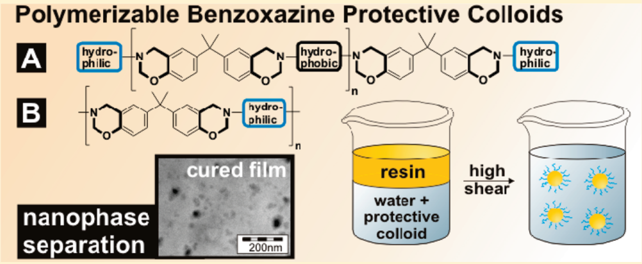
Macromolecules
ARTICLE
pubs.acs.org/Macromolecules

Benzoxazine Miniemulsions Stabilized with Multifunctional Main-chain Benzoxazine Protective Colloids

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

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

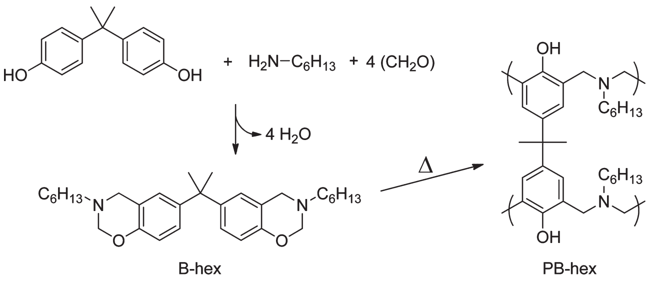
ABSTRACT: The morphology control of thermoset systems is one of the key challenges to obtain high performance materials like structural adhesives or advanced protective coatings. Usually applied from solvents, it is highly desirable to transfer this concept to environmentally benign aqueous dispersions, although typical disadvantages like increased water uptake or reduced adhesion have to be minimized. In this respect, we introduce two different types of main-chain benzoxazine protective colloids, one of them additionally showing a lower critical solution temperature (LCST) characteristics, that provide colloidal stability in dispersion and become covalently incorporated into the network upon curing to suppress typical negative side effects. Furthermore, these multifunctional agents can be designed to undergo simultaneously a tailored chemically induced phase separation (CIPS) in order to obtain a desired morphology and to improve the overall mechanical and thermal properties of the resulting thermoset materials. The two examples were characterized by ^{1}H NMR, FT-IR, DSC, and TGA. The colloidal stability was characterized by DLS and turbidity measurements. The thermoset morphologies were investigated by TEM.



1. INTRODUCTION

As indicated by active publication of numerous patents and publications in the field of benzoxazine chemistry, this innovative material class has gained increasing interest over the past decade. The ability of true self-polymerization, the high design flexibility and the excellent properties of the resulting thermosets have drawn attention to this biheterocycle and motivated research and industry to focus on this vivid field of research.[1,2] In 1944, Holly and Cope reported the synthesis of 1,3-benzoxazines by the combination of a primary amine, a phenolic derivate, and formaldehyde.[3] The enormous number of possible combinations by varying amine and phenolic component offers a huge library of different benzoxazine derivates. An example is given in Scheme 1. The thermally activated curing reaction occurs without the addition of catalysts or initiators and can lead, depending on the molecule design, to highly cross-linked thermoset materials with highly competitive properties compared to "classical" thermosets as epoxy or phenolic resins. The excellent mechanical properties as high modulus, high strength and high glass transition temperature (T_g) in combination with other advantages as storage stability of the resins at room temperature, low heat release and low dimensional shrinkage during curing and superior FST (fire, smoke, toxictiy) open a wide range of possible applications[1] from composite materials over brake adhesives to printed circuit boards. The use of benzoxazines and their attention in general industry is therefore expected to grow significantly in the near future.

Scheme 1. Principle of Synthesis and Polymerization of Difunctional Benzoxazines Using the Example of B-hex and the Resulting Cross-Linked Polymer PB-hex

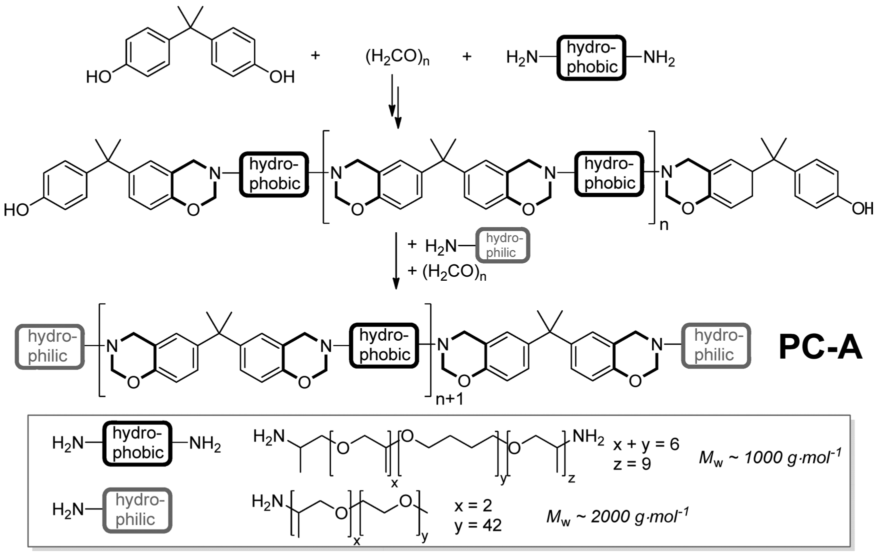


Recent activities in the field of benzoxazine chemistry focus on the replacement of monofunctional amines and phenols by difunctional species. Replacing only one component leads to molecules with two benzoxazine units, a possible solution to increase the cross-linking density in the cured samples. Taking it one step further by starting from a difunctional amine and a difunctional phenol, prepolymers (the correct definition according to the IUPAC guideline) with repeating benzoxazine units in the main chain can be obtained.[4−17] Not only can these prepolymers cross-link via thermally activated ring-opening polymerization, they also behave like thermoplastic materials of good solubility and processability. The resulting cured polybenzoxazines show resistance to creep, good dimensional stability and excellent thermal and chemical resistance. In

Received: April 28, 2011
Revised: June 20, 2011
Published: June 30, 2011

dx.doi.org/10.1021/ma200973g | Macromolecules 2011, 44, 5650–5658

Scheme 2. Three-Step–One-Pot Synthesis of Protective Colloid Type A (PC-A) Containing Hydrophobic Blocks in the Main Chain and Hydrophilic End Blocks

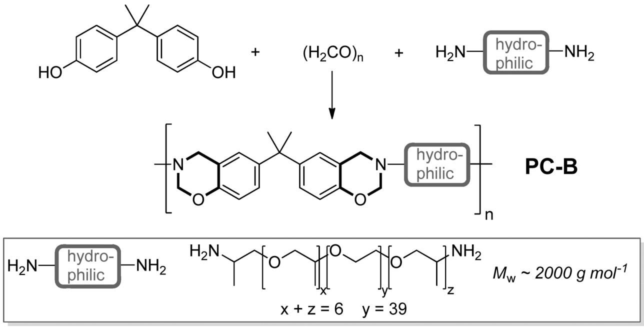


combination with the "classical" benzoxazine thermosets mechanical properties can be improved significantly.[17,18]

In this article, we fuse benzoxazine chemistry with the field of water-based emulsions to show once more the versatility of this material class. We investigated the synthesis and characterization of multifunctional main-chain benzoxazine prepolymers and their ability to function as protective colloids to stabilize o/w-miniemulsions of benzoxazine resins. Miniemulsions are defined as heterogeneous mixtures of small droplets with diameters of 50–500 nm. These particles can be obtained using high shear forces created by devices as ultrasonic tips or high pressure homogenizers of different geometries. Stabilization is achieved by only a small amount of a surface active molecule, usually a surfactant, and an additional osmotic agent that suppresses interdroplet diffusion. Several review articles on this interesting and growing field of research were published in the past.[19–21]

Benzoxazine protective colloids in our definition represent thermally (co)polymerizable surface active multifunctional prepolymers with hydrophilic polymeric blocks and benzoxazine moieties in the polymer backbone. Those molecules combine the advantages of the concepts for nonionic benzoxazine surfactants[22] and high molecular weight multifunctional prepolymers.[16–18] In analogy to the previously described concept for nonionic benzoxazine surfactants, benzoxazine protective colloids can circumvent problems caused by the mobility of the stabilizer since they contain (co)polymerizable moieties that chemically bond to the benzoxazine network during curing. Typical problems include reduction of wettability or paintability in adhesive applications, decrease in strength of adhesive joints and promotion of corrosion or fracture failure by serving as nucleation points for these processes. Additionally to that and in congruence to the structurally similar high molecular weight multifunctional prepolymers, our protective colloids allow tailoring of chemical induced phase separation (CIPS) and the resulting nano- and microphase separation upon curing at the same time. It shall be noted that this concept can be easily transferred to other thermoset resin systems which exhibit copolymerization ability with benzoxazines, e.g., epoxides.

Scheme 3. One-Step Synthesis of Protective Colloid Type B (PC-B) Containing Hydrophilic Blocks in the Main Chain



2. EXPERIMENTAL SECTION

2.1. Materials. Bisphenol A, paraformaldehyde, hexylamine and toluene were used as received from Aldrich. Polyether monoamine Surfonamine L-200, the hydrophilic PEO-based diamine Jeffamine ED-2003 and the hydrophobic PTMO-based XTJ-542 were used as received from Huntsman Corporation.

2.2. Synthesis of Benzoxazine Protective Colloids. Benzoxazine protective colloid type A (PC-A) was prepared in a two-step reaction (Scheme 2). In step one a hydrophobic multifunctional main-chain benzoxazine prepolymer was created starting from Bisphenol A, paraformaldehyde and a hydrophobic polyether diamine. In the second step hydrophilic polymeric end-blocks were attached. Benzoxazine protective colloid type B (PC-B), a hydrophilic multifunctional main-chain benzoxazine prepolymer, was created in accordance to the first step of the PC-A synthesis from Bisphenol A, paraformaldehyde and a hydrophilic polyether diamine (Scheme 3).

Protective Colloid Type A (PC-A). To a suspension of paraformaldehyde (0.44 mol) and Bisphenol A (0.1 mol) in toluene in a round-bottom flask, a solution of the hydrophobic PTMO-based diamine XTJ-542 (0.1 mol) in toluene is added. The mixture is stirred under reflux for 4 h. Bisphenol A (0.02 mol) and paraformaldehyd (0.044 mol) are added and the solution is stirred under reflux for another 2 h. The solvent is removed and the molten hydrophilic monoamine Surfonamine L-200 (0.075 mol) and paraformaldehyde (0.165 mol) is added. The mixture is stirred for 3 h at 80 °C. The crude mixture is dissolved in water and the insoluble residues are filtered out. After evaporation of water the product is degassed for 2 h at about 6×10^{-1} mbar and 80 °C. A yellowish solid was obtained (yield ~82%).

Protective Colloid Type B (PC-B). To a suspension of paraformaldehyde (0.44 mol) and Bisphenol A (0.1 mol) in toluene in a round-bottom flask, a solution of the hydrophilic PEO-based diamine Jeffamine ED-2003 (0.1 mol) in toluene is added. The mixture is stirred under reflux for 5 h. After evaporation of the solvent the product is degassed for 2 h at about 6×10^{-1} mbar and 80 °C. A yellowish solid was obtained (yield ~87%).

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 viscous resin. 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 SEC analysis. Because of the presence of ring-opened structures and oligomeric structures, the yield has been calculated to be around 88%.

2.3. Preparation of Polybenzoxazine Films. One g of the benzoxazine protective colloid and 4 g of the benzoxazine resin were transferred to an aluminum dish (o.d. = 5 cm), mixed and then cured at 180 °C for 3 h in an autoclave at 6 bar. Depending on the chemical nature of the protective colloid, turbid or transparent films were received.

2.4. Preparation of Benzoxazine Miniemulsions. Two different approaches were applied to prepare benzoxazine miniemulsions.[22] Either emulsification of the pure resin at elevated temperatures (pure resin method) or emulsification of resin solution in chloroform at room temperature followed by solvent evaporation was carried out (resin solution method).

Pure Resin Method. Unless otherwise noted, o/w-miniemulsions with a water/resin weight ratio of 4:1 were synthesized. A certain amount (Table 2) of protective colloid was solubilized in 80 g of water (continuous phase) and heated to 80 °C. Slow addition of 20 g of the preheated resin (dispersed phase) under mixing with a rotor−stator mixer afforded the preemulsion. In the next step, the preemulsion was homogenized at 80 °C in a high-pressure homogenizer (4 cycles) and let to cool down to rom temperature.

Resin Solution Method. Unless otherwise noted, o/w-miniemulsions with a water/resin/solvent weight ratio of 8:1:1 were synthesized. A certain amount (Table 2) of protective colloid was solubilized in 80 g water (continuous phase). Twenty ml of a 50 wt % resin solution in chloroform were added under mixing 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). The auxiliary solvent was evaporated by stirring in an open beaker in a fume hood 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 H210Z (200 μm) and H210Z (400 μm). FT-IR spectra were recorded with Bruker spectrometer model IFS66v/s. ^{1}H NMR spectra were obtained on a Bruker UltraShield 400 (400 MHz) instrument. Size exclusion chromatography (SEC) was measured with Waters Alliance instrument with UV detector 2487 (254 nm) or refractive index detector 2410. DMSO was used as a carrier solvent at a flow rate of 0.9 mL·min^{-1} at 35 °C. Three polystyrene gel columns (Waters Styragel HR1, 3 and 5) were used with measurable molecular weights from 1×10^2 to 2×10^7. Polystyrene standards were used for calibration to determine M_n and M_w/M_n. Differential scanning calorimetry (DSC) was measured on a TA Instruments Q1000 analyzer. Samples (6−7 mg) were heated from −90 to 300 °C at a heating rate of 2 °C·min^{-1} under nitrogen. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q5000 analyzer. Samples (6−7 mg) were heated from room temperature to 500 °C at a heating rate of 2 °C·min^{-1} under nitrogen. 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. Turbidity experiments were carried out on a Metrohm 662 turbidity photometer.

Table 1. Apparent Molecular Weights and Polydispersity of the Protective Colloids Determined by SEC (Eluent: DMSO), as Well as the Amounts of Hard and Soft Segments in the Prepolymer

	M_w	M_n	PDI	"soft" part[a]	"hard" part[a]
PC-A	14 600	6400	2.3	89.0	11.0
PC-B	25 800	10 700	2.4	86.7	13.3

[a] In wt % of the total weight of the resulting polymer.

3. RESULTS AND DISCUSSION

Protective colloid type A (PC-A) was synthesized by the polycondensation of a hydrophobic poly(ether diamine) of a molecular weight (M_w) of about 1000 g·mol^{-1}, bisphenol A and paraformaldehyde followed by the attachment of terminal hydrophilic PEO based poly(ether monoamine) (M_w ~2000 g·mol^{-1}) by condensation and formation of benzoxazine (Scheme 2). To ensure a high molecular weight, the first step was carried out in a 1:1 ratio of diamine to diphenol. An additional step, the addition of bisphenol A, was necessary to create bisphenol A end groups that are needed to attach hydrophilic segments. In case of protective colloid type B (PC-B) the target structure was synthesized in one step from a hydrophilic poly(ether diamine) (M_w ~2000 g·mol^{-1}), bisphenol A and paraformaldehyde (Scheme 3).

Both structures can be defined as multifunctional main-chain benzoxazine prepolymers that contain polymeric blocks and benzoxazine units in an alternating order. In general polybenzoxazines are hydrophobic materials of low water uptake. This property is highly desired for most applications and a standard measure in material science. Because of the introduction of hydrophilic poly(ethylene oxide), solubility in water is achieved which is quite unusual for this class of materials. Ishida et al. reported of main-chain benzoxazine prepolymers containing hydrophilic polyether segments in the backbone.[17] Surface-active behavior and their application as protective colloids were not reported.

Both systems were analyzed in detail. Table 1 gives the apparent molecular weights (M_w and M_n) and the polydispersity index (PDI) of these main-chain benzoxazine prepolymers determined by size exclusion chromatography (SEC). The achieved molecular weights are rather low regarding the molecular weight of the oligomeric precursors. This phenomenon could be explained by the limited mobility of the chains in the course of molecular weight increase and the resulting decreased accessibility of the amine groups. Furthermore, the percentage of "soft" polyether blocks and "hard" benzoxazine units has been calculated based on the molecular weight of the amine precursors and the molecular weight of the resulting "hard" benzoxazine structure units in the polymer under the assumption of discrete molecular weights. These values influence the cross-linking-density in the cured state and of course the chemically induced phase separation (CIPS) when incorporated in a thermosetting matrix. The higher the "hard" amount, the more cross-linking sites are available.[18]

Since each molecule contains several benzoxazine structures, ring-closed and ring-opened structures coexist and are randomly distributed along the polymer backbone. Therefore, it is virtually impossible to selectively remove ring-opened structures. Even though the ring open structures cannot actively contribute to the ring-opening polymerization, they still act as linking units between two soft segments. Furthermore, they can be incorporated into the network by covalent bonding as a reaction partner or by hydrogen bonding contribution. The degree of ring-closure is given in the ^{1}H NMR section.

3.2. Characterization of Benzoxazine Protective Colloids. *FT-IR Analysis.* The chemical structure of the protective colloids PC-A and PC-B were confirmed by FT-IR analysis. The FT-IR spectrum of PC-A is shown in Figure 1A. The formation of the oxazine ring is proved by the characteristic benzoxazine signal at 1243 cm^{-1} which corresponds to the asymmetric stretching vibration of C—O—C in the oxazine ring. The C—O—C symmetric stretching mode of the oxazine ring overlaps with the strong absorption band of the polyether C—O—C stretching vibration at 1112 cm^{-1}. The characteristic vibrations of the trisubstituted aromatic ring in the benzoxazine can be found at around 1498 and 926 cm^{-1}. Figure 1B shows the FT-IR spectrum of PC-B. In analogy, the asymmetric stretching vibration of C—O—C in the oxazine ring can be found at 1241 cm^{-1}. The target structure can be further confirmed by the peaks at 1513 and 918 cm^{-1} which can be assigned to trisubstituted aromatic ring vibrations. As in the case of PC-A the strong absorption band of the polyether C—O—C stretching vibration at 1113 cm^{-1} hides the C—O—C symmetric stretching mode of the benzoxazine ring.

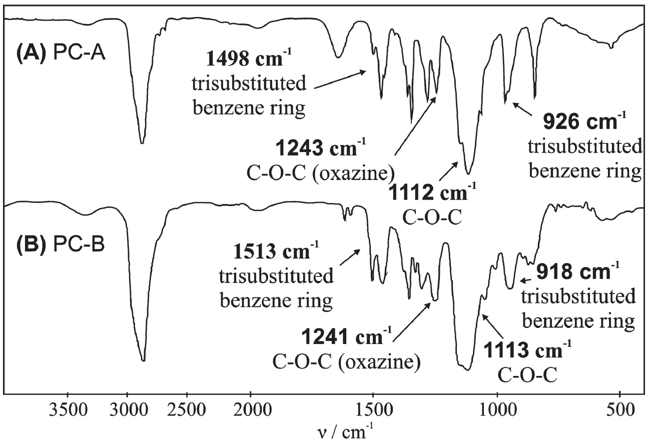


Figure 1. FT-IR spectra of protective colloid type A (A) and type B (B).

^{1}H NMR Analysis. Further confirmation of the target structures was achieved by ^{1}H NMR spectroscopy. Figure 2 shows the ^{1}H NMR spectrum of PC-A. The existence of the oxazine ring can be proved by the two characteristic methylene group signals at 4.1 ppm (Ar—CH$_2$—N) and 4.9 ppm (O—CH$_2$—N). The aromatic protons of Bisphenol A can be found in the region of 6.7 to 7 ppm. The resonance peaks between 3.2 and 3.8 ppm were assigned to the methylene groups in the polyether backbone neighboring oxygen and the methyl end group of the hydrophilic end blocks. Since the peaks of the inner methylene groups of the tetramethylene block at 1.7 ppm overlap with the methyl groups between the benzene rings, a degree of ring-closure cannot be calculated with high accuracy. The peaks at 7.3 ppm (chloroform) and 2.1 ppm (water residues) can be assigned to solvent residues.

Figure 3 shows the ^{1}H NMR spectrum of PC-B. The two characteristic methylene group signals of the benzoxazine ring appear at 4.0 ppm (Ar—CH$_2$—N) and 4.9 ppm (O—CH$_2$—N), the aromatic protons at 6.6 to 7.1 ppm. The resonance peaks between 3.3 and 3.7 ppm were assigned to the methylene and methine groups in the polyether backbone. 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. A ring closure degree of 66% was calculated from the ratio of the integral of the methylene group at 4.9 ppm and the methyl group integral at 1.6 ppm. The signals at 7.3 ppm (chloroform) and 2.1 ppm (water residues) again represent solvent peaks.

3.3. Miniemulsification and Colloidal Stability. The main-chain benzoxazine prepolymers were investigated in terms of their abilities to stabilize o/w-emulsions of hydrophobic

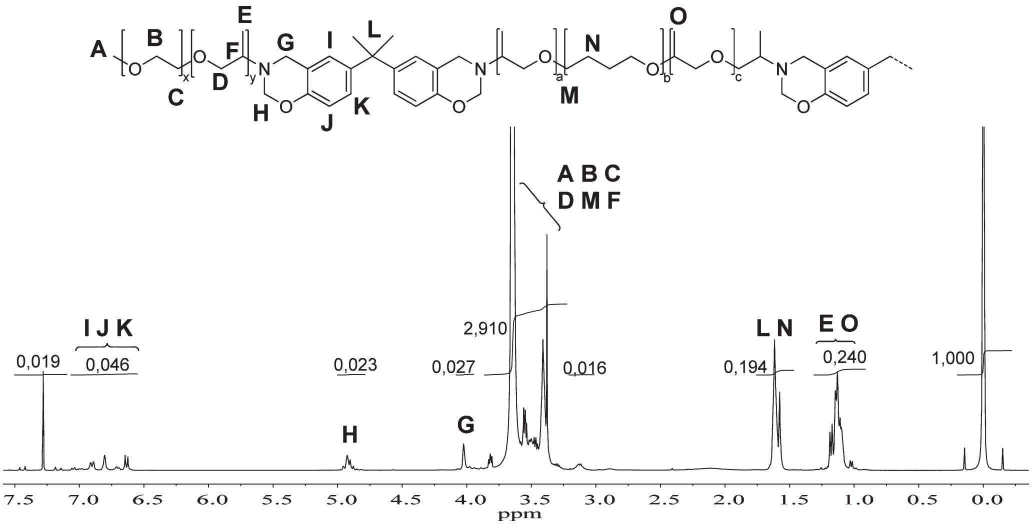


Figure 2. ^{1}H NMR of protective colloid type A in CDCl$_3$.

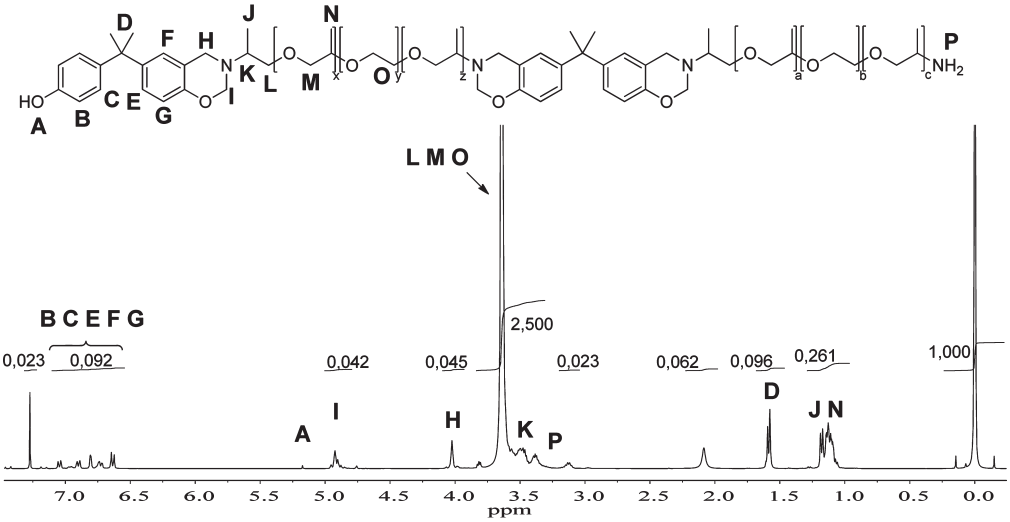


Figure 3. ^{1}H NMR of protective colloid type B in $CDCl_3$.

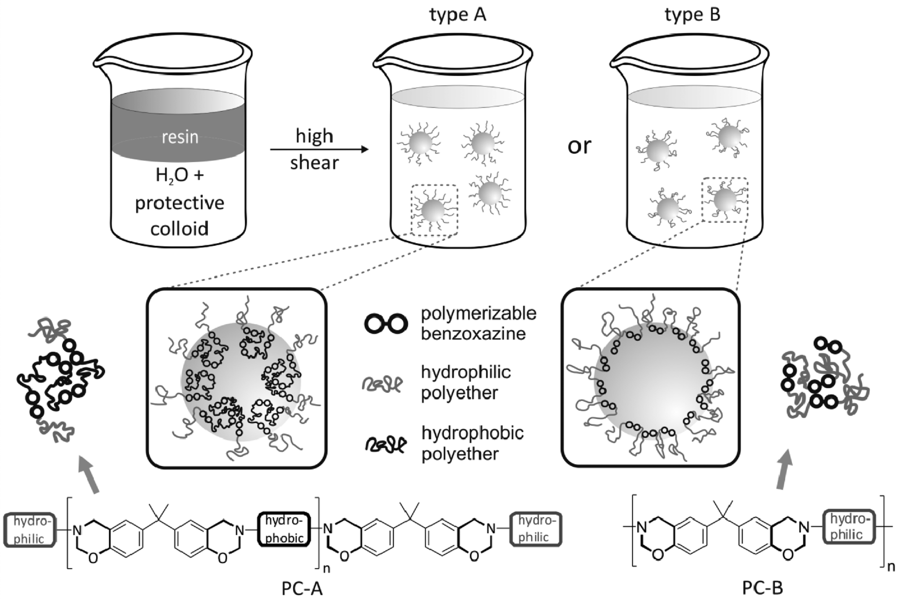


Figure 4. Preparation principle of benzoxazine miniemulsions stabilized by two different benzoxazine-based protective colloids.

benzoxazine resin (Figure 4). Because of the high hydrophobicity and the high viscosity of the benzoxazine dispersed phase, an additional (ultra)hydrophobe is not necessary.

B-hex represents a difunctional *N*-aliphatic benzoxazine resin synthesized from Bisphenol A, hexylamine and formaldehyde.[22,23] We like to point out that this resin as most other benzoxazine resins contains about 10% of oligomeric and ring-opened structures. These side products are desirable since they can suppress crystallization, show slight catalytic behavior in the curing process arising from free acidic phenol groups[24−26] and have major influence on the viscosity. The viscosity of the benzoxazine resin is of great importance for the emulsification procedure. Synthesizing a miniemulsion is based on fission and fusion processes of nanodroplets created by high shear forces. In our experiments a high pressure homogenizer generates these forces by pumping the preemulsion through channels of small diameter and special geometry. Comparably large droplets in the micrometer regime of the preemulsion are raptured into pieces and partially merge again since the interface sometimes cannot be stabilized fast enough. The resulting miniemulsion is a product of the diffusion and absorption rate of the stabilizer, in our case the protective colloid, and the time of energy insertion to the system. With increasing viscosity the effectiveness of the fission step decreases rapidly and the expected size distribution broadens. In the worst case after exceeding a viscosity limit a stable miniemulsion cannot be prepared. On the basis of recently published results,[22] a temperature of 80 °C was chosen to perform the experiments to ensure a viscosity of about 200 mPa·s. Another possibility is the use of resin solutions in an organic auxiliary solvent. The solvent is carefully evaporated in an additional step after the miniemulsification without destroying the droplets.

Both methods, pure resin and resin solution method, were successfully applied to PC-A. Table 2 gives the particle diameters

Table 2. Particle Diameters Obtained by DLS of Miniemulsions Stabilized by Benzoxazine Protective Colloids (Water/Resin Ratio of 4/1 by Weight and Water/Resin/$CHCl_3$ Ratio of 8/1/1 by Weight)

protective colloid (PC)	PC-A						PC-B
dispersed phase	B-hex					B-hex in $CHCl_3$	B-hex in $CHCl_3$
c(PC) (g/L)[a]	20	40	60	80	120	40	40
d_{vol} (nm)	440	404	310	292	247	149	126
d_{vol}/d_{num}	2.38	2.09	2.21	2.44	2.91	1.67	1.31
estimated area per PC on particle (nm^2)[b]	3.97	2.16	1.88	1.49	1.18	2.56	6.12
estimated area per PEO block on particle (nm^2)[b]	1.98	1.08	0.94	0.75	0.59	1.28	0.51

[a] c in cont. phase (H_2O). [b] Based on d_{vol} from DLS measurements, M_w from SEC results (discrete molecular weight), spherical particles, and the assumption that all surface active molecules are completely located at the droplet interface.

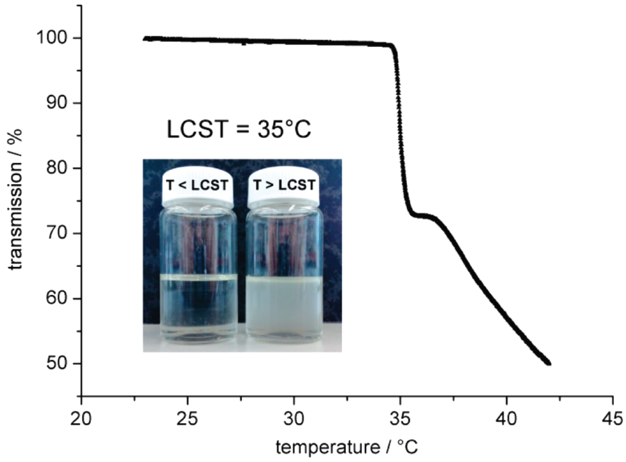


Figure 5. Turbidity photometric measurement of protective colloid type B; the strong decrease in transmission at 35 °C represents the lower critical solubility temperature (LCST) The photo shows a solution of PC-B in water at temperatures below and above the LCST. The turbidity of the sample on the right shows the insolubility of PC-B when the LCST is exceeded.

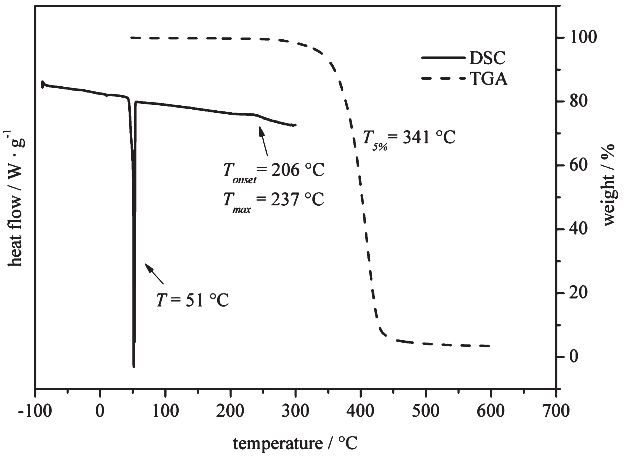


Figure 6. Thermal analysis of PC-A by DSC (solid line) and TGA (dashed line). The heating rates in both cases were 2 K·min^{-1}.

and polydispersity values (d_{vol}/d_{num}) obtained by dynamic light scattering (DLS) for these miniemulsions. The water/resin weight ratio was kept constant in case of the pure resin method at 4/1. Monomodal miniemulsions were obtained in all cases. Particle sizes can be easily adjusted by variation of the protective colloid concentration. An increasing amount of protective colloid leads to decreasing particle sizes in a size range from 200 to 500 nm and polydispersities of about 2 to 2.5. Below the critical value of 20 g·L^{-1} the miniemulsions became instable. Also the resin solution method was successfully applied. Narrower distributions of around 1.7 were achieved due to the lower viscosity of the dispersed phase and the resulting increased effectiveness of the fission process. The given particle sizes were measured after evaporation of the solvent. Furthermore, the theoretical interfacial particle area per protective colloid molecule and per poly(ethylene oxide) block were estimated based on the assumption that all the surface active stabilizing molecules are completely located at the vicinity of the droplet interface. Interestingly for the PC-A the estimated areas per stabilizing molecule are of the same order of magnitude than for the lower M_w and structurally more simple polymerizable benzoxazine surfactants.[22] This indicates that the functional hydrophobic part of the PC-A is almost completely immersed into the droplet inside and does not contribute to the overall colloidal particle stabilization. Following our design concept this hydrophobic benzoxazine main-chain segment acts in the miniemulsion state predominantly as an anchor moiety only. Contrary to that and as can be expected from theory the PEO blocks contributes predominantly to the steric stabilization of the particles (Table 2).

In case of PC-B, the situation was found to be interestingly different. During the preparation of the sample for the pure resin method, which includes preheating the protective colloid solution in water to 80 °C, the turbidity of the sample was investigated. Turbidity photometric measurements of a PC-B solution were carried out (Figure 5) indicating the existence of a lower critical solution temperature (LCST) at 35 °C. Driven by entropic interactions, the polymer molecules agglomerate and finally precipitate out causing a turbid solution at temperatures exceeding the LCST. To our knowledge this behavior was not reported before in the field of benzoxazine chemistry. However, this LCST transition can be additionally explained by a comparison with structurally vaguely related segmented polymers based on polyurethane chemistry. In one selected case methylene diisocyanate (MDI) was used as a hard segment in conjunction with PEO as soft segment. In a similar manner, a LCST-behavior was observed and investigated in more detail.[27]

Because of the LCST of PC-B, only the resin solution method was applicable in order to emulsify the benzoxazine resin formulation at lower temperatures. In fact even narrower distributions and smaller particle sizes as in the case of PC-B were

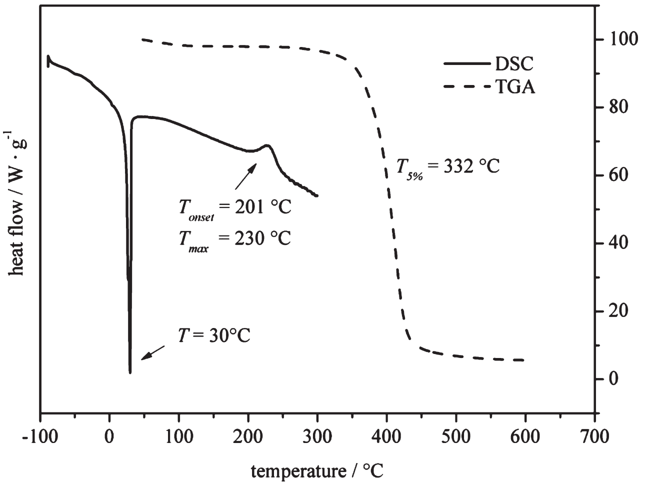


Figure 7. Thermal analysis of PC-B by DSC (solid line) and TGA (dashed line). The heating rates in both cases were 2 K·min^{-1}.

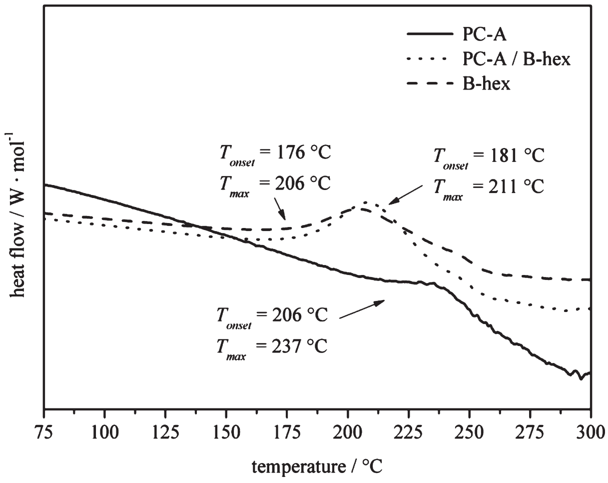


Figure 8. DSC overlay of the curing peaks of B-hex, PC-A, and a 4/1 molar mixture of B-hex and PC-A based on the theoretical molar masses. The heating rate in each measurement was 2 K·min^{-1}.

obtained. Interestingly the estimated average interfacial area per stabilizing molecule is much larger compared to the PC-A system, what can in part be explained from the higher M_w of the PC-B. On the other hand the average area per stabilizing PEO-block is comparably smaller. This can be interpreted as an indication that the PA-B is located to a larger content at the interface of the particle due to an overall higher hydrophilicity.

Thinking one step further, the thermo-responsive behavior of PC-B can be used to destabilize miniemulsions on command. Increasing the temperature above 35 °C leads to a collapse of the hydrophilic PEO-blocks and destroys the ability to stabilize the emulsion droplets. The result is the fusion of particles followed by the deposition of the benzoxazine resin. This procedure could be an interesting tool to create benzoxazine coatings by thermo-induced film formation.

3.5. Thermal Analysis and Copolymerization Behavior. For many practical applications benzoxazines have to withstand temperatures up to 250 °C for a period of several hours. High thermal stability and resistance against decomposition in this temperature range is an important issue. Figures 6 and 7 show the dynamic scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) diagrams for PC-A and PC-B respectively, recorded with a heating rate of 2 K·min^{-1} under nitrogen atmosphere. The $T_{5\%}$ values of 352 °C for PC-A and 355 °C for PC-B indicate excellent thermal stability. The degradation onset temperatures (T_{onset}) are well above 300 °C. The DSC diagrams show a distinct endothermic melting peak at 51 °C for PC-A and 30 °C for PC-B resulting from the high crystalline PEO polymer chains. For PC-A, the maximum of the exothermic curing peak ($T_{\max}$) can be found at 237 °C with $T_{\text{onset}} = 206$ °C. Similar values with $T_{\max} = 230$ °C and $T_{\text{onset}} = 201$ °C were observed for PC-B. PC-B homopolymerizes at slightly lower temperatures than PC-A. A possible explanation is the better flexibility of PC-B since the segment length between the hard units is higher than in the case of PC-A allowing less H-bonding and $\pi-\pi$-interaction.

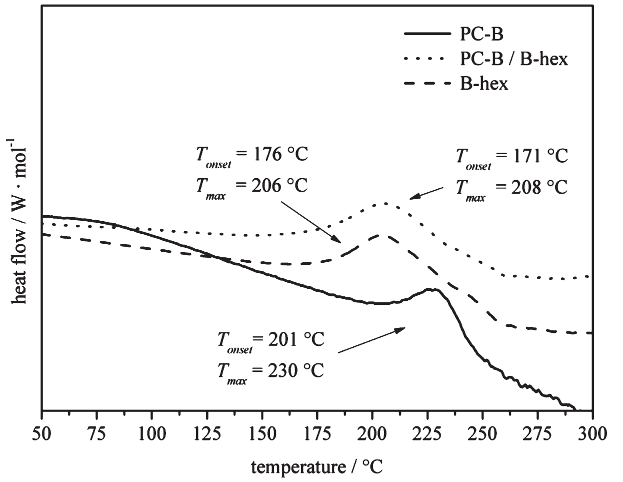


Figure 9. DSC overlay of the curing peaks of B-hex, PC-A, and a 4/1 molar mixture of B-hex and PC-A based on the theoretical molar masses. The heating rate in each measurement was 2 K·min^{-1}.

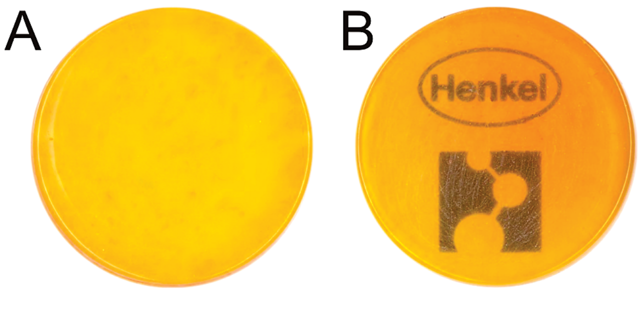


Figure 10. Cured films of PC-A (**A**) and PC-B (**B**) (20 wt %) in B-hex. The transparency of the film B indicates the compatibility of PC-B and resin as demonstrated by the visibility of the MPI-P/Henkel logo placed under the samples. Film A shows the formation of larger PC-A domains indicated by the opaqueness of the sample.

For practical applications, the copolymerization behavior of B-hex with the dispersed colloids is of major importance. The main benzoxazine fraction in the miniemulsion is the hydrophobic benzoxazine resin which is also true from the application point of view. Even though we need to be sure that the stabilizer will be incorporated into the network during curing. To ensure that fact, we carried out several DSC experiments of B-hex resin/colloid mixtures. Then 20 mol % of PC-A or PC-B was mixed

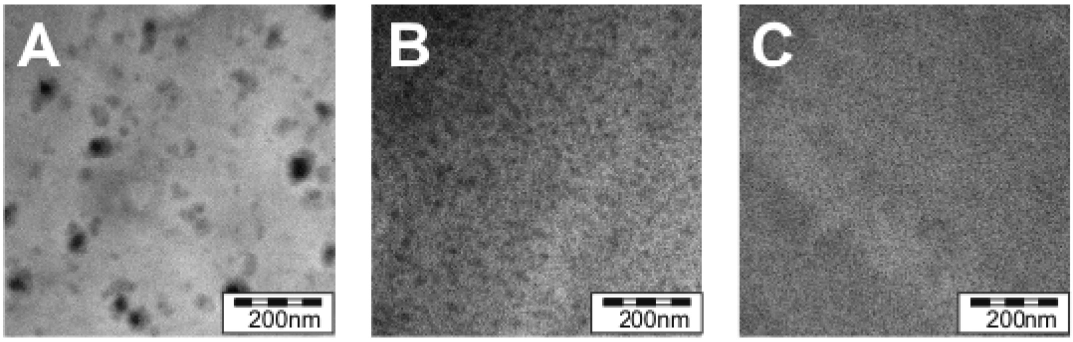


Figure 11. TEM images of the cured films of PC-A (A) and PC-B (B) (20 wt %) in B-hex and the cured pure B-hex reference sample (C). Large domains of up to 100 nm can be found in image A whereas image B shows small domain sizes of around 10 nm.

with B-hex and the resulting DSCs were analyzed (Figure 8 and 9). As before, the heating rate was 2 K·min^{-1} under nitrogen atmosphere. The DSCs show broad peaks caused by ring-opened species that function as acidic and therefore catalytic impurities. The copolymerization occurs at slightly higher temperatures than the homopolymerization of the pure resin. Both systems outstand the homopolymerization of PC-A in terms of lower temperatures of about 25 °C. The most important information regarding copolymerization behavior is the missing exothermic peak at 237 °C in the resin-colloid-mixture. This observation proves that both species copolymerize and that PC-A is fully incorporated into the network.

A similar argumentation is valid for PC-B. An individual peak in the DSC can be observed for the resin/PC-B-mixture.

The experiments prove that complete copolymerization and incorporation of the protective colloid occurs in both cases at relatively low temperatures compared to the curing peak of pure protective colloid.

3.6. Compatibility. The morphological behavior of films of cured protective colloid/B-hex mixtures was investigated. PC-B/B-hex mixtures (20 wt %) resulted in yellow transparent films (Figure 10B). It should be pointed out that identical films are obtained by drying of the emulsions. The MPI-P/Henkel logo which is placed under the film is clearly visible. The protective colloid is compatible with the resin and formation of domains is not observed. In case of PC-A, the situation is quite different. The film is opaque, the logo under the film is invisible. This indicates the formation of larger PC-A domains within the network that due to their size scatter light more intensively and therefore let the sample to appear opaque. It shall be noted that the described concept allows tailoring the overall interaction parameter χ.[18] This way the chemically induced phase separation (CIPS) can be used to adjust and control a desired morphology for various thermosetting resins and therefore to improve their overall mechanical and thermal properties.

This investigation is due to a combination of effects resulting from the molecular weight and the chemical nature of the protective colloid and its segments. This behavior was discussed in detail in an earlier publication.[18]

3.6. Transmission Electron Microscopy (TEM). To get a microscopic view on the morphology and prove the transferability of the advanced chemically induced phase separation and toughening concept described for multifunctional thermoplastic main-chain benzoxazine prepolymers,[18] transmission electron microscopy (TEM) investigations were carried out (Figure 11). The images are labeled in consistency with the images of Figure 10. Both samples containing protective colloid show formation of nanodomains due to nanophase separation as indicated by the differences in contrast of domains and matrix. Whereas the pure B-hex reference sample **C** shows no signs of such morphology.

The domains show a gradient in contrast from the center of the domain to the matrix in consistency with the toughening model described in an earlier publication.[18] Sample **A**, shows domain sizes of up to 100 nm in contrast to sample **B** with sizes of around 10 nm.

4. CONCLUSION

The concept of benzoxazine main-chain prepolymers was successfully transferred to aqueous systems for the first time. For this purpose, hydrophilic PEO soft segments were introduced as structural elements in this novel and highly versatile material class. Because of these modifications and their unique structural nature these materials not only have the ability to copolymerize with various thermoset resins—including benzoxazines and epoxides among others—but also can provide colloidal stability for aqueous resinous dispersions. Because these multifunctional surface active agents become covalently incorporated into a thermoset matrix upon curing many negative side effects that can be typical observed in dispersion systems can be minimized. For example, an inferior performance concerning water resistance and/or adhesive strength is often observed in coatings and adhesives derived from water compared over traditional, but environmentally unfavorable solvent based systems. The disadvantageous side effects of many water-based material in this respect are mainly resulting from diffusion and migration processes of the surface active colloidal stabilizer agents used traditionally for dispersion chemistry. Following our concept, the undesired formation of surface active aggregates that increase water uptake and the adsorption and consequently blocking of important interfaces for strong adhesion are minimized due to the covalent incorporation into the thermoset network.

Two different structural types of hydrophilic−hydrophobic main-chain benzoxazines were synthesized and characterized in detail. Because of their working principle as surface active stabilizer of higher molecular weight the hydrophilic−hydrophobic main-chain benzoxazines were named as multifunctional protective colloids. The protective colloid of type A (PC-A) carries the hydrophilic PEO segments at the terminal ends. Contrary to that the protective colloid of type B (PC-B) contains the hydrophilic PEO moieties distributed throughout the whole polymer backbone in a segmented way interrupted in an alternating fashion by the main-chain benzoxazine hard segments.

The chemical structure of PC-A and PC-B was investigated and proven by ^{1}H NMR and FT-IR. Their thermal properties were analyzed by TGA and DSC. The DSC measurements were not only used to observe the homopolymerization of the main-chain benzoxazines but also to follow their copolymerization behavior with B-hex as benzoxazine resin example. Interestingly and quite beneficial from application point of view complete conversions for these resin formulations where already obtained at lower temperatures than for the corresponding homopolymerizations of the protective colloids. It shall be noted that the colloidal stabilization and copolymerization is also possible with various other thermoset materials, e.g. *N*-aromatic benzoxazines, epoxides, oxethanes, etc. just to name a few and mixtures thereof.

In respect of their stabilizing ability PC-A and PC-B were investigated using the miniemulsion technology as a tool to emulsify resinous mixtures using surface active agents. Colloidal stable dispersions with average volume weighted particle sizes between 200 and 500 nm measured by DLS were obtained. The particle size was depending on the protective colloid concentration and following a clear and expected trend. The higher the concentration of surface active agent is, the smaller are the corresponding particles. Furthermore, the particle size distribution was influenced by the preparation method. As expected, using an auxiliary solvent which was removed afterward, lead to smaller and narrower particle size distributions were obtained. The solvent method was also applied to utilize PC-B for emulsification and colloidal stabilization at lower temperatures. This became necessary, because interestingly this material shows a LCST transition at 35 °C as proven by turbidity measurements.

Finally the morphologies of cured films of B-hex with 20 wt % PC-A or PC-B were investigated by TEM. Nanodomains were formed with domain sizes of up to 100 nm in case of PC-A and 10 nm for PC-B films. The domains are covalently bonded to the matrix and show a gradient in contrast as described in an earlier publication.[18]

■ ACKNOWLEDGMENT

We like to express our gratitude to Rainer Schönfeld, Stefan Kreiling, and Thomas Huver from Henkel Adhesive Research for the fruitful discussions. Furthermore, we thank Lothar Unger and Ursula Tenhaef for their laboratory support. We like to thank Huntsman Corporation for complementary samples of different soft segments.

■ REFERENCES

(1) Ghosh, N. N.; Kiskan, B.; Yagci, Y. *Prog. Polym. Sci.* **2007**, *32* (11), 1344–1391.

(2) Yagci, Y.; Kiskan, B.; Ghosh, N. N. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47* (21), 5565–5576.

(3) Holly, F. W.; Cope, A. C. *J. Am. Chem. Soc.* **1944**, *66* (11), 1875–1879.

(4) Takeichi, T.; Kano, T.; Agag, T. *Polymer* **2005**, *46* (26), 12172–12180.

(5) Chernykh, A.; Liu, J. P.; Ishida, H. *Polymer* **2006**, *47* (22), 7664–7669.

(6) Agag, T.; Takeichi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45* (10), 1878–1888.

(7) Yeganeh, H.; Razavi-Nouri, M.; Ghaffari, M. *Polym. Adv. Technol.* **2008**, *19* (8), 1024–1032.

(8) Kiskan, B.; Demiray, G.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (11), 3512–3518.

(9) Velez-Herrera, P.; Doyama, K.; Abe, H.; Ishida, H. *Macromolecules* **2008**, *41* (24), 9704–9714.

(10) Nagai, A.; Kamei, Y.; Wang, X. S.; Omura, M.; Sudo, A.; Nishida, H.; Kawamoto, E.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (7), 2316–2325.

(11) Chou, C. I.; Liu, Y. L. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (19), 6509–6517.

(12) Chernykh, A.; Agag, T.; Ishida, H. *Polymer* **2009**, *50* (2), 382–390.

(13) Garea, S. A.; Iovu, H.; Nicolescu, A.; Deleanu, C. *Polym. Test.* **2009**, *28* (3), 338–347.

(14) Wang, L.; Zheng, S. *Polymer* **2009**, *51* (5), 1124–1132.

(15) Kiskan, B.; Aydogan, B.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47* (3), 804–811.

(16) Liu, J.; Agag, T.; Ishida, H. *Polymer* **2010**, *51* (24), 5688–5694.

(17) Agag, T.; Geiger, S.; Alhassan, S. M.; Qutubuddin, S.; Ishida, H. *Macromolecules* **2010**, *43* (17), 7122–7127.

(18) Sawaryn, C.; Landfester, K.; Taden, A. *Polymer* **2011**10.1016/j.polymer.2011.04.064.

(19) Landfester, K. *Angew. Chem., Int. Ed.* **2009**, *48* (25), 4488–4507.

(20) Guyut, A.; Landfester, K.; Schork, F. J.; Wangd, C. *Prog. Polym. Sci.* **2007**, *32* (12), 1439–1461.

(21) Antonietti, M.; Landfester, K. *Prog. Polym. Sci.* **2002**, *27* (4), 689–757.

(22) Sawaryn, C.; Landfester, K.; Taden, A. *Macromolecules* **2010**, *43* (21), 8933–8941.

(23) Kaushik, M.; Bhatnagar, N.; Varma, I. K. *Int. J. Plastics Technol.* **2005**, *9*, 377–384.

(24) Ishida, H.; Rodriguez, Y. *Polymer* **1995**, *36* (16), 3151–3158.

(25) Ning, X.; Ishida, H. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32* (5), 921–927.

(26) Ning, X.; Ishida, H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32* (6), 1121–1129.

(27) Okamura, H.; Suzuki, K.; Mori, T.; Minagawa, K.; Masuda, S.; Tanaka, M. In *Chain behavior in model homogeneous ER fluids depending on temperature*, Nice, France, Jul 09−13, 2001; Nice, France, 2001; pp 2385−2391.