Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 8933–8941 **8933**
DOI: 10.1021/ma101169g

Benzoxazine Miniemulsions Stabilized with Polymerizable Nonionic Benzoxazine Surfactants

Christian Sawaryn,[†,‡] Katharina Landfester,[†] and Andreas Taden*[,†,‡]

[†]*Max-Planck-Institute for Polymer Research, Mainz, Germany, and* [‡]*Henkel AG & Co. KGaA, Adhesive Research, Düsseldorf, Germany*

Received May 31, 2010; Revised Manuscript Received September 21, 2010

ABSTRACT: For the first time, the concept of polymerizable nonionic benzoxazine surfactants is described. Different target structures with varying hydrophobic−lipophilic balance (HLB) values were synthesized and successfully tested for the miniemulsification of two N-aliphatic and N-aromatic benzoxazine resins. As a model system, the difunctional benzoxazine surfactant bis(3,4-dihydro-2*H*-3-(polypropyleneoxide-*block*-polyethyleneoxide-1,3-benzoxazinyl)isopropane (B2000) was analyzed in detail via FT-IR, ^{1}H NMR, surface tension measurements, and thermal analysis such as DSC and TGA. Additional to the colloidal stability of the benzoxazine miniemulsions, investigations focused on the surfactant copolymerization behavior and compatibility with other resins. It was found that despite the observed slow homopolymerization the described surfactants easily undergo copolymerization with the model benzoxazine resins.

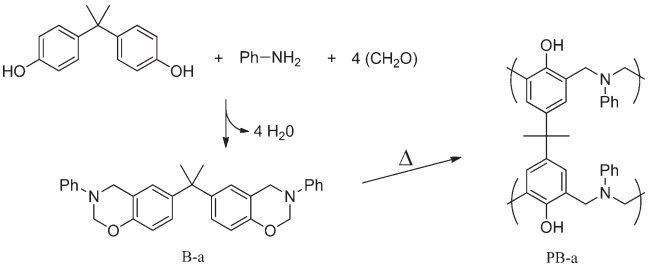
1. Introduction

Benzoxazine resins have gained much interest over the past decade because they can provide a highly competitive combination of properties compared with more "classical" thermoset materials like epoxy or phenolic resins. Depending on the molecular design, benzoxazines can form highly cross-linked thermoset materials after polymerization with excellent mechanical properties like high modulus, high strength, and high glass-transition temperature (T_g).[1] Typical additional advantages are the storage stability of the monomer resins at room temperature, the low heat release and low dimensional shrinkage during the curing reaction, and superior FST (fire, smoke, toxicity) properties of the polymerized material compared with those of epoxy. Most often, benzoxazine monomers are designed as multireactive resins and form highly cross-linked thermosets after cure.[2] The corresponding thermosetting polybenzoxazines can be used as polymer matrix in composite materials, for example, in carbon fiber laminates for aerospace or high-performance racing cars. Other applications are, for example, printed circuit boards or brake adhesives. Because of the advantages described above, it is expected that the use of benzoxazines will grow significantly in the near future and become an important part in general industry.

These expectations are also driven from the synthetic point of view because benzoxazine resins can be easily manufactured from inexpensive raw materials as primary amines, formaldehyde, and phenols. Because of these widely adjustable preconditions, the benzoxazine chemistry offers a highly flexible degree of monomer design.[3−10] The curing reaction shows a true self-polymerizing behavior that allows the polymerization to occur without the addition of initiators or curatives. The general reaction scheme of the synthesis and curing reaction is shown in Scheme 1 using the example of a difunctional benzoxazine monomer based on bisphenol A and aniline.

The group of Ishida et al. was pioneering this field of research and published several ground-breaking contributions.[11−16] Endo et al. have recently investigated the polymerization reaction in more detail and found strong support for intermediate iminium structures that gives a further insight into the benzoxazine polymerization mechanism.[17,18] For a broader overview on this interesting chemistry, the reviews of Yagci are recommended.[1,19]

Scheme 1. Principle of Synthesis and Polymerization of Difunctional Benzoxazines Using the Example of B-a and the Resulting Crosslinked Polymer PB-a



In this Article, the transfer of benzoxazine chemistry to the field of water-based emulsions is shown. We describe the synthesis of benzoxazine resin miniemulsions stabilized with polymerizable nonionic benzoxazine surfactants (Figure 1). Miniemulsions, in general, represent heterogeneous mixtures of small droplets with diameters between 50 and 500 nm, which are produced using high shear forces. The droplets are stabilized by only a low amount of surfactant and an additional osmotic agent that prevents inter-droplet diffusion. Miniemulsions have gained increasing attention over the last several years; consequently, several review articles were published on this topic, which are also recommended to the interested reader.[20,21]

In contrast with commercially available (nonionic) surfactants, benzoxazine surfactants will be used because they contain (co)polymerizable moieties and will become part of the polybenzoxazine network after curing. Nonpolymerizable surfactants show certain mobility during film formation and the initial steps of the curing reaction and therefore can diffuse and segregate in bulk or at interfaces. In particular, for adhesive applications or the interaction between different interfaces, this behavior is usually disadvantageous and unwanted. For example the

*To whom correspondence should be addressed.

Published on Web 10/13/2010

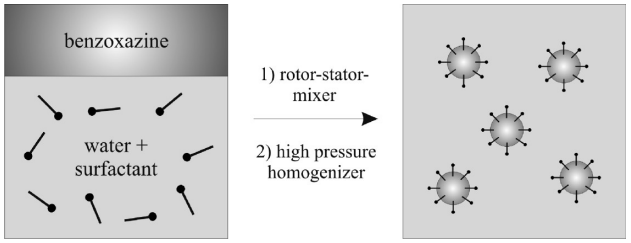
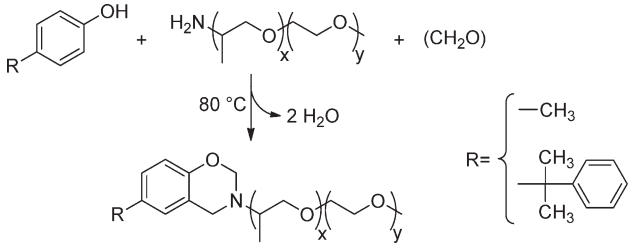
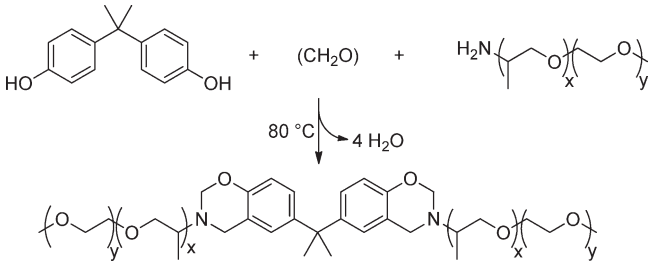


Figure 1. Principle of the miniemulisification of benzoxazine resins in aqueous phase.

Scheme 2. Synthesis of Thermally Polymerizable Benzoxazine Nonionic Surfactants



Scheme 3. Synthesis of Thermally Polymerizable Benzoxazine Nonionic Gemini Surfactants



wettability or paintability is most often reduced. Another consequence is in many cases the lowering of the maximum bond strengths in adhesive joints that can be achieved. Other applications like coatings for corrosion protection can also be affected in negative ways by mobile surfactants or self-forming surfactant aggregates. In addition to a decreased adhesion, such mobile surfactants or surfactant aggregates can also weaken the coating as such because of the creation of domains with higher water content, lower cross-linking density, and lower glass-transition temperature. Therefore, they can, for example, serve as nucleation points for corrosion or fracture failure. The polymerizable benzoxazine-based surfactants described here do help to circumvent these disadvantages because they get incorporated into the polybenzoxazine network upon curing.

2. Experimental Section

2.1. Materials. Bisphenol A, 4-cumylphenol, *p*-cresol, aniline, phenol, 4,4′-methylene dianiline, and paraformaldehyde were used as received from Aldrich.

Polyether monoamines (Surfonamine L-100, L-200, L-300) and Lutensol AT50 were used as received from Huntsman and BASF, respectively.

2.2. Syntheses of Benzoxazine Nonionic Surfactants. Benzoxazine surfactants were prepared from a phenol component, paraformaldehyde, and a polyether monoamine, as shown in Schemes 2 and 3. Abbreviations for the different polyetheramines and the resulting surfactants are listed in Tables 1 and 2, respectively.

p-Cresol- and 4-Cumylphenol-Based Surfactants. The synthesis of pC2000 and CuPh2000 was performed by a solventless method. In a round-bottomed flask, amine-functionalized polyether (10 mmol), phenol component (10 mmol), and paraformaldehyde (20 mmol) were stirred at 80 °C for 2 h. To remove reaction water, a vacuum was applied while stirring at 80 °C for another 3 h. The crude mixture was further purified by GPC column with dichloromethane as eluent on neutral, porous styrene divinylbenzene copolymer beads of 200−400 mesh size. Yellowish solids were obtained (yield ∼85%).

Table 1. List of Hydrophilic Polymeric Amine Components Used for the Synthesis of the Benzoxazine Surfactants

polyetheramine (PEA)	MW (g/mol)	PPO/PEO (x/y)
PEA1000	1000	3/19
PEA2000	2000	2/42
PEA3000	3000	8/58

Table 2. Nomenclature and HLB Values of the Benzoxazine Surfactants

	PEA1000	PEA2000	PEA3000
p-cresol (HLB)[a]		pC2000 (18)	
4-cumylphenol (HLB)		CuPh2000 (17)	
bisphenol A (HLB)	B1000 (14)	B2000 (18)	B3000 (16)

[a] Hydrophilic−lipophilic balance (Griffin).

Bisphenol-A-Based Gemini Surfactants. B1000, B2000, and B3000 were prepared by analogy to the procedure described for pC2000 and CuPh2000.

Because of the difunctionality of bisphenol A, the molar ratio of phenol, polyetheramine, and paraformaldehyde was changed from 1:1:2 to 1:2:4. Yellowish solids were obtained (yield ∼75%).

3,3′-(Methylenedi-4,1-phenylene)bis[3,4-dihydro-2H-1,3-benzoxazine](P-mda)/N-phenyl-3,4-dihydro-2H-1,3-benzoxazine (P-a) Resin Mixture (3:2 wt % Ratio). P-mda/P-a mixed resin was prepared in a one-pot synthesis. To 700 mL of toluene, paraformaldehyde (540.7 mmol, 16.24 g, 10% excess), 4,4′-methylene dianiline (72.9 mmol, 14.45 g), phenol (245.8 mmol, 23.13 g), and aniline (100 mmol, 9.31 g) were added and refluxed for 5 h under stirring. The reaction mixture was washed three times with 1 N NaOH aqueous solution and three times with deionized water. After removal of solvent via rotary evaporator, the product was heated to 80 °C for another 2 h while high vacuum was applied to remove the residual solvent. The procedure afforded a yellow highly viscous resin. The yield was almost quantitative. The amount of ring-opened structures was quantified by ^{1}H NMR, giving the value of 13%. The amount of oligomeric structures was calculated to be 11% based on GPC analysis.

6,6′-(Propane-2,2-diyl)bis(3-hexyl-3,4-dihydro-2H-1,3-benzoxazine) (B-hex). To 200 mL of toluene, paraformaldehyde (1.1 mol, 36.04 g), bisphenol A (0.25 mol, 57.07 g), and hexylamine (0.5 mol, 50.56 g) were added and refluxed for 5 h under stirring. The reaction mixture was washed three times with 1 N NaOH aqueous solution and three times with deionized water. After removal of solvent via rotary evaporator, the product was heated to 80 °C for another 2 h while high vacuum was applied to remove residual solvent. The procedure afforded a transparent highly viscous resin. The yield was almost quantitative. The amount of ring-opened structures was quantified by ^{1}H NMR, giving the value of 12%. The amount of oligomeric structures was calculated to be 10% based on GPC analysis.

3,3′-(Methylenedi-4,1-phenylene)bis[3,4-dihydro-2H-1,3-benzoxazine] (P-mda). To 200 mL of toluene, paraformaldehyde (1.1 mol, 36.04 g), bisphenol A (0.25 mol, 57.07 g), and aniline (0.5 mol, 46.57 g) were added and refluxed for 5 h under stirring. The reaction mixture was washed three times with 1 N NaOH aqueous solution and three times with deionized water. After removal of solvent via rotary evaporator, the product was heated to 80 °C for another 2 h while high vacuum was applied to remove residual solvent. The procedure afforded a transparent

orange solid. The yield was almost quantitative. The amount of ring-opened structures was quantified by ^{1}H NMR, giving the value of 11%. The amount of oligomeric structures was calculated to be 8% based on GPC analysis.

N-Phenyl-3,4-dihydro-2H-1,3-benzoxazine (*P-a*). To 200 mL of toluene, paraformaldehyde (1.1 mol, 36.04 g), phenol (0.5 mol, 47.06 g), and aniline (0.5 mol, 46.57 g) were added and refluxed for 5 h under stirring. The reaction mixture was washed three times with 1 N NaOH aqueous solution and three times with deionized water. After removal of solvent via rotary evaporator, the product was heated to 80 °C for another 2 h while high vacuum was applied to remove residual solvent. The procedure afforded a crystalline yellowish solid. The yield was almost quantitative. A ring-closure degree of 90% was determined by ^{1}H NMR. No signs for oligomeric structures were found.

2.3. Preparation of Polybenzoxazine Films. One gram of the polymerizable surfactant B2000 and 4 g of resin were placed in an aluminum dish (Ø = 5 cm), mixed, and then cured at 180 °C for 3 h in an autoclave at 6 bar pressure to give transparent polybenzoxazine films.

2.4. Preparation of Benzoxazine Miniemulsions. Miniemulsions were prepared by two different methods. In method 1 (pure resin method), the pure resin was emulsified at elevated temperatures, which ensured a low viscosity. In method 2 (resin solution method), the resin was dissolved in chloroform and emulsified at room temperature. After emulsification, the solvent was evaporated to give the final miniemulsion.

Pure Resin Method. Unless otherwise noted, aqueous miniemulsions were prepared with a water/resin weight ratio of 4:1. The surfactant was dissolved in 80 g of water (continuous phase) and heated to a certain temperature, 70 °C for P-mda/P-a and 80 °C for B-hex systems. Twenty grams of the preheated resin (dispersed phase) was slowly added to the continuous phase under mixing with a rotor-stator mixer to afford the pre-emulsion. The pre-emulsion was transferred to a high-pressure homogenizer and miniemulsified at 70 and 80 °C, respectively (four cycles). The ready-made miniemulsion was allowed to cool to room temperature.

Resin Solution Method. Twenty milliliters of a 50 wt % solution of resin in chloroform was slowly added to the continuous phase (80 g water plus surfactant). The system was mixed with a rotor-stator mixer at room temperature to afford the preemulsion. Miniemulsification was carried out in a high-pressure homogenizer at room temperature (four cycles). To evaporate the solvent, miniemulsion was stirred in an open beaker for several hours.

2.5. Instrumentation. Miniemulsification was carried out on a Microfluidics M-100Y Microfluidizer processor at 11 000 psi using the chamber sequence (1) H210Z (200 μ) and (2) H210Z (400 μ). FT-IR spectra were obtained with Bruker spectrometer model IFS66v/s. ^{1}H NMR spectra were recorded on a Bruker UltraShield 400 (400 MHz) instrument. Optical microscopy was carried out on an Olympus BX60 microscope. TEM pictures were obtained on a Philips CM12 instrument. Dynamic viscosity of the resins was measured using TA Instruments ARES rheometer (plate/plate). Differential scanning calorimetry (DSC) was measured on a TA Instruments Q1000 analyzer. Samples (6 to 7 mg) were heated from −90 to 300 °C at a heating rate of 2 °C/min under nitrogen. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q5000 analyzer. Samples (6 to 7 mg) were heated from room temperature to 500 °C at a heating rate of 2 °C/min under nitrogen. Surface tension was measured on a Dataphysics DCAT 11 instrument by Du Noüy ring method at 25 °C. Particle diameters were determined via scattering experiments on a NICOMP 380 particle sizer at a scattering angle of 90° using a red laser diode at a wavelength of 635 nm. The temperature was 23 °C.

3. Results and Discussion

Benzoxazines of technical interest are commonly hydrophobic materials and only show very limited water solubility. In fact, for the typical applications mentioned in the introduction, chemists and engineers are aiming for low water uptake materials to maintain a very high T_g under "wet" conditions.[22] Compared with most cured epoxy resins, such polybenzoxazines usually have a lower water uptake and a better T_g retention. In contrast with that, the polymerizable nonionic benzoxazine surfactants described here show a quite unusual structure and corresponding properties; for example, they are amphiphilic and fairly water-soluble.

Such surfactants consist of a hydrophobic headgroup with at least one benzoxazine unit as main motive and at least one hydrophilic tail based on poly(ethylene oxide) (PEO). The synthesis of polymerizable benzoxazine surfactants is described in Schemes 2 (mono surfactant) and 3 (gemini surfactants).

A similar concept of structurally related naphthoxazine-functional poly(propylene oxide)s has already been reported.[23] As a basis for the synthesis of different benzoxazine surfactants, three phenolic derivatives were applied corresponding to three different types of hydrophobic head groups: *p*-cresol, 4-cumylphenol, and bisphenol A. The previous two result in the formation of so-called monobenzoxazines, and the latter one yields a difunctional benzoxazine derivative after synthesis, which can be considered as a gemini surfactant.[24] As the nonionic, hydrophilic tail PEO of different molecular weight is applied. For the synthesis of the target structures, three different polyetheramines consisting of poly(propylene oxide)-*block*-poly(ethylene oxide) (PPO/PEO) block copolymers with a terminal primary amine functionality were applied. The amine group is bound to a short hydrophobic PPO chain end that contributes in the final benzoxazine surfactant structure to the hydrophobic headgroup. The main fraction of the polyetheramines consists of a longer hydrophilic PEO chain compared with the corresponding PPO block. The molecular weight, the PPO/PEO ratio, and the abbreviations for the three different used polyetheramines are shown in Table 1.

The starting materials described above were used for the synthesis of a set of different benzoxazine surfactants with systematic variations in the headgroup structure and the PEO chain length. Overall, five different benzoxazine surfactants were synthesized, and their constitution and nomenclature are shown in Table 2. The theoretical values for the hydrophobic−lipophilic balance (HLB) according to Griffin[25,26] were calculated from the different molecular weight fractions within the target structures and are listed also listed in Table 2.

The calculated HLB values for all surfactants range from 14 to 18 and indicate a predominant hydrophilic character and potential ability for the stabilization of oil-in-water (o/w) emulsions. All of these surfactants were tested in this respect (see later). To obtain reliable analytical results, we further purified the surfactants by preparative size exclusion column (SEC) chromatography to remove possible nonreacted polyetheramines residues and, in the case of the B2000, possible monosubstituted species. All surfactants were analyzed, and the exemplary analytical results are discussed for the gemini-surfactant B2000 in more detail. This difunctional benzoxazine "gemini" surfactant was used most often in due course, and the corresponding analytical results can be considered to be a role model for the other surfactants based on our concept.

3.1. Characterization of Benzoxazine Surfactants. *FT-IR Analysis.* The chemical structure of the surfactants was confirmed by FT-IR analysis. Figure 2 shows the infrared absorption of monomer B2000. The characteristic benzoxazine signal at 1243 cm^{-1} corresponds to the asymmetric stretching vibration of C−O−C in the oxazine ring. In conjunction with the peaks at 1500 and 919 cm^{-1}, which can be assigned to trisubstituted aromatic ring vibrations, the infrared spectra clearly show the presence of the target structure. A strong absorption band can be detected at

1114 cm^{-1}, resulting from the polyether C−O−C stretching vibration, which is overlapping and hides the C−O−C symmetric stretching mode of the benzoxazine ring.

^1H NMR Analysis. The structure of the benzoxazine surfactants was further confirmed by ^1H NMR spectroscopy. Figure 3 shows the ^1H NMR spectra of B2000. The two characteristic methylene group signals of the benzoxazine ring appear at 4.0 (Ar−CH_2−N) and 4.9 ppm (Ar−CH_2−O), and those of the aromatic protons appear at 6.6 to 7.0 ppm. The resonance peaks in the range from 3.4 to 3.8 ppm were assigned to the methylene groups next to the oxygen in the polyether backbone and the methyl end groups of the chains. The signals at 1.6 and 1.1 ppm are the resonance peaks of the methyl groups between the benzene rings and the methyl groups in the polypropylene block. The peaks at 7.3 (chloroform) and 1.9 ppm (water residues) are solvent peaks.

From the ratio of the methylene integral at 4.9 ppm and the methyl integral at 1.6 ppm, the ring closure degree of this benzoxazine monomer can be calculated, giving a value of ~75%. A ring closure degree of 75% for the monomeric B2000 surfactant sample still represents the fact that the vast majority of the surfactant molecules obtain at least one polymerizable unit and can therefore copolymerize efficiently. In the case of the monofunctional benzoxazine surfactants, the same ring closure degree would translate into the situation that one-quarter of the molecules does not carry a polymerizable group and would therefore not covalently bound to the polymer network upon curing. Despite their missing ability for polymerization, the ring-opened structures most likely maintain a certain degree of surface activity and therefore should also be suitable for emulsification and stabilization issues. However, regarding the attempted technical application, these insights and thoughts lead us to the decision to use the B2000 as the main surfactant molecule and role model within this contribution.

Surface Tension. In Figure 4, the surface tension development of benzoxazine surfactant B2000 solutions as a function of concentration at room temperature is shown. The surface tension values were determined by the Du Noüy ring tensiometer method and clearly show the surface activity of the material. A defined critical micellation concentration (cmc) value is not found. As desired, the surface tension decreases strongly already at low concentrations of B2000 until at ca. 1 g/L a surface tension value of ca. 45 mN/m is reached. A further increase in the surfactant concentration still reduces the surface tension but to a much lower extent. From this point on, even a 10-fold increase in concentration to 10 g/L only leads to a surface tension decrease to ca. 40 mN/m. It is likely that already at a concentration of 1 g/L the air−water interface is completely covered with the B2000

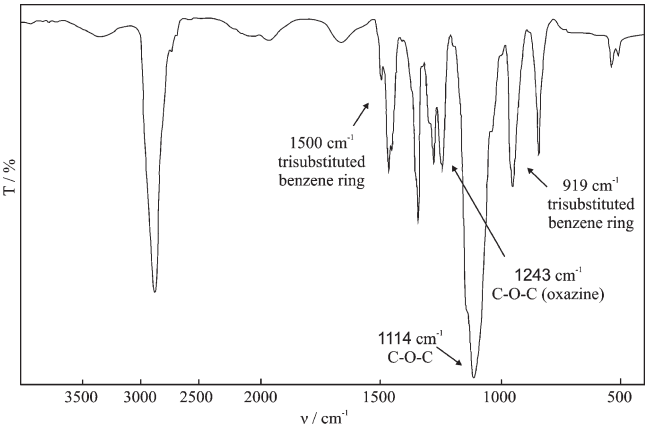


Figure 2. FT-IR spectrum of benzoxazine surfactant B2000.

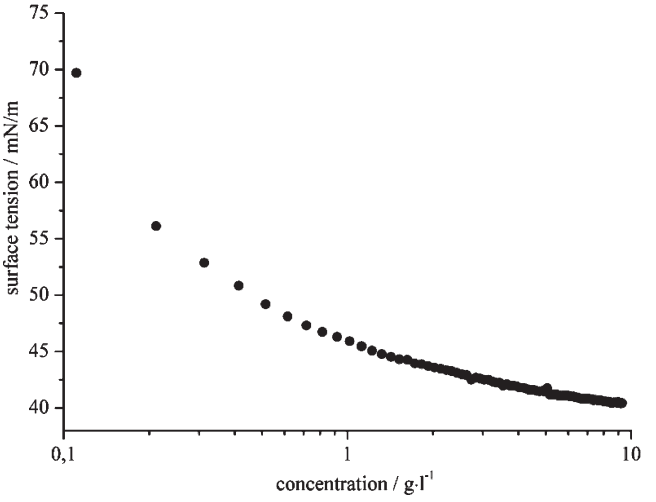


Figure 4. Surface tension of benzoxazine surfactant B2000 as a function of concentration determined by Du Noüy ring tensiometer.

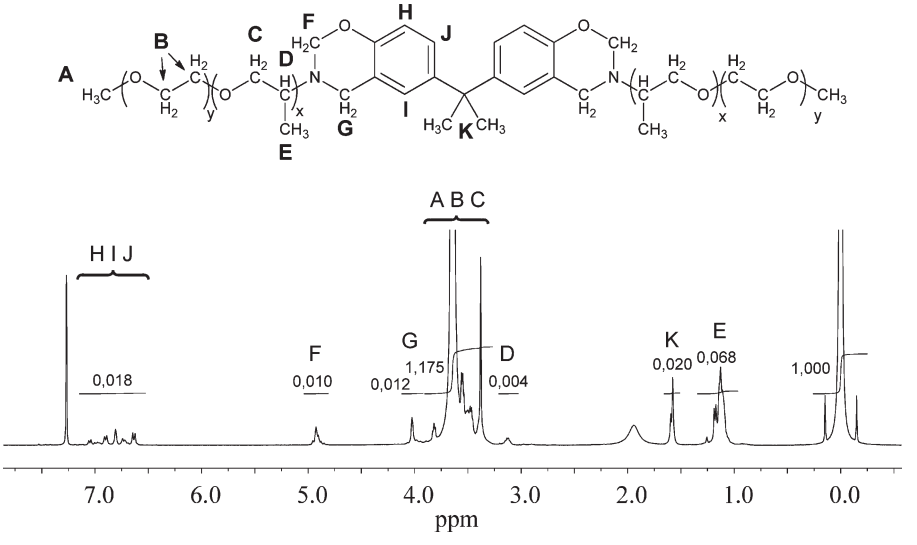


Figure 3. ^1H NMR spectrum of benzoxazine surfactant B2000 in chloroform.

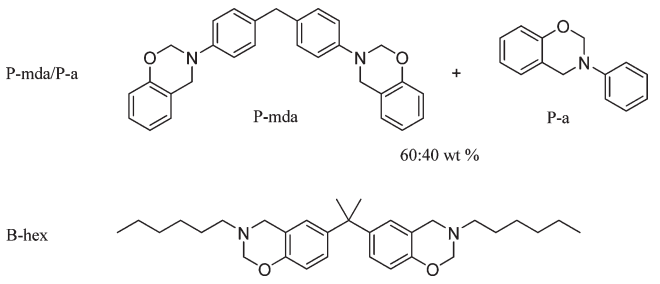


Figure 5. Resin monomer structures of B-hex and P-mda/P-a used as dispersed phase for the miniemulsion experiments.

molecules and that corresponding surfactant aggregates (micelles) are formed within the continuous aqueous phase. A further investigation of the surfactant by dynamic light scattering (DLS) and isothermal titration calorimetry (ITC) gave no reproducible and significant information about the cmc and the formation of defined aggregates. The relatively small further decrease in the surface tension at higher concentrations can probably be attributed to packing phenomena of the sterically demanding B2000 molecules at the air−water interphase and certain corresponding compressibility.

3.2. Miniemulsification and Colloidal Stability. The surfactants described above were tested for their emulsifying and stabilizing effect concerning o/w emulsions of hydrophobic benzoxazine resins. Two different benzoxazine resins were used as the disperse phase for this purpose, namely, P-mda/P-a and B-hex. The idealized monomeric structures of these resins are given in Figure 5. P-mda/P-a is a N-aromatic benzoxazine resin mixture that is synthesized in a one-pot procedure, yielding mono- and difunctional monomeric benzoxazine structures at the same time. This resin was already described by the group of Gu[27] as a potential high-performance resin for the production of fiber-reinforced composites by infusion processes due to a relatively low viscosity. In fact, the monomeric P-a can be considered as a "reactive diluent" that lowers the viscosity and increases the modulus of the cured material at the same time.[27,28] In contrast with that, the B-hex represents a N-aliphatic benzoxazine resin based on bisphenol A, hexylamine, and formaldehyde only.[29]

It shall be noted that these benzoxazine resins do partially contain oligomeric and ring-opened structures because these side products prove to be beneficial to a certain extent in several ways. First of all, the benzoxazine oligomers can prevent the crystallization of the monomer; this makes the handling of the resin much more convenient. Second, the ring-opened phenolic structures show a slight catalytic character and help to increase the curing kinetics.[30,31] For a possible industrial synthesis of benzoxazines, it is furthermore important that the workup procedure can be simplified as much as possible and that the overall yield of the reaction is, in general, very high. In this relationship, the process becomes more sustainable and environmentally friendly because less waste is produced when a certain degree oligomers and ring-opened structures can be tolerated. Last, but not least, the oligomer distribution has a strong effect on the viscosity of the resin material, which is crucial in many applications, for example, for infusion processes or the fabrication of preimpregnated fibers (prepregs).

The viscosity of the resins is also one of the main criteria for the miniemulsification process. Miniemulsions are created by a fission and fusion procedure involving very high sheer forces. Larger droplets from the starting pre-emulsion

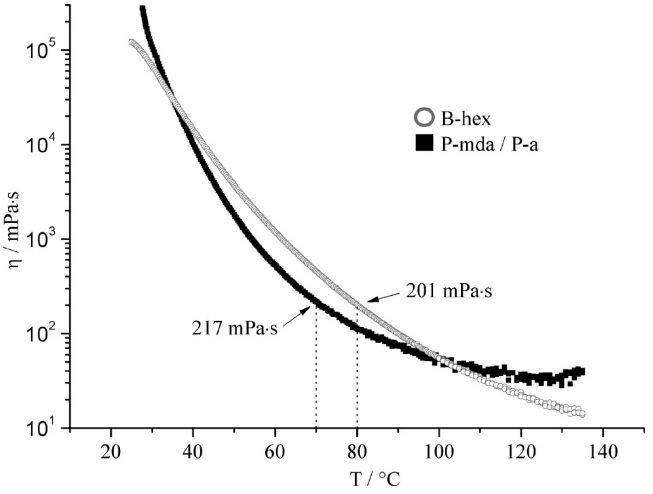


Figure 6. Viscosity−temperature dependencies of the resins B-hex (○) and P-mda/P-a (■) that were used as dispersed phase in miniemulsion. Emulsification was performed at viscosities of ~200 mPa·s.

Table 3. Particle Diameters of Miniemulsions Prepared by the Pure Resin Method with Varying B2000 Surfactant Concentrations and a Fixed Water/Resin Ratio of 4/1 by Weight

disp. phase	P-mda/P-a					B-hex	
c(B2000) (g/L)[a]	25	37,5	50	62,5	75	25	62,5
d_{vol} (nm)	417	340	274	238	212	425	194
d_{vol}/d_{num}	2,18	2,17	1,90	1,95	1,74	2,19	1,66

[a] c in cont. phase (H_2O).

are torn into pieces and partially fused together again because the newly created interfaces cannot be stabilized quickly enough because of the limited surfactant diffusion and adsorption. The final miniemulsion represents an equilibrium state from this interplay after a short period of energy insertion to the system. However, if the viscosity of the disperse phase is much higher than that for the continuous phase, then the droplet fission step is less effective. As a consequence, the miniemulsion particle size distribution becomes broader, and the average particle size becomes bigger. In the worst case, the whole process becomes unfavorable, and a stable miniemulsion cannot be obtained.

The viscosity−temperature dependencies of the resins B-hex and P-mda/P-a are shown in Figure 6. The miniemulsification of the pure resins was performed at viscosities of ~200 mPa·s at elevated temperatures of 70−80 °C. Alternatively, the resins were dissolved in chloroform to give very low viscous 50 wt % solutions, which where then subsequently used as disperse phase. In this case, the miniemulsification itself was performed at room temperature. Afterward, the chloroform was removed by careful evaporation out of the droplet without destroying the miniemulsion stability.

Table 3 summarizes the DLS results obtained from the miniemulsification of P-mda/P-a and B-hex with the surfactant B2000 at different concentrations via the pure resin method. The water/resin ratio was kept constant at 4/1 by weight. In all cases, monomodal miniemulsions were obtained. In accordance with the literature, the particle sizes can be adjusted by variation of surfactant concentration. The average particle size decreases with increasing surfactant concentration in the size range between 200 to 500 nm with values of d_{vol}/d_{num} of ~2 as a measure for the polydispersity. A surfactant concentration of 20 g/L appeared to be a critical value, below which the miniemulsions showed instability.

The gemini B2000 surfactant was compared with the different synthesized monofunctional benzoxazine surfactant

Table 4. Particle Diameters of Miniemulsions with P-mda/P-a As the Disperse Phase Stabilized by Different Surfactants (Water/Resin Ratio: 4/1 wt %) Prepared by the Pure Resin Method[a]

surfactant	B1000	B2000	B3000	pK2000	CuPh2000	Lut AT50
d_{vol} (nm)	$905_{(78\%)}$/365	417	449	462	452	477
d_{vol}/d_{num}	4,16	2,18	1,14	2,11	1,10	3,10
modality	bi	mono	mono	mono	mono	mono

[a] Surfactant concentration in the aqueous phase was kept constant at 25 g/L.

molecules and with the commercially available Lutensol AT50 (Table 4), a nonionic (and nonpolymerizable) surfactant that carries a C_{16}/C_{18} chain as the hydrophobic part and PEO with 50 repeat units on average as the hydrophilic tail. The miniemulsification in this test series was always performed with the pure P-mda/P-a resin mixture at 70 °C, a fixed water/rein ratio of 4/1, and an identical surfactant concentration of 2.5 wt % to the continuous aqueous phase. With the exception of the B1000, all surfactants gave under these conditions monomodal particle size distributions. In other words, the usage of B1000 yielded the least stable system, which can be explained by the comparably shortest PEO chain, which is responsible for the steric repulsion of the droplets and their stabilization against coalescence. Interestingly, most of the benzoxazine surfactants gave similar or even better DLS results compared with the nonionic surfactant Lutensol AT50. The use of B3000 and CuPh2000 gave reproducibly very narrow monomodal particle size distributions. These two benzoxazine surfactants do have a slightly lower HLB value compared with B2000 and pK2000, which gave similar results and a polydispersity of ~2. It can be speculated that the differences in the amphiphilic character of the described surfactants do lead to these trends in observation.

3.3. Crystallization versus Stability. Although stable benzoxazine miniemulsions with reasonable and comparable DLS data were obtained with both resins used as disperse phase, the samples based on P-mda/P-a showed a tendency to coagulate and "solidify" after several days of storage at room temperature. In comparison with that, the B-hex samples stayed perfectly stable, even after several weeks or months of storage. This behavior was observed almost independently from the surfactant type, solid content, or surfactant concentration of the samples. The reason for this behavior can be explained from the optical microscope pictures shown in Figure 7. In the case of the P-mda/P-a miniemulsions, a slight but enduring tendency for the formation of large needles can be observed, whereas this process is absent for the B-hex samples. Obviously a macroscopic crystallization takes place from the N-aromatic benzoxazine resin miniemulsion and finally leads to destabilization. In fact, the sample not only coagulates but also "solidifies" at higher solid contents. This is due to the stiff needles that come into contact in an irregular pattern and leave a high amount of space vacant where the water from the starting aqueous miniemulsion is included. A similar behavior in a different miniemulsion system was already previously investigated in more detail and describes the formation of macroscopic molecular crystals induced by an transition from amorphous to crystalline in the miniemulsion particles and the awakening of "super van der Waals interactions".[32]

In fact, the crystallization from a miniemulsion based on the above-mentioned driving force is difficult to prevent by surfactant variation only and practically always leads to coagulation. The best way to avoid or at least to slow this destabilization mechanism seems to be to avoid the crystallization itself, as is proven for the B-hex system. These considerations are supported by the investigation of the pure P-mda and P-a miniemulsions, which were synthesized for comparison. Indeed, the pure systems do have a more pronounced needle formation tendency compared with the P-mda/P-a mixture and coagulate even faster. Obviously, the P-mda/P-a resin mixture is a first step toward crystallization suppression due to a molecular heterogeneity. It shall be noted in this context that the presence of oligomers and partially ring-opened structures again proves to have a beneficial side effect because the crystallization can potentially be slowed or prevented completely.

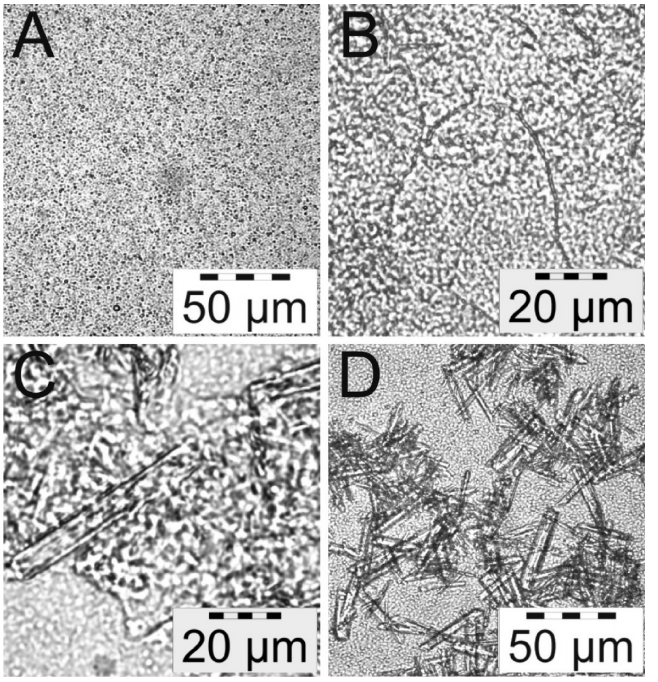


Figure 7. Images of (A) B-hex, (B) P-mda/P-a, (C) P-mda, and (D) P-a miniemulsions obtained by an optical microscope. The existence of needle-shaped particles in P-mda and P-a containing miniemulsions causes instability.

As previously mentioned, the benzoxazine miniemulsions were prepared by either the pure resin or the resin solution method. The resin solution method has the disadvantage that the solvent used as an auxiliary additive to facilitate the miniemulsification step needs to be removed afterward without destroying the miniemulsion stability as such. Therefore, the auxiliary solvent needs to be evaporated very carefully under mild conditions to avoid coagulation. As model solvent, chloroform was used for this purpose, even knowing that this solvent very likely prohibits any commercial process transcription. Nevertheless, in Figure 8, it can be seen from an example based on B-hex that this procedure does lead to much smaller and narrower particle size distributions compared with the pure resin method. It shall be noted that in principle this resin method can also be performed with other hydrophobic solvents different from chloroform. Typical candidates would, for example, be cyclohexane, ethylacetate, or toluene (azeotropic removal).

3.4. Thermal Analysis and Copolymerization Behavior. In practice, almost all possible applications of the benzoxazine miniemulsions do involve a film formation, followed by curing at high temperatures. Very often, the curing of benzoxazines is performed at 180 °C for several hours, but (post)curing temperatures of up to 250 °C can also be applied in special cases. Therefore, it is important that the benzoxazine surfactants do show a high thermal stability and do not decompose under the curing conditions. The TGA diagrams of B1000, B2000, and B3000 under an air atmosphere can be

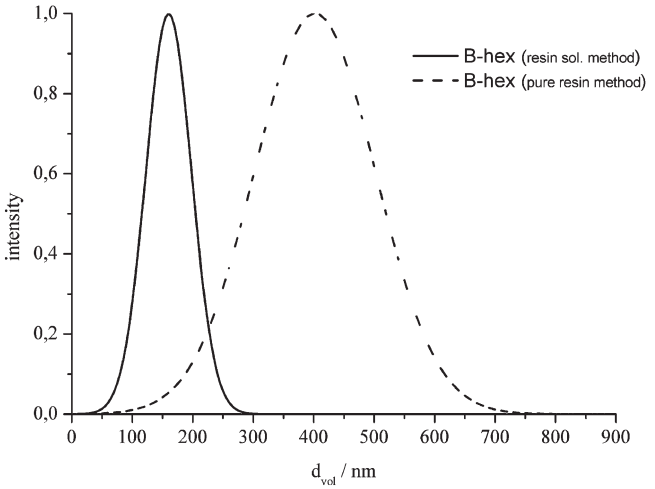


Figure 8. Particle size distribution (d_{vol}) of B-hex miniemulsions prepared by two different methods. (c(B2000) = 25 g/L; water/resin ratio: 8/1 wt %).

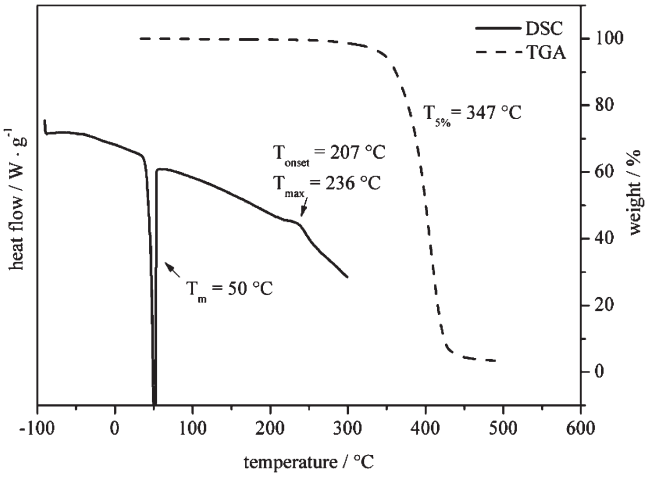


Figure 9. Thermal analysis of B2000 by DSC (solid line) and TGA (dashed line). The heating rates in both cases were 2 K/min.

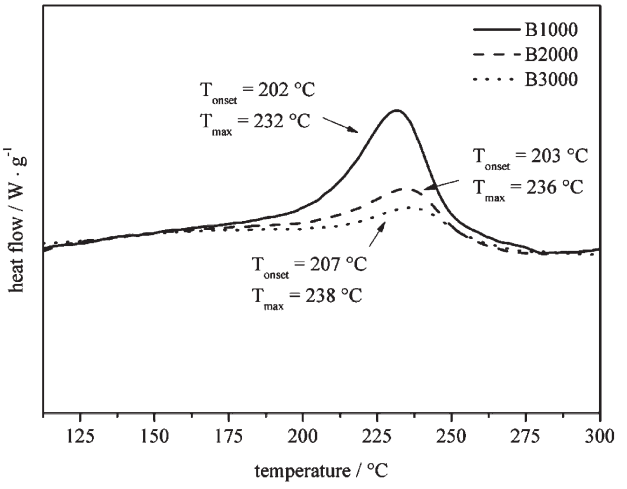


Figure 10. DSC overlay of the benzoxazine gemini surfactants B1000, B2000, and B3000. The heating rate in each measurement was 2 K/min.

found in Figure S1 of the Supporting Information and prove that the surfactants have an excellent thermal stability. Furthermore, the surfactants should copolymerize with the benzoxazine resins used as the disperse phase. In Figure 9, the exemplary thermal analysis of the B2000 is shown. The DSC and the TGA diagrams were recorded with a heating rate of 2 K/min and under a nitrogen atmosphere. The TGA shows an excellent thermal stability signified by a $T_{5\%}$ value of 347 °C. The degradation onset temperature T_{onset} lies well above 300 °C. The DSC diagram shows a pronounced melting transition at T_m = 50 °C from the highly crystalline PEO chain. The exothermic curing of B2000 can be observed at relatively high temperatures with T_{onset} = 207 °C and T_{max} = 236 °C.

A DSC overlay of the homopolymerizations of B1000, B2000, and B3000 are shown in Figure 10. It can be clearly seen that with a higher molecular weight of the polyether chain the homopolymerization is shifted to higher temperatures. Because the investigated benzoxazine surfactants from this series are almost identical to the electronic point of view, this behavior can only be explained by the differences in steric demand of the substituent to the nitrogen atom in the polymerizable benzoxazine unit. The larger the steric hindrance due to the N-polyether substituent, the slower the homopolymerization kinetics. It seems to be surprising that concerning the molecular weight of the substituent, even in the range between 1000 and 3000 g/mol, visible shifts in the polymerization kinetics can be found. The deceleration in the homopolymerization kinetics seems to reach slowly an upper limit between B2000 and B3000 because the difference in the T_{max} values become smaller.

Besides the slow homopolymerization behavior in general, it can be seen that the peaks in the DSC are rather broad. This can be at least partially attributed to the molecular weight distribution of the polyether substituents. Because the attached polyether chains carry a certain polydispersity in molecular weight, they also differ in size and steric demand, which finally corresponds to a variation in the activation barrier for the polymerization. Another major influence on the broadness of the peaks is ring-opened species that function as acidic impurities.

Even more important than the homopolymerization of the benzoxazine surfactants is their copolymerization with the disperse phase. It is obvious from an application point of view that a low amount of surfactant is beneficial and should be always preferred. Therefore, the main benzoxazine fraction of the described benzoxazine miniemulsions will, in practice, always consist of the hydrophobic benzoxazine resins. However, as previously mentioned, even a small fraction of surfactant can still lead to negative side effects if it does not become incorporated into the overall polymer network after curing. Several DSC measurements were conducted to clarify the polymerization reaction of the B2000 with the P-mda/P-a resin and the B-hex resin. Additionally, to the pure material samples two mixtures with 20 mol % B2000 and the two different benzoxazine systems based on the theoretical molar masses were analyzed. All measurements were recorded under the same conditions with a heating rate of 2 K/min. The results are displayed in the overlay diagrams of Figures 11 and 12, respectively.

The pure N-aliphatic B-hex resin is polymerizing at lower temperatures than those of the N-aromatic P-mda/P-a resin system. The homopolymerization of the surfactant occurs at significantly higher temperatures and is noticeable broader than that for both resin systems investigated.

Figure 11 shows that B2000 in combination with P-mda/P-a results in an exothermic curing peak that appears at almost the same temperatures as the pure P-mda/p-a system and is furthermore of comparable width. No signs can be found that residual B2000 still homopolymerizes at higher

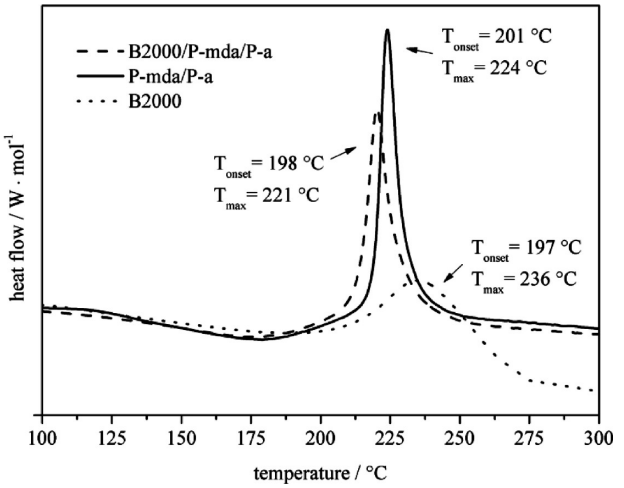


Figure 11. DSC overlay of the curing peaks of P-mda/P-a, the surfactant B2000, and a 4/1 molar mixture of P-mda/P-a with B2000 based on the theoretical molar masses. The heating rate in each measurement was 2 K/min.

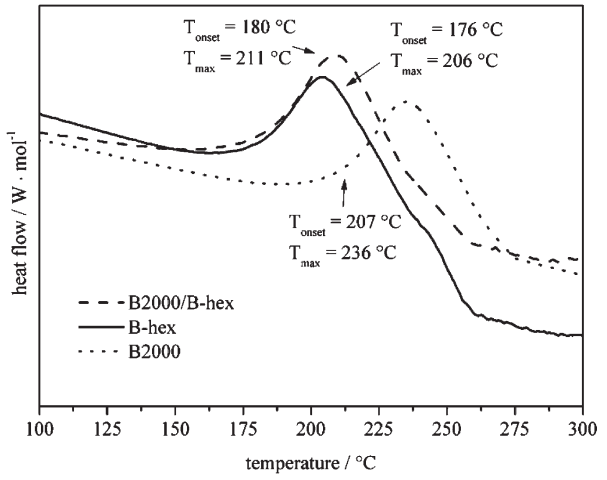


Figure 12. DSC overlay of the curing peaks B-hex, the surfactant B2000, and a 4/1 molar mixture of B-hex with B2000 based on the theoretical molar masses. The heating rate in each measurement was 2 K/min.

temperatures. This data strongly suggests that all B2000 surfactant molecules copolymerize with the N-aromatic benzoxazine and get incorporated into the polybenzoxazine network already under relatively mild curing conditions. Figure 12 shows that in the case of B2000, in combination with B-hex, the exothermic curing peak also appears at almost the same temperatures as those for the pure B-hex system and is in a similar manner of comparable width. Most important is that no residual B2000 is left over for a polymerization at higher temperatures. Therefore, the results can be interpreted in a way that the B2000 surfactant is also in this N-aliphatic benzoxazine system incorporated completely under relatively mild curing conditions.

3.5. Compatibility. Finally, the compatibility of the benzoxazine surfactants was tested with B-hex and P-mda/P-a. Mixtures with 20 wt % of B2000 in the benzoxazine resins were cured at 180 °C for 3 h to give a ca. 3 mm thick film of the respective polybenzoxazine network. As can be seen from Figure 13, the polymerized samples were in both cases transparent and perfectly compatible, even with high surfactant loading. The color of the samples is identical to the ones obtained with the pure resin systems after curing under the same conditions. Furthermore, the Lutensol AT50 was also tested in the same manner (Supporting Information, Figure S2). In this case, the polymerized B-hex sample appears slightly more turbid but still compatible. The corresponding P-mda/P-a sample, however, becomes completely opaque upon curing, which indicates the formation of surfactant domains within the network that are large enough to scatter light effectively.

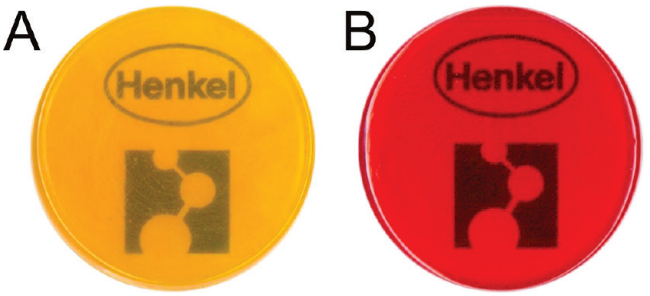


Figure 13. Cured films of B2000 (20 wt %) in (A) B-hex and (B) P-mda/P-a with a thickness of ~3 mm. The transparency indicates the compatibility of surfactant and resin, as demonstrated by the visibility of the MPI-P/Henkel logo placed underneath the samples.

4. Conclusions

Several polymerizable nonionic benzoxazine surfactants were synthesized with varying HLB values and tested for the miniemulsification of two N-aliphatic and N-aromatic benzoxazine resins named B-hex and P-mda/P-a, respectively. Stable miniemulsions with monomodal particle size distributions were obtained already at low surfactant concentrations. All synthesized surfactants gave better results than the commercial Lutensol AT50 reference surfactant with the exception of the benzoxazine surfactant based on the comparably smallest PEO chain length of $M_w \approx 1000$ g/mol as hydrophilic moiety. Stable miniemulsions were prepared following two different homogenization methods, one based on processing the pure resins at elevated temperatures and the other one based on benzoxazine resin solutions, followed by solvent evaporation. The solvent evaporation method did lead, in general, to smaller particles and narrower particle size distributions but requires an additional manufacturing step. The colloidal stability of the systems involving the P-mda/P-a was limited to a couple of days only, even when the starting miniemulsions did show good DLS results after homogenization. It could be shown that the origin of this instability is related to severe interparticle attraction due to crystallization, which practically cannot be avoided by surfactant stabilization only. Contrary to that, the B-hex miniemulsions showed no crystallization tendency and stayed perfectly stable, even over longer time periods.

As a model system for the concept of polymerizable benzoxazine surfactants, the difunctional Gemini benzoxazine surfactant B2000 based on bisphenol A was analyzed in detail. The structure of this compound was proven via FT-IR and ^{1}H NMR spectroscopy. Ring-opened structures were also identified. The overall ring closure degree was determined to a degree of 75%. Surface tension measurements clearly showed the surface activity of B2000.

Special focus was laid on the surfactant copolymerization behavior with the B-hex and P-mda/P-a, respectively. Interestingly, it was found that despite the observed slow homopolymerization, the B2000 easily undergoes copolymerization with these model benzoxazine resins.

Acknowledgment. We thank Stefan Kreiling, Rainer Schönfeld, and Thomas Huver from Henkel Adhesive Research for the

fruitful discussions. The laboratory support from Lothar Unger and Ursula Tenhaef is acknowledged.

Supporting Information Available: TGA of B1000, B2000, and B3000 and cured films of Lutensol AT50 (20 wt %) in B-hex and P-mda/P-a.This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ghosh, N. N.; Kiskan, B.; Yagci, Y. *Prog. Polym. Sci.* **2007**, *32*, 1344–1391.
(2) Ishida, H.; Allen, D. J. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1019–1030.
(3) Takeichi, T.; Agag, T. *High Perform. Polym.* **2006**, *18*, 777–797.
(4) Liu, Y. H.; Zhang, W.; Chen, Y.; Zheng, S. X. *J. Appl. Polym. Sci.* **2006**, *99*, 927–936.
(5) Lin, C. H.; Cai, S. X.; Leu, T. S.; Hwang, T. Y.; Lee, H. H. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3454–3468.
(6) Allen, D. J.; Ishida, H. *J. Appl. Polym. Sci.* **2006**, *101*, 2798–2809.
(7) Agag, T.; Takeichi, T. *Macromolecules* **2003**, *36*, 6010–6017.
(8) Liu, Y. L.; Chou, C. I. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5267–5282.
(9) Andreu, R.; Espinosa, M. A.; Galia, M.; Cadiz, V.; Ronda, J. C.; Reina, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1529–1540.
(10) Kiskan, B.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1670–1676.
(11) Ning, X.; Ishida, H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1121–1129.
(12) Dunkers, J.; Ishida, H. *Spectrochim. Acta, Part A* **1995**, *51*, 1061–1074.
(13) Low, H. Y.; Ishida, H. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1935–1946.
(14) Schnell, I.; Brown, S. P.; Low, H. Y.; Ishida, H.; Spiess, H. W. *J. Am. Chem. Soc.* **1998**, *120*, 11784–11795.
(15) Wang, Y. X.; Ishida, H. *Polymer* **1999**, *40*, 4563–4570.
(16) Ishida, H.; Sanders, D. P. *Macromolecules* **2000**, *33*, 8149–8157.
(17) Sudo, A.; Kudoh, R.; Nakayama, H.; Arima, K.; Endo, T. *Macromolecules* **2008**, *41*, 9030–9034.
(18) Kudoh, R.; Sudo, A.; Endo, T. *Macromolecules* **2009**, *42*, 2327–2329.
(19) Yagci, Y.; Kiskan, B.; Ghosh, N. N. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5565–5576.
(20) Landfester, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 4488–4507.
(21) Antonietti, M.; Landfester, K. *Prog. Polym. Sci.* **2002**, *27*, 689–757.
(22) *ASTM Standard D7028, "Standard Test Method for Glass Transition Temperature (DMA Tg) of Polymer Matrix Composites by Dynamic Mechanical Analysis (DMA)*; ASTM International: West Conshohocken, PA, 2001.
(23) Yildirim, A.; Kiskan, B.; Demirel, A. L.; Yagci, Y. *Eur. Polym. J.* **2006**, *42*, 3006–3014.
(24) Menger, F. M.; Keiper, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1907–1920.
(25) Griffin, W. C. *J. Soc. Cosmet. Chem.* **1954**, *5*, 249–256.
(26) Griffin, W. C. *J. Soc. Cosmet. Chem.* **1949**, *1*, 311–326.
(27) Xiang, H.; Ling, H.; Wang, J.; Song, L.; Gu, Y. *Polym. Compos.* **2005**, *26*, 563–571.
(28) Dansiri, N.; Yanumet, N.; Ellis, J. W.; Ishida, H. *Polym. Compos.* **2002**, *23*, 352–360.
(29) Kaushik, M.; Bhatnagar, N.; Varma, I. K. *Int. J. Plast. Technol.* **2005**, *9*, 377–384.
(30) Ishida, H.; Rodriguez, Y. *Polymer* **1995**, *36*, 3151–3158.
(31) Ning, X.; Ishida, H. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 921–927.
(32) Taden, A.; Landfester, K.; Antonietti, M. *Langmuir* **2004**, *20*, 957–961.