because of a lower dielectric constant than in the surrounding water and an unusual polarity gradient between the surface and core of the micelle. Secondly, the transition state of the reaction can be stabilized because of an interaction with the headgroup of the amphiphile. And third, there is a concentration effect on the reaction by incorporation of the reactants into the micelle. This concentration effect also leads to an increase in acidity on anionic surfaces and an increase of basicity on cationic surfaces in comparison to the bulk water phase.

Micellar effects have been observed in all fields of chemistry [9] and even in coordination catalysis [10]. There are examples in solvolytic reactions, oxidation, reduction, and C–C coupling reactions [11]. In this paper, we focused on the hydrogenation of the C–C double bond of α -amino acid precursors and on C–C bond forming reactions.

In the beginning of our work, only a few papers in hydrogenation were known. Nuzzo *et al.* [12] found in rhodium complex-catalyzed hydrogenations with N,N-bis(diphenylphosphinoethyl) succinic acid monoamide as a ligand in water only in the presence of sodium dodecylsulfate (SDS) any activity. Shilov and coworkers [13] described that, in the presence of phospholipids, the nitrogen reduction catalyzed by an artificial

nitrogenase system is very selectively enhanced. We also received from Kagan and Samuel a personal communication about experiments with surfactants in aqueous hydrogenation reactions, but this work was not published and not continued [14].

EXPERIMENTAL

Materials

Substrates for hydrogenation were synthesized as described in previous papers: methyl (Z)- α -acetamido-cinnamate [15] and the precursors of α -benzamidophosphonic acid and α -benzamidophosphinic acid esters [16]. All saturated amphiphiles were purchased by Aldrich (USA, Germany) and Fluka (Switzerland). The triblock copolymers (Synperonics and Pluronics) were a gift from C.H. Erbslöh, Krefeld (Germany). *N*-palmitoylprolinates and *N*-palmitoylprolylprolinates were synthesized in accordance with [17]. Polymerizable amphiphiles are described in [18], and the preparation of amphiphilized inorganic supports is partly given in [19]. An example of new developments is described below. The synthesis of selected polymer-surfactant complexes is given in [20].

Water-soluble phosphines and their palladium complexes for Suzuki coupling reactions were prepared in accordance with [21]. All reagents for the Suzuki reaction and also for the hydroformylation were purchased by Aldrich. This supplier was also the source for [Rh(cod)2]BF₄ and for BPPM.

Analytical methods. All synthesized compounds were characterized by elemental analysis (Leco, C, H, N, S automatic analyzer), ¹H-, ¹³C-, and ³¹P-NMR spectroscopy (Bruker ARX 400), and FTIR (Nicolet Magna 550). Enantiomeric excesses were measured by GLC (Hewlett Packard chromatograph 5880 A) with a 10 m

Table 1. Asymmetric hydrogenation of methyl (Z)- α -acetamidocinnamate under aqueous micellar conditions

Surfactant	$t_{1/2}$, min	ee^* , %
None in water	90	78
None in methanol	2	90
Anionic: sodium dodecylsulfate	6	94
Cationic: cetyltrimethylammonium hydrogen sulfate	5	95
Zwitterionic: N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate	5	93
Nonionic: polyoxyethylene(10)hexadecylether (Brij 56)	7	95

Note: Conversion is higher than 99%. Reaction conditions: 25°C, 0.1 MPa H₂, H₂O; Cat = [Rh(cod)₂]BF₄ + L* + surfactant.

* GLC data.

capillary coated with XE-60 (L)-N-tert-butylvalinamide (FID, at 150°C) or HPLC (Hewlett Packard, HP 1090, column Chiral OD-H; eluent: hexane : 2-propanol = 9 : 1 or column Chiral AD; eluent: hexane : ethanol = 95 : 5).

Molecular weights of polymerized micelles and tri-block copolymers were determined with a membrane osmometer (Knauer, Germany) and by gel permeation chromatography (Hewlett Packard HP 1090; column SDV 5 μ , PSS, Mainz). The size of assemblies was determined by dynamic light scattering (Coulter N4 plus) and by electron microscopy (Zeiss, transmission electron microscope 912 OMEGA).

Critical micelle concentrations (CMCs) of new amphiphiles were measured by a dye solubilization method (1-(2-pyridylazo)-2-naphthol) and by the concentration dependence of the surface tension with the Nouy ring method (tensiometer of Lauda Te Ic/3, Germany).

Microassays of Rh and Pd were performed with an atomic absorption spectrometer AA 300 of Perkin-Elmer (USA).

Methods

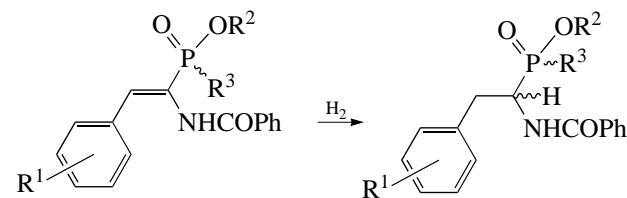
Hydrogenation. All operations were made under exclusion of oxygen in a vigorously stirred thermostatted reaction vessel which is connected with a burette also thermostatted (25 \pm 0.1°C) for hydrogen. Typical procedures were performed with 1 mmol substrate, 0.01 mmol catalyst, and from 0.2 up to 0.5 mmol

amphiphile in 15 mL of solvent (as a rule water) at 1 bar (0.1 MPa) hydrogen. The consume of hydrogen was measured volumetrically. After the end of the reaction, the aqueous phase was extracted two times with 5 mL of chloroform and the organic phase analyzed by GLC or HPLC (see above and Tables 1 and 2).

The pH-controlled hydrogenation was regulated by a pH-stat with 0.18 M KOH and 0.18 M HClO₄ connected with a PC as described in [22]. The asymmetric hydrogenation in a membrane reactor is described in [20].

General procedure for Suzuki reactions. All operations were carried out in an argon atmosphere. Sodium carbonate decahydrate (11.6 g, 45 mmol) and the amphiphile (3.4 mmol) were dispersed in 15 mL of water in a 100-mL water jacketed vessel with a magnetic stirrer. Two separately prepared solutions of 13.5 mmol of the haloarene in 15 mL of toluene and 15 mmol of the phenylboronic acid in 15 mL of ethanol were added, and the first sample for GLC was taken (HP 5890; column HP1; program: 2 min at 50°C, then 10°C/min up to 260°C). The reaction vessel was heated at 78°C, and the catalyst (0.01 mmol) added under vigorous stirring (1000 rpm). The progress of the reaction was followed by GLC. After the end of the reaction, the product was purified by column chromatography (Merck silica gel 40; eluent: *n*-heptane : ethylacetate = 7 : 1).

Polymerization of unsaturated amphiphiles in a micellar state. The UV-polymerization was performed using the UV irradiation equipment of Gräntzel,

Table 2. Asymmetric hydrogenation of α -benzamidophosphinic acid and α -benzamidophosphonic acid derivatives under micellar conditions with $[\text{Rh}(\text{COD})_2]\text{BF}_4 + \text{BPPM}$ as catalytic system

No.	R ¹	R ²	R ³	Amphiphile	t _{1/2} , min	ee, %
1	H	Et	Me	CTAH ₂ SO ₄	18	99
2	H	Et	Me	SDS	6	98
3	H	Et	Me	Tween 40	36	97
4	4-Me	Et	Ph	SDS	10	96
5	4-iPr	Et	Ph	SDS	240	93
Substrate : amphiphile : Rh-BPPM = 50 : 100 : 1						
6	4-Me	Me	OMe	SDS	5	99
7	4-Cl	Me	OMe	CTAH ₂ SO ₄	7	99
8	4-Me	Me	OMe	CTAH ₂ SO ₄	8	99
9	4-F	Me	OMe	CTAH ₂ SO ₄	12	99
10	2-F	Me	OMe	CTAH ₂ SO ₄	13	99
11	4-Cl	Me	OMe	SDS	4	98
12	4-NO ₂	Me	OMe	SDS	6	98
13	4-F	Me	OMe	SDS	6	98
14	4-F	Me	OMe	Tween 40	9	98
15	4-Me	Me	OMe	Tween 40	11	98
16	4-CF ₃	Me	OMe	CTAH ₂ SO ₄	14	98
17	4-iPr	Me	OMe	SDS	15	98
18**	3-F	Me	OMe	CTAH ₂ SO ₄	20	98
19	4-iPr	Me	OMe	CTAH ₂ SO ₄	30	98
20**	3-F	Me	OMe	SDS	7	96
21	4-CF ₃	Me	OMe	SDS	11	96
Substrate : amphiphile : Rh-BPPM = 100 : 20 : 1						

Note: Conversions are higher than 99% in each case. Without amphiphiles, Rh deposition was observed. Reaction conditions: 25°C, 0.1 MPa H₂. CTAH₂SO₄ is cetyltrimethylammonium hydrosulphate.

* According to HPLC.

** Chiralpak AD column.

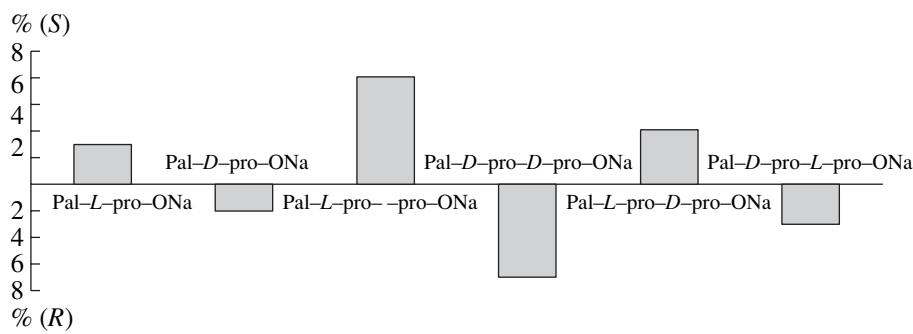


Fig. 2. Chiral induction by chiral micelles (prolineamphiphiles) within hydrogenation methyl (Z)- α -acetamidocinnamate in the presence of an achiral catalyst [Rh(COD)(BDPP)BF₄]. Rh : amphiphile : AE = 1 : 20 : 100.

Karlsruhe (Germany), at 185 nm or alternatively at 254 nm in the presence of a radical initiator as communicated in [18]. Polymerization by a low-temperature plasma was carried out in the absence of a radical initiator in a newly-developed thin-film rotation reactor in collaboration with Ehlbeck and Maaß from the Leibniz Institute of Low-Temperature Plasma Physics in Greifswald. A detailed description of the reactor is given in a patent [23].

Syntheses

Synthesis of silica-bound undecyltrimethylammonium bromide (see Scheme 4). The supported material was prepared in four steps. Commercially available 11-bromoundec-1-ene was reacted with trichlorosilane in the presence of a catalytic amount of H₂PtCl₆ to yield the hydrosilylation product according to a procedure in [24]. The trichlorosilyl group was solvolyzed within 2 h by methanol at room temperature to the trimethoxysilyl group [25]. Quaternization was carried out with two equivalents of trimethylamine in methanol for 3 h at room temperature. The resulting ω -trimethoxysilyl-undecyltrimethylammonium bromide was linked to a silica support as described below. Elemental analysis (C, H, N, Br) gave a loading of 0.47 mmol/g.

General procedure for linking trialkoxysilyl groups on silica. All experiments were performed in an argon atmosphere. To 10 g of silica gel 60 (Merck, 0.040–0.063 mm) dried in vacuum (1 mbar) at 200°C for 12 h was added a solution of 10 mmol of the trialkoxysilyl compound in 40 mL of toluene. The mixture was shaken for 2 h at room temperature and then refluxed for an additional 2 h. About 20 mL of toluene was distilled off and after that 40 mL of toluene was added. Again 20 mL was distilled off. The mixture was filtered under argon, and the residue washed with four 80-mL portions of hot toluene, 60 mL of hot ethanol, and two 20-mL portions of diethyl ether. The product was then dried in vacuum overnight.

RESULTS AND DISCUSSION

In 1992, we observed that in water the nearly insoluble substrate methyl (Z)- α -acetamidocinnamate with the scarcely soluble chiral rhodium phosphine complex gave only low activities and very low enantioselectivities in a water medium. Especially in comparison with results in methanol, there is a large decrease; however, by adding a small amount of a surfactant to the aqueous mixture, the activity and enantioselectivity were significantly enhanced. As summarized in Table 1, the headgroups of the amphiphiles can be anionic, cationic (with restrictions), zwitterionic, or nonionic. The effect depends on the concentration and is only visible above the CMC [26].

It was also possible to hydrogenate with the same aqueous micellar system a series of phosphonic and phosphinic acid derivatives with great success [27]. Table 2 shows a selection of the experiments. In the case of α -benzamidophosphinic acid esters, the rate of hydrogenation (activity) depends strongly on the alkyl or aryl substituent at the phosphorus (entries 1–5). The enantioselectivity was really satisfying in all examples.

The source of enantioselectivity is the chiral ligand BPPM ((2S,4S)-N-tert-butoxycarbonyl-2-diphenylphosphino-4-diphenylphosphinomethyl-pyrrolidine) in the rhodium complex (see Table 1). We tried to achieve a chiral induction by chiral micelles in the presence of an achiral hydrogenation-active complex [17].

Figure 2 contains results with stereoisomeric sodium *N*-palmitoylprolinates and stereoisomeric sodium *N*-palmitoylprolylprolinates as amphiphiles. The chiral induction is low but unambiguous: sodium *N*-palmitoyl-*L*-proline gave the product with an (*S*)-configuration; the *D*-proline gave an (*R*)-configured product. The effect can be amplified with *L,L*-prolylproline or *D,D*-prolylproline as the headgroup. With *L,D*- or *D,L*-prolylprolines, the configuration of the product is directed by the configuration of the *N*-palmitoylprolyl part; that means the chiral induction occurs near the zone of the transition from the headgroup to the hydrophobic tail. This region in an aqueous micelle is called “palisade layer” [28]. In our opinion, the substrate is located in a region of medium polarity,

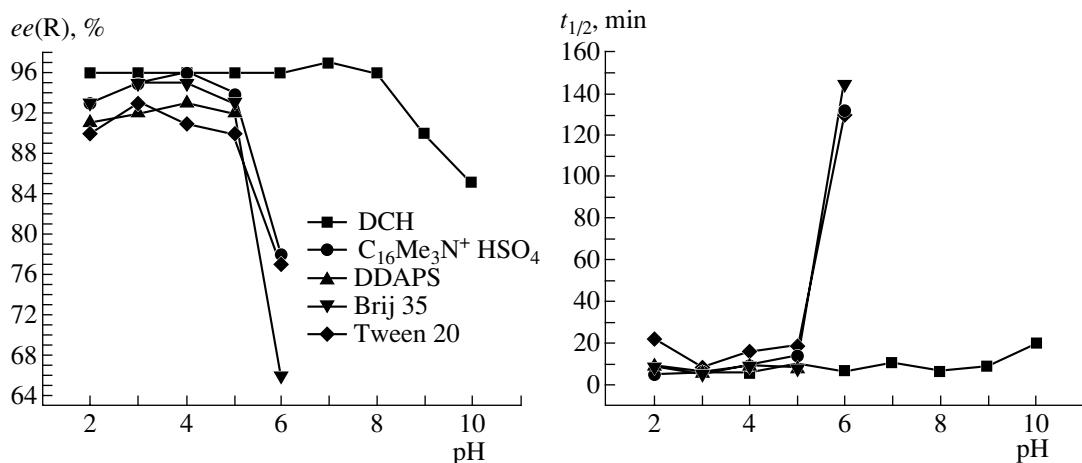


Fig. 3. pH-dependence of activity and enantioselectivity within asymmetric hydrogenation under micellar conditions.

whereas the ionic rhodium complex is embedded in the polar headgroup.

Asymmetric hydrogenation follows a mechanism via hydride intermediates [29] and in water is strongly dependent on the pH [30]. Amphiphiles have a significant influence on this behavior. Figure 3 displays the influence of different types of amphiphiles for the asymmetric hydrogenation of methyl (Z)- α -acetamido-cinnamate by a systematic change in the pH.

With all types of amphiphiles, there is a constant enantioselectivity and a constant activity between pH 2 and 5. Only anionic surfactants such as SDS were an exception and gave constant values between pH 2 and 8 [22]. Probably, anionic aqueous micelles are more closed than cationic, zwitterionic, and nonionic micelles [31]. Because of the low concentration (just above the CMC) and the inertness of several anionic micelle-forming amphiphiles, their use seems to be a good alternative to buffer systems for optimal hydrogenation reaction conditions. The application of supramolecular systems is not restricted to hydrogenation reactions [32]. As an example from our laboratory, we present in Fig. 4 the influence of different amphiphiles on the palladium-catalyzed Suzuki coupling of *p*-iodoanisole

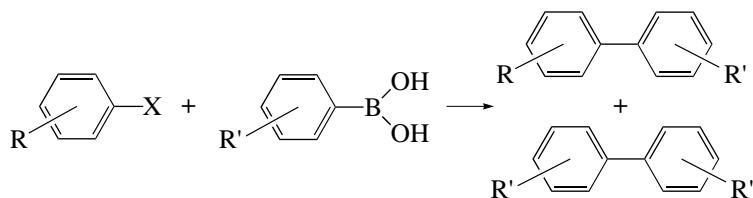
and *p*-tolylboronic acid at 78°C (Scheme 1) in a biphasic system with water and toluene [33].

The amphiphiles here could have the function of phase-transfer reagents, but only micelle forming amphiphiles (with one chain $> C_{10}$) were active as cocatalysts. We considered that there is a competition between micellar and phase-transfer effects [34].

Sometimes, the achievements with amphiphiles in the enhancement of rate and selectivity are fascinating, but unfortunately micellar systems are not really stable multiphase systems. The amphiphile can contaminate the product and complicate a phase separation because of a soap effect. As a rule, micelles are not even suitable for retention in a membrane reactor. A way out should be the immobilization of amphiphiles.

Three principal methods will be discussed here: (1) the polymerization of unsaturated amphiphiles in a micellar system; (2) the use of polymeric amphiphiles, which can form micelles in aqueous dispersions; and (3) the linking of amphiphiles on the surface of inorganic or organic supports (synthesis of amphiphilized polymers).

The chance to polymerize micelles as intact supramolecules depends on the location of the unsatur-



Reaction conditions: 15 mmol PhB(OH)₂, 13.5 mmol *p*-iodoanisole, tolyene : ethanol : water = 15 : 15 : 15 (in vol.), substrate : catalyst = 1350, 0.01 mmol PdCl₂[Ph₂P(CH₂)₄SO₃K]₂, surfactant, 45 mmol Na₂CO₃.

Scheme 1. Suzuki coupling under the aqueous two-phase condition.

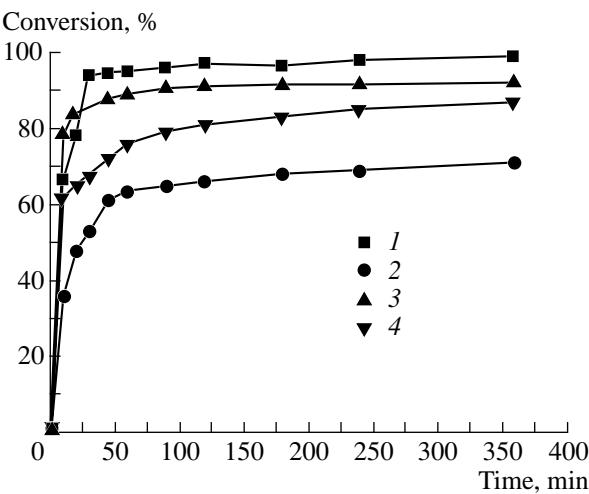


Fig. 4. Influence of different amphiphiles on Suzuki coupling in an aqueous two-phase system (see Scheme 1). (1) $\text{C}_{12}\text{Me}_3\text{N}^+\text{Br}^-$, (2) without surfactant, (3) $\text{C}_{12}\text{Me}_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$, and (4) SDS.

ation in the molecule. Terminal double bonds in hydrophobic chains are much less reactive than, e.g., unsaturated ester groups (acrylates or methacrylates) linked to the polar headgroup. The principle of the micelle polymerization for two types of unsaturated amphiphiles is shown in Fig. 5.

The polymerization should have a topological (entropic) advantage because of the aggregation, but the dissociation is a very fast process and could be faster than the polymerization reaction. Some authors doubt that a micelle is polymerizable [35], but, as a matter of fact, polymerized amphiphiles often have the size of micelles and result in spherical particles in aqueous dispersions [36].

The polymerization was realized by irradiation of UV in the presence of organic initiators, e.g., AIBN (α,α' -azobisisobutyronitrile), or by the influence of low-temperature plasma [23] in special reactors. Table 3 gives a comparison of the results in UV and plasma reactors. Molecular weights and reaction time are satisfying in the plasma process, but the selectivity is relatively low because of side reactions with water-derived radicals.

Selected unsaturated amphiphiles and their use in asymmetric hydrogenation in a supramolecular (monomeric) and a macromolecular (polymeric) state are given in Table 4 [37]. In all cases, the polymerized micelles gave comparable or better results with respect to activity and enantioselectivity than the supramolecular species, but one has to consider that most unsaturated amphiphiles have no optimal structure for micelle formation. In the polymerized micelle, the step to a spherical self-organization seems to be facilitated. As a rule, in the work-up procedure, the phase separation is much easier with polymerized amphiphiles than with monomeric amphiphiles.

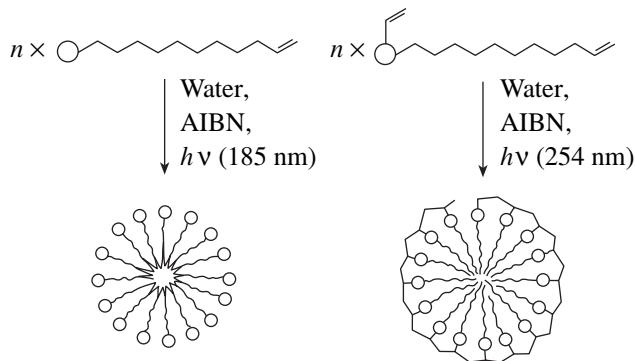
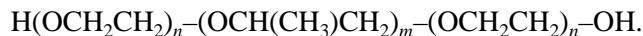


Fig. 5. Polymerization of micelles (idealized).

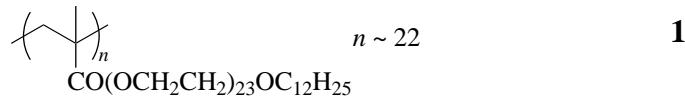
A formal alternative to polymerized micelles would be micelles formed by amphiphilic polymers. One example is the application of commercially available polyoxyalkylene block copolymers of the general structure



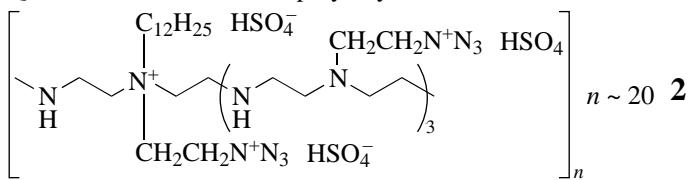
(Synperonic, Pluronics) [38]. The polyoxyethylene wings are hydrophilic; the polyoxypropylene part is hydrophobic. We checked a series of polymers in the micellar asymmetric hydrogenation of methyl (*Z*)- α -acetamidocinnamate and found good activities and enantioselectivities especially for Synperonics with 56 units ($m = 56$) in the polyoxypropylene part [39]. Interestingly, the polyoxyethylene wings are much more variable (n between 5 and 132). In our experience, Pluronics are also excellent phase-transfer reagents in the hydroformylation of 1-dodecene [40].

Another concept was the synthesis and application of polymer-surfactant complexes [20, 41]. Three examples are presented in Scheme 2. The principle consists in a polymerization or copolymerization of unsaturated amphiphilic monomers in the presence of saturated micelle-forming surfactants, which were irreversibly involved in the macromolecule. Dependent on the size of the polymer, it is able to form more-or-less large aqueous micelles. The first example (**1**) is the polymerized polyoxyethylene dodecylether methacrylate with SDS (sodium dodecylsulfate) as the surfactant, the second one (**2**) is a polymerized hydrogen sulfate of quaternized polyethyleneimine in the presence of Tween 20 (polyoxyethylene(20)sorbitan-monododecanoate), and the third one is a poly(*N*-isopropylacrylamide-co-dodecyl methacrylate) with SDS (**3**).

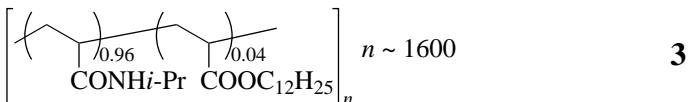
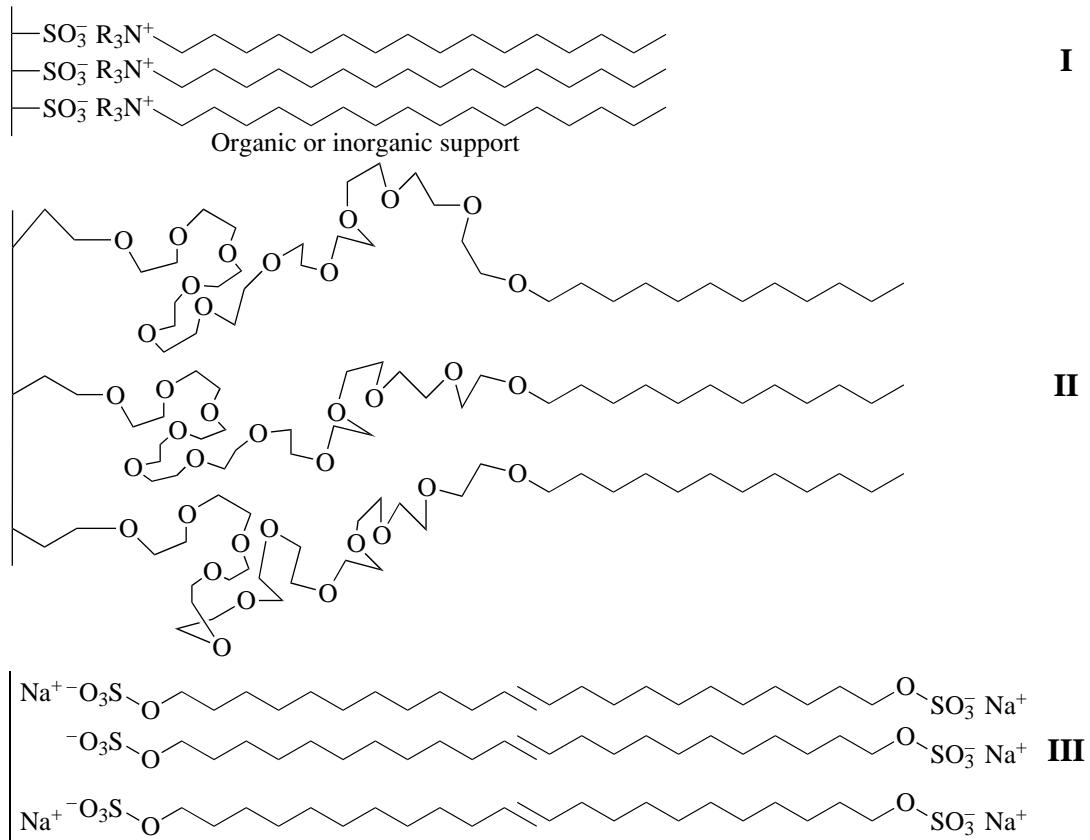
Especially **3** with $n = 1600$ is a large molecule and was used as a nonpenetrating catalyst-support in a membrane reactor. The flow diagram of this reactor is given in Fig. 6. The reactor is a closed pressure cylinder (up to 5 bar) with a mechanical stirrer and adapters for vacuum, argon, or hydrogen, the permeated product, and the take-off for analytical samples [20]. For a membrane a YM 10 with a cutoff of 10000 Da (Amicon/Millipore, Eschborn, Germany) was used. Figure 7 shows

Poly(oxyethylene)₂₃dodecylether methacrylate/SDS

Quaternized and sulfated polyethylene imine/Tween 20



Poly(N-isopropylacrylamide-co-dodecylmethacrylate)/SDS

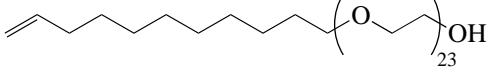
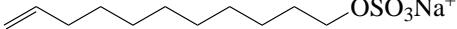
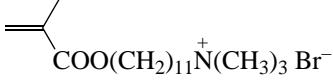
**Scheme 2.** Three examples of polymer–surfactant complexes.**Scheme 3.** Examples of amphiphilized polymers.

the recycling protocol for seven cycles with polymer **3** as the support.

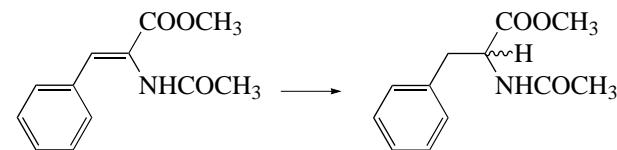
The enantioselectivity is almost constant within the experiment, while the turnover (conversion) decreased

after the third cycle, and the isolable yield of the product (methyl (S)-phenylalaninate) after each cycle is at a low level from the beginning. Probably, the permeability of the membrane is not sufficient, and the product is

Table 3. Comparison of UV with low-temperature plasma polymerization

Monomer	UV with initiator 8 h				Plasma without initiator		
	185 nm		254 nm				
	conversion, %	mw, g/mol	conversion, %	mw, g/mol	conversion, %	mw, g/mol	time, h
	100	17000	100	3900–16000	90	12500	4
	95	900–1900	100	4300	70	10000	8
	100	6100–8900	100	4000–31000	100	5000	0.5

mw is molecular weight.

Table 4. Use of polymerized amphiphiles

	$t_{1/2}$, min	$ee (R)$, %	Reaction time, min
Nonionic amphiphiles			
$(C_2H_4O)_{23}(CH_2)_9CH=CH_2$ monomer	6	95	21
polymer	7	94	50
Anionic amphiphiles			
$CH_2=CH-(CH_2)_9OSO_3Na$ monomer	35	85	50
polymer	6	91	40
Cationic amphiphiles			
$CH_2=C(CH_3)COOCH_2CH_2OOC(CH_2)_{10}N^+(CH_3)_3HSO_4^-$ monomer	65	83	200
polymer	31	87	90

Note. Conversion is higher than 99%. Reaction conditions: 25°C, 0.1 MPa H₂, H₂O; Cat = [Rh(cod)₂]BF₄ + BPPM; Rh : amphiphile : substrate = 1 : 20 : 100. Without amphiphile: $t_{1/2}$ = 90 min, ee = 78%, Rh deposition was observed.

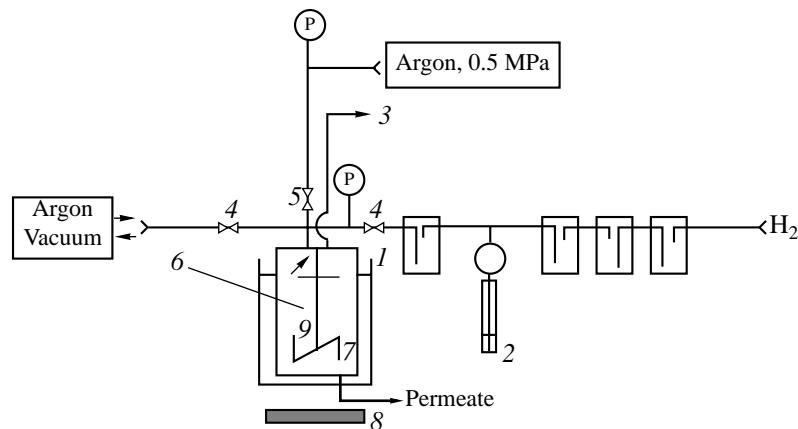


Fig. 6. Flowchart of a membrane reactor for asymmetric hydrogenation: (1) thermostat (25°C); (2) safety valve; (3) sampling; (4) stop valve; (5) metering valve; (6) stirring cell; (7) membrane; (8) magnetic stirrer; (9) stirring bar; (P) pressure gauge.

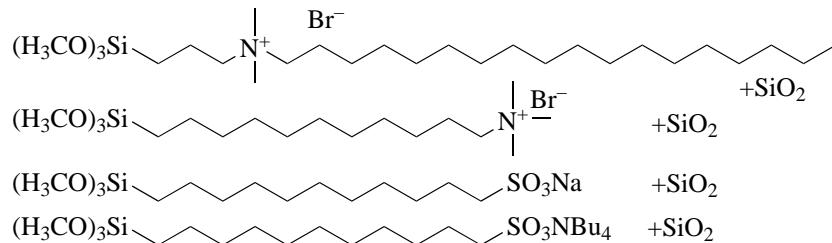
enriched in the reaction chamber. More encouraging are the results for the retention. Especially rhodium was sufficiently retained while the loss of the ligand and also of the polymer-surfactant complex is more significant.

In conclusion, the concept of using polymerized and polymeric micelles in a membrane reactor is encouraging, but the results are not satisfying up to date. The most important problem will be the finding of stable and regenerable membranes. A future aspect would be the application of ceramic membranes. Finally, Scheme 3 displays three types of amphiphilized inorganic supports [19]. Type **I** is an amphiphilization by ionic exchange on a sulfonated silica with a hexadecyltrimethylammonium cation; type **II** is an amphiphilic polyoxyethylene dodecylether covalently bound to silica; and type **III** is a sodium dodecylsulfate adsorbed on alumina. This surfactant could not be removed by washing with water and is probably in interaction with a free surfactant molecule. This type is called "admicelle" and plays an interesting role in surface chemistry [42].

The effect of the amphiphilized polymers on the asymmetric hydrogenation of methyl (Z)- α -acetamido-cinnamate is given in Table 5. In comparison with the surfactant-free experiment, the three types of amphiphilized polymers had the effect on activity and

enantioselectivity that we expected. The influence of the polymers was slightly less than that of the monomers in micelles but always comparable. The importance of such immobilization can be demonstrated in Table 6, which contains a recycling experiment with ten cycles for ionic exchanger **1**.

The enantioselectivity was almost stable and in the last experiment increased, perhaps because of a stereoselective adsorption of the product. In cycles 1 through 9, the amphiphilized polymer was only separated by filtration, and the aqueous phase was extracted with chloroform. After cycle 9, the extraction was done in the presence of the polymer. The rhodium complex was embedded in the amphiphilic layer within all steps. Leaching of rhodium could not be observed during the recycling procedure. Comparing the amphiphilic layer on the support with aqueous supramolecular micelles, the surface of the support seems to be much more hydrophobic, and the hydrophilic part is arranged near the support. Actually, the amphiphilized support reacts in aqueous suspension like an aqueous micelle, but we are now trying improved models presented in Scheme 4 [43].



Scheme 4. New developments in amphiphilized polymers.

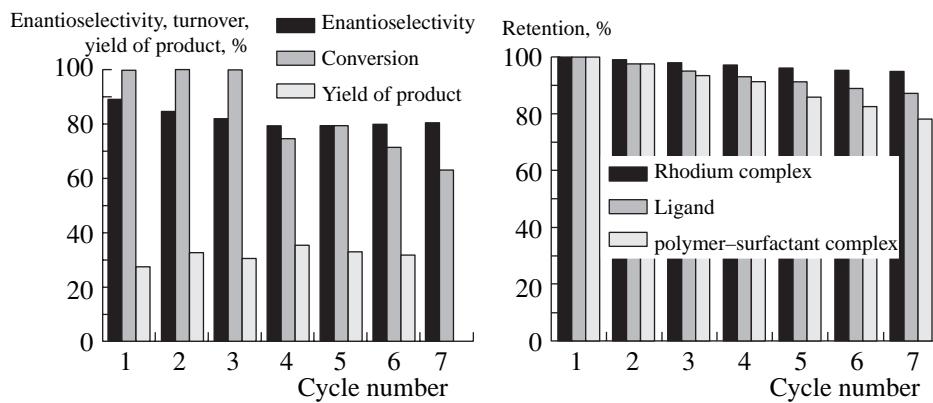


Fig. 7. Recycling protocols for a membrane reactor with polymer–surfactant complex **3** and membrane YM 10 (cutoff 10000 Da). Turnover here was like conversion.

The unsaturated monomers derived from 1-undecene were hydrosilylated with triethoxysilane or trimethoxysilane, respectively. A linking to SiO_2 or Al_2O_3 via the trialkoxysilyl group is a classical immobilization procedure. Hydrosilylation and anchoring depend on the type of hydrophilic headgroup and are sometimes difficult to realize. The cationic types could be seen as immobilized cationic micelles or alternatively as immobilized ionic liquids [44]. Both topics are presently very actual.

Finally, we should compare our immobilized polymers with the concept of supported aqueous phase catalysis (SAPC) [45]. In both models, hydrophobic

Table 5. Effect of amphiphilized polymers* on the asymmetric hydrogenation of methyl α -acetamidocinnamate (1 mmol substrate, 0.01 mmol $[\text{Rh}(\text{COD})(\text{BPPM})]\text{BF}_4$, 0.2 mmol amphiphile in 20 ml water at 25°C)

Amphiphile	$t_{1/2}$, min**	Optical yield, % ee***
without	~90	78****
$\text{C}_{16}\text{N}^+\text{Me}_3\text{HSO}_4^-$	5	95
Silica ion exchanger 1	11	92
$\text{C}_{12}(\text{OCH}_2\text{CH}_2)_{12}\text{OH}$	5	95
Silica bound surfactant 2	24	93
$\text{C}_{12}\text{OSO}_3\text{Na}$ (SDS)	6	94
Alumina adsorbed SDS 3	8	90

Notes: * Approximate surfactant concentration at the solid phase: (1) 0.63, (2) 0.31, and (3) 0.25 mmol/g.

** $t_{1/2}$ is the half-time of the hydrogenation.

*** Measured by GC (see Table 1).

**** Rh-precipitation.

and hydrophilic centers are in the neighborhood of the surface of the support, and substrate and catalyst are free-movable in these phases. Obviously, the polar and nonpolar phases are fixed much stronger on the amphiphilized polymers, and the chances of recycling are improved.

CONCLUSIONS

Amphiphiles as assemblies in water can promote chemical reactions. The separation of product and catalyst is often difficult because of the surface activity of the amphiphiles. Polymeric amphiphiles for the embedding of catalysts enable phase separation by filtration or membrane filtration, respectively. The polymerization of unsaturated amphiphiles is possible by UV irradiation or by activation in a low-temperature plasma. Another successful reaction medium is given by supported (immobilized) amphiphiles.

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REFERENCES

1. Bergethon, P.R. and Simons, E.R., *Biophysical Chemistry. Molecules to Membranes*, New York: Springer, 1990, p. 99.
2. Behr, A. and Keim, W., *Erdöl, Erdgas, Kohle, Petrochem.*, 1987, vol. 103, p. 126.

3. Vogt, D., *Aqueous-Phase Organometallic Chemistry*, Cornils, B. and Herrmann, W.A., Eds., Weinheim: Wiley-VCH, 1998, p. 541.
4. Cornils, B. and Kuntz, E.G., *Aqueous-Phase Organometallic Chemistry*, Cornils, B. and Herrmann, W.A., Eds., Weinheim: Wiley-VCH, 1998, p. 271.
5. Moroi, Y., *Micelles. Theoretical and Applied Aspects*, New York: Plenum Press, 1992.
6. Blokzijl, W. and Engberts, J.B.F.N., *Angew. Chem.*, 1993, vol. 105, p. 1610; *Angew. Chem., Int. Ed. Engl.*, 1993, vol. 32, p. 1545.
7. Morawetz, H., *Adv. Catal.*, 1969, vol. 20, p. 341.
8. Brown, J.M., Baker, S.K., Colens, A., and Darwent, J.R., *Enzymic and Nonenzymic Catalysis*, Dunnill, P., Wiseman, A., and Blakebrough, N., Eds., Chichester: Horwood, 1980, p. 111.
9. Fendler, J.H., *Membrane Mimetic Chemistry*, New York: Wiley, 1982.
10. Scrimin, P., *Supramolecular Control of Structure and Reactivity*, Hamilton, A.D., Ed., Chichester: Wiley, 1996, p. 101.
11. Oehme, G., *Aqueous-Phase Organometallic Chemistry*, Cornils, B. and Herrmann, W.A., Eds., Weinheim: Wiley-VCH, 1998, p. 191.
12. Nuzzo, R.G., Haynie, S.L., Wilson, M.E., and Whiteside, G.M., *J. Org. Chem.*, 1981, vol. 46, p. 2861.
13. Didenko, L.P., Makhaev, V.D., Shilova, A.K., and Shilov, A.E., *Prepr. 4th Int. Symp. Homogen. Catal.*, Leningrad, 1984, vol. II, p. 102.
14. Cited in Oehme, G., Paetzold, E., and Selke, R., *J. Mol. Catal.*, 1992, vol. 71, p. L1.
15. Cook, A.H., Harris, G., and Heilborn, G., *J. Chem. Soc.*, 1948, p. 1060.
16. Brovarets, V.S., Zyuz, K.V., Budnik, L.N., et al., *Zh. Obshch. Khim.*, 1993, vol. 63, p. 1259.
17. Grassert, I., Schinkowski, K., Vollhardt, D., and Oehme, G., *Chirality*, 1998, vol. 10, p. 754.
18. Fuhrmann, H., Grassert, I., Schareina, T., et al. *Macromol. Chem. Phys.*, 2001, vol. 202, p. 426.
19. Flach, H.N., Grassert, I., Oehme, G., and Capka, M. *Colloid Polym. Sci.*, 1996, vol. 274, p. 261.
20. Fuhrmann, H., Dwars, T., Michalik, D., et al., *Adv. Synth. Catal.*, 2003, vol. 345, p. 202.
21. Paetzold, E., Kinting, A., and Oehme, G., *J. Prakt. Chem.*, 1987, vol. 329, p. 725.
22. Grassert, I., Kovács, J., Fuhrmann, H., and Oehme, G., *Adv. Synth. Catal.*, 2002, vol. 344, p. 312.
23. FRG Patent Application 10102465A1, 2002.
24. Tamao, K., Yoshida, J.-I., Yamamoto, H., et al., *Organometallics*, 1982, vol. 1, p. 355.
25. Ryan, J.W., Menzie, G.K., and Speier, J.L., *J. Am. Chem. Soc.*, 1960, vol. 82, p. 3601.
26. Grassert, I., Paetzold, E., and Oehme, G., *Tetrahedron*, 1993, vol. 49, p. 6605.
27. Dwars, T., Schmidt, U., Fischer, C., et al., *Angew. Chem.*, 1998, vol. 110, p. 3033; *Angew. Chem., Int. Ed.*, 1998, vol. 37, p. 2851.
28. Rosen, M.J., *Surfactants and Interfacial Phenomena*, 2nd ed., New York: Wiley, 1989, p. 172.
29. Halpern, J., *Asymmetric Synthesis*, Morrison, J.D., Ed., London: Academic Press, 1985, vol. 5, p. 41.
30. Joó, F., Kovács, J., Bényei, A.Cs., et al., *Chem. Eur. J.*, 2001, vol. 7, p. 193.
31. Papp, E., Bányai, I., and Joó, F., *React. Kinet. Catal. Lett.*, 2000, vol. 69, p. 23.
32. Savelli, G., Germani, R., and Brinchi, L., *Reactions and Syntheses in Surfactant Systems*, Texter, J., Ed., New York: Marcel Dekker, 2001, p. 175.
33. Paetzold, E. and Oehme, G., *J. Mol. Catal. A: Chem.*, 2000, vol. 152, p. 69.
34. Battal, T. and Rathman, J.F., *Reactions and Syntheses in Surfactant Systems*, Texter, J., Ed., New York: Marcel Dekker, 2001, p. 359.
35. Hamid, S. and Sherrington, D., *J. Chem. Soc., Chem. Commun.*, 1986, p. 937.
36. Paleos, C.M., *Polymerization in Organized Media*, Paleos, C.M., Ed., Philadelphia: Gordon and Breach, 1992, p. 183.
37. Oehme, G., Grassert, I., Paetzold, E., et al., *Coord. Chem. Rev.*, 1999, vols. 185–186, p. 585.
38. Nonionic Surfactants. *Polyoxyalkylene Block Copolymers*, Nace, V.M., Ed., New York: Marcel Dekker, 1996.
39. Drexler, K., Meisel, R., Grassert, I., et al., *Macromol. Chem. Phys.*, 2000, vol. 201, p. 1436.
40. Paetzold, E., Oehme, G., Fischer, C., and Frank, M., *J. Mol. Catal. A: Chem.* (in press).
41. Fuhrmann, H., Grassert, I., Holzhüter, G., et al., *New J. Chem.*, 2002, vol. 26, p. 1675.
42. *Surfactant Adsorption and Surface Solubilization*, Sharma, R., Ed., ACS Symp. Ser. no. 615, Washington, D.C.: ACS, 1995.
43. Moineau, C., Iovel, I., and Oehme, G. (unpublished).
44. Wasserscheid, P. and Keim, W., *Angew. Chem.*, 2000, vol. 112, p. 3926; *Angew. Chem., Int. Ed.*, 2000, vol. 39, p. 3772.
45. Arhancet, J.P., Davis, M.E., Merola, J.S., and Hanson, B.E., *Nature*, 1989, vol. 339, p. 454.