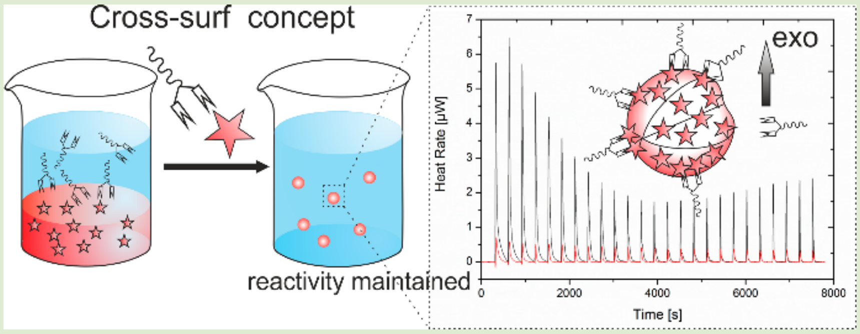
ACS Macro Letters
Letter
pubs.acs.org/macroletters

Alternative Pathway for the Stabilization of Reactive Emulsions via Cross-Linkable Surfactants

Ann-Christin Bijlard,[†,‡] Svenja Winzen,[†] Kenji Itoh,[‡] Katharina Landfester,[†] and Andreas Taden*[,†,‡]

[†]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
[‡]Henkel AG & Co. KGaA, Henkelstr. 67, 40191 Düsseldorf, Germany

S *Supporting Information*



ABSTRACT: Highly reactive emulsions were stabilized by employing a surfmer analogous concept. An interfacial reaction between an emulsion droplet and a cross-linkable reactive surfactant was used to provide colloidal stability and simultaneously maintain the majority of the reactive groups. Polyaddition-type reaction between epoxy and amine was chosen as a model system to spontaneously and covalently bond the surfactant to the emulsion droplets. The interfacial reaction was monitored via isothermal titration calorimetry analysis. With this method, the increased colloidal stability could be attributed to a reaction rather than a pure physical adsorption. The maintained reactivity of the emulsion droplets enables consecutive conversions with coreactive components, e.g., for cross-linking reactions, corrosion protection, or functional coatings.

Soft matter, stimuli-responsive colloids have gained tremendous interest over the recent years.[1−3] Nanocapsules, for example, offer the possibility to transfer chemical actives into media they would usually not be compatible with or prematurely react. Most frequently orthogonal reactions are used to create stimuli-responsive, protective shells of significant thickness surrounding the active to maintain reactivity and enable triggered release. This way temperature, pH, light, redox activity, enzymes, and other physicochemical interactions can be applied to stimulate self-healing, catalysis, or drug release properties.[4,5]

However, in some cases the formation of a protective shell may negatively influence or even hinder the final application. As a consequence, a lot of effort has been made to reduce the shell thickness and to achieve quantitative release.[6] This work instead focuses on preserving the active material solely by an interfacial reaction with a reactive surfactant to yield an ultrathin stabilizing layer. The majority of the reactive material remains active and provides a low latency for consecutive reactions, which can be triggered by comparably weak external stimuli, like film formation.

Reactive surfactants have proven to exceed the performance of pure physisorbed surfactants in many cases due to their covalent incorporation into the polymer structure.[7,8] Often referred to as surfmers, they consist of amphiphilic molecules with a polymerizable unit and are especially known for free radical emulsion polymerization to obtain systems with improved coating adhesion and water resistance.[9,10] Beyond that, surfmers can be utilized to provide additional functionality, e.g., improved cell interactions[11] or CO_2 response.[12] The surfmer concept was further employed for polyaddition reactions, i.e., in benzoxazine[13] or polyurea[14] based systems. These approaches all have in common that (i) the functionality of the surfmer equals the functionality of the monomer and (ii) that the reactive species are fully consumed upon the respective polymerization reactions.

In this contribution, however, emulsion droplets were stabilized by an interfacial reaction between the active material and the reactive surfactant (schematic representation in Figure 1). Polyaddition-type reaction between an amine and a reactive cross-linkable surfactant ("cross-surf") containing epoxy groups was used as a model system. High sheer force miniemulsification was utilized to obtain small, narrowly distributed nanodroplets. Miniemulsion droplets are typically not densely covered with surfactant molecules and often referred to as "critically stabilized".[15] In this respect the cross-surf concept and its ability to react with amine droplets can hardly be

Received: October 5, 2014
Accepted: October 22, 2014
Published: October 23, 2014

© 2014 American Chemical Society

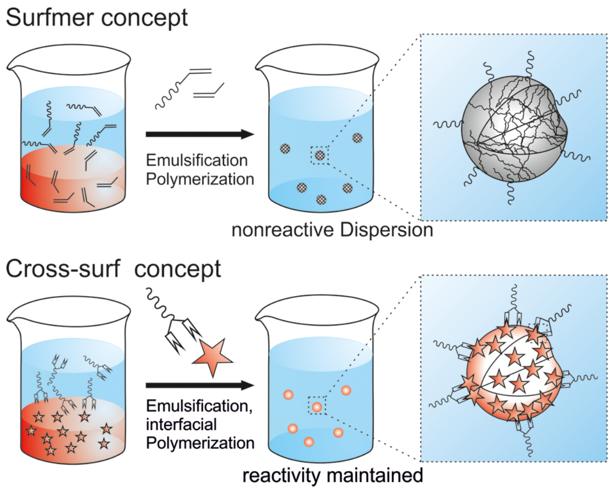


Figure 1. Comparison of the surfmer concept to the cross-surf concept which allows the effective stabilization of active materials via interfacial reactions.

considered as an encapsulation mechanism or dense shell formation and might be seen as soft interface functionalization (or deactivation) instead. Scheme 1 reflects the utilized surfactants and the amine in a simplified manner, and more detailed synthetic and analytical information can be found in the Supporting Information (SI).

In brief, an oligomeric epoxy surfactant (ES) was synthesized, comprising a bifunctional reactive glycidyl headgroup and a nonionic, mainly poly(ethylene oxide) (PEO) based tail. Its hydrophilic-lipophilic balance (HLB value) was calculated to be 14.9 which classifies it for the stabilization of oil-in-water (o/w) emulsions.[16] The molecular weight was determined via SEC and end group analysis of the epoxy groups (see Figure S1, SI) to be $M_n \sim 8000$ g/mol, which corresponds to an average number of $n = 2.9$. A hydrophobic phenalkamine was utilized as the amine species, which is known as a highly reactive epoxide curing agent even at low temperatures.[17] A nonreactive reference surfactant (nrES) with identical backbone was synthesized by converting the epoxide groups with formic acid.[18] Furthermore, an additional nonreactive surfactant (nrES2) was synthesized, which will be discussed later.

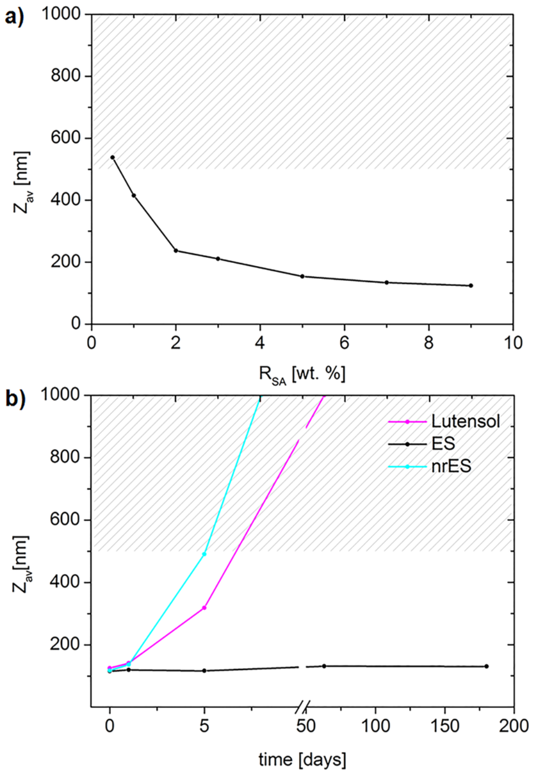
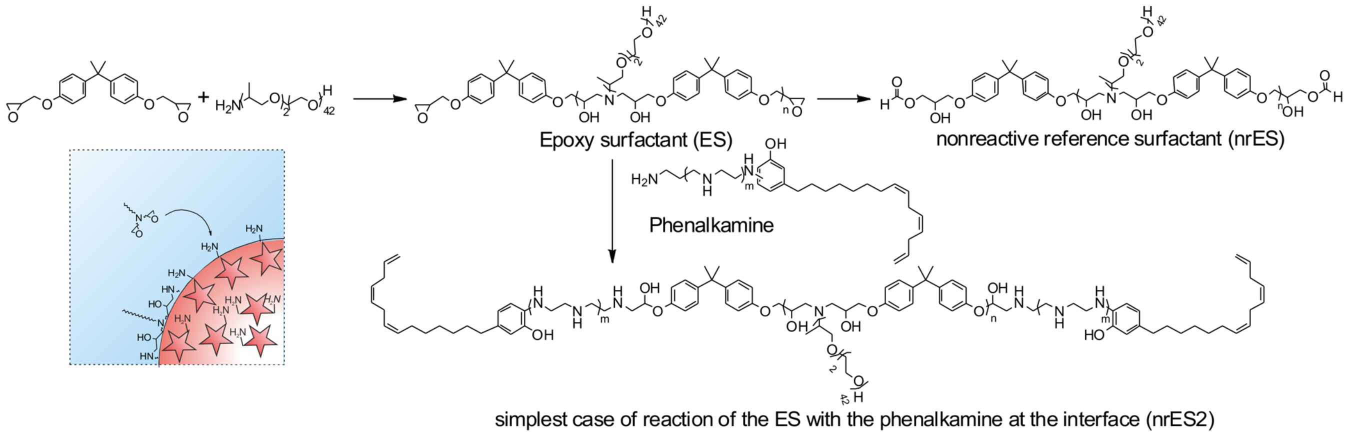


Figure 2. (a) Dependency of the particle size on ES concentration. (b) Colloidal stability of the ES (7 wt %) in comparison with the nonreactive references.

In a first step, the ability of the ES to stabilize the phenalkamine emulsion was investigated by varying the concentration ratio of the ES to the dispersed phase. Figure 2a illustrates that the *z*-average particle size decreases from 415 to 124 nm when the surfactant to amine ratio is increased from 0.5 wt % to 9 wt %. It was not possible to achieve colloidal stability with commonly used surfactants like SDS or CTAB. The use of the nonionic surfactant Lutensol AT50 ($C_{16/18}EO_{50}$) initially produced stable emulsions but had a limited long-term stability to a few days as shown in Figure 2b. A strong increase in particle size and partial phase separation was observed. With the ES, however, a drastically increased stability for over 6 months of storage was found. To show that the increased stability was attributed to an interfacial reaction,

Scheme 1. Synthesis of the Reactive Epoxy Surfactant (Cross-Surf; ES) and the Nonreactive Reference (nrES) and the Simplest Case of Interfacial Reaction of the ES and the Phenalkamine (nrES2)



emulsions with the nrES were prepared that also showed a strong increase in particle size.

The maximum surface area that can be stabilized per ES molecule, assuming full coverage, was calculated to be 8.7 nm^2 at 7 wt % ES. For comparison, in a standard recipe of a styrene miniemulsion with 5 wt % Lutensol AT50 a maximum surface coverage of 2.6 nm^2 per surfactant molecule was reported.[19] The larger surface area coverage of the ES can be explained by their difference in chemical structure and molecular weight. Please note that both systems correspond to approximately 1.5 mg/m^2 surface coverage, which is in good agreement to other miniemulsions stabilized by macromolecular surfactants and would relate to a shell thickness of 1.5 nm if a density of 1 g/cm^3 is assumed.[20] The real thickness of the stabilization layer is of course depending on various parameters like adsorption, depletion, branching, and solvent−polymer interactions.[21] However, even with the ES covalently reacting at the interface a dense shell formation is not likely, and an ultrathin stabilization layer is formed instead, which can easily be broken upon weak stimuli.

We chose isothermal titration calorimetry (ITC) to more closely investigate the droplet−surfactant interaction.[22−25] ITC is a well-known method to follow polymer−surfactant interactions or micellation or to investigate interfacial processes in emulsion.[26] A freshly prepared emulsion which was prestabilized with Lutensol was diluted to a droplet concentration of 1 × 10^{-6} mM which was calculated according to the DLS data (153 nm). A 1 mM surfactant solution was titrated into the emulsion and into distilled water as a blank experiment to subtract the heat of dilution as shown in Figure 3a. Two experiments were carried out as references. First, the nonreactive surfactant was titrated into the amine miniemulsion with all other parameters kept constant. Second, the reactive surfactant was titrated into a nonreactive miniemulsion. For this purpose an epoxy miniemulsion was chosen since it is structurally comparable to the headgroup of the surfactant. A number concentration in the cell was estimated similar to the amine miniemulsion on the basis of the DLS data (241 nm).

For the titration of the epoxy surfactant to the amine emulsion as shown in Figure 3b, a strong heat release can be observed which reaches a plateau after approximately 14 titration steps. The enthalpy of the process was determined by a fit according to an independent binding model and was found to be about −343 kJ/mol of surfactant.[27,28]

The reference experiments however show different trends. The titration of the nonreactive surfactant to the amine miniemulsion shows a slightly endothermic process. The second control experiment shows a comparable result. It can thus be concluded that the generated heat observed for the reactive surfactant is not attributed to a physical adsorption process but rather to the exothermic reaction between the epoxy group and the amine at the interface. The result that the reaction between the ES and the reactive amine miniemulsion reaches a plateau also shows that the reaction seems to be restricted to the droplet−water interface due to the high reactivity of the amine.

It was not possible to isolate the pristine polymers from the interfacial reaction (see SI); therefore, additional investigations were carried out in bulk. Because the amine is present in excess at the interface a model reaction was carried out with a molecular ratio of the ES to the phenalkamine of 1:2 at first, which resulted in a cross-linked gel. The primary amine groups are expected to dominate the reaction, and accordingly an excess of 1:4 gave a water-soluble product which served as an additional reference surfactant nrES2 hereafter (see Scheme 1). An analogously prepared miniemulsion with this surface active, but nonreactive, surfactant had a particle size of Z_{av} = 228 nm compared to Z_{av} = 134 nm for the ES stabilized emulsion. This may be a hint that not only nrES2 is formed at the interface but also cross-linked products. However, the overall amount of polymer formed is fairly low.

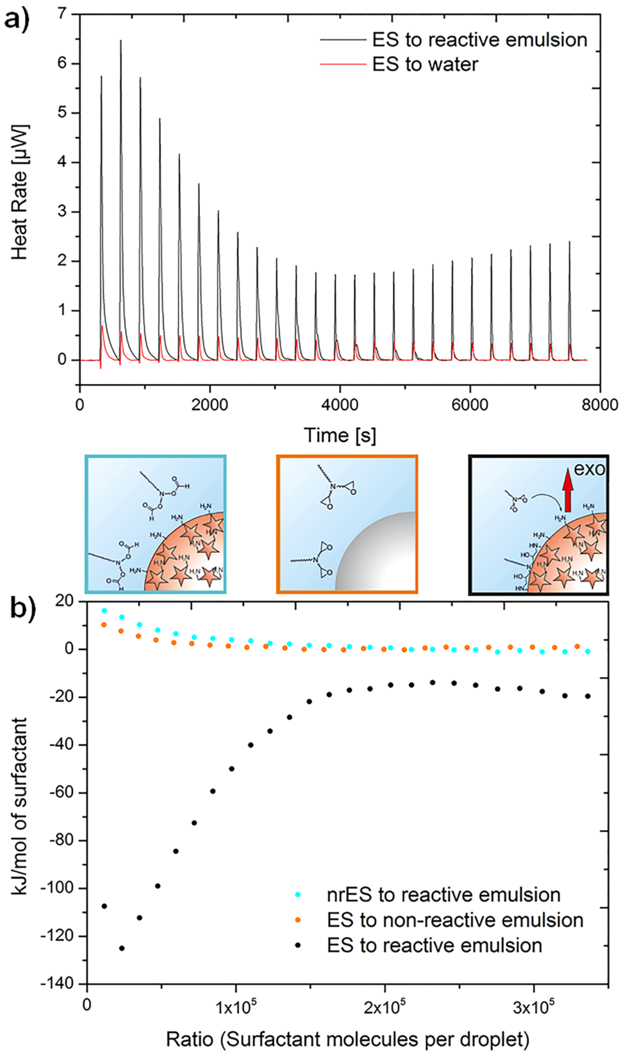


Figure 3. (a) Exemplary raw ITC signals from the titration of the ES to the amine miniemulsion and to water to subtract the heat of dilution. (b) Integrated results of the heat change per mole surfactant versus the surfactant to droplet ratio showing the cross-linking of the ES at the interface.

Generally, this approach enables us to preserve the majority of the active material thus allowing the system to be used for consecutive reactions, which was demonstrated by polymerizing an epoxide resin. A thermosetting polymer network could be formed by stoichiometrically mixing with the epoxy emulsion which already served as reference for the ITC experiments. Homogenous, nontacky, and free-standing films were obtained after drying at room temperature (see Figure 4).

The curing reaction was determined via rheology measurements at 70 °C to enable the evaporation of the aqueous phase within reasonable time. The moduli displayed in Figure 4a show a strong increase and hardening reaction upon film formation, further signified by the damping factor tan δ, which

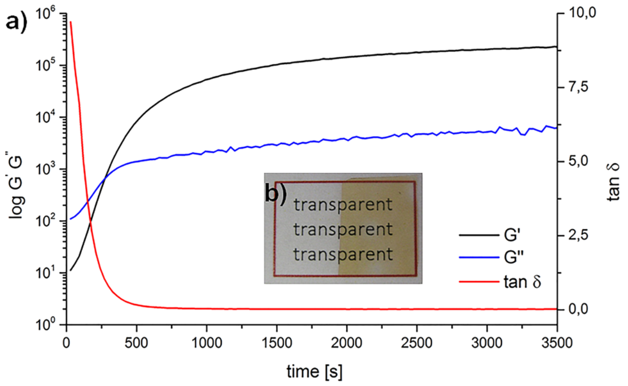


Figure 4. (a) Oscillatory rheology measurements upon curing reaction to demonstrate the maintained reactivity of the amine. (b) Room-temperature cured film.

shows the conversion from a predominantly viscos (tan $\delta > 1$) toward an elastic material (tan $\delta < 1$). SEM measurements of the cured film showed a very homogeneous film with no traces of shell or shell-like remains visible (Figure S6, SI).

In conclusion, our proposed cross-surf concept is able to stabilize reactive compounds without the need of dense encapsulation. Reactive epoxide surfactants were utilized for interfacial polyaddition with amine nanodroplets and followed by ITC experiments that clearly indicate an interface deactivation with an ultrathin stabilization layer formed. Further investigations need to be carried out to fully understand and tune the interfacial reaction which will be studied by increasing the number of epoxide groups in the surfactant to favor interfacial cross-linking. The vast majority of the active amine component remains unaffected and can be utilized for consecutive reactions, which can be triggered by comparably soft stimuli, like room-temperature film formation. The overall characteristics render the cross-surf concept highly interesting for various applications and products, e.g., coatings, adhesives, self-healing systems, and corrosion protection.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, characterization methods, miniemulsion preparation, and characterization of the surfactants and the phenalkamine. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: taden@mpip-mainz.mpg.de and/or andreas.taden@henkel.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Sandra Seywald, Ute Heinz, Burkhard Eschen, and Marion Cornils for analytical and laboratory support.

■ REFERENCES

(1) Hsu, L.; Weder, C.; Rowan, S. J. *J. Mater. Chem.* **2011**, *21*, 2812−2822.

(2) Stuart, M. A. C.; Huck, W. T. S.; Genzer, J.; Muller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. *Nat. Mater.* **2010**, *9*, 101−113.

(3) Fleige, E.; Quadir, M. A.; Haag, R. *Adv. Drug Delivery Rev.* **2012**, *64*, 866−884.

(4) Esser-Kahn, A. P.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. *Macromolecules* **2011**, *44*, 5539−5553.

(5) Motornov, M.; Roiter, Y.; Tokarev, I.; Minko, S. *Prog. Polym. Sci.* **2010**, *35*, 174−211.

(6) Caruso, M. M.; Blaiszik, B. J.; White, S. R.; Sottos, N. R.; Moore, J. S. *Adv. Funct. Mater.* **2008**, *18*, 1898−1904.

(7) Li, W.; Min, K.; Matyjaszewski, K.; Stoffelbach, F. o.; Charleux, B. *Macromolecules* **2008**, *41*, 6387−6392.

(8) Guyot, A.; Tauer, K. In *Polymer Synthesis*; Springer: Berlin Heidelberg, 1994; Vol. *111*, pp 43−65.

(9) Guyot, A. *Adv. Colloid Interface Sci.* **2004**, *108−109*, 3−22.

(10) Unzué, M. J.; Schoonbrood, H. A. S.; Asua, J. M.; Goñi, A. M.; Sherrington, D. C.; Stähler, K.; Goebel, K.-H.; Tauer, K.; Sjöberg, M.; Holmberg, K. *J. Appl. Polym. Sci.* **1997**, *66*, 1803−1820.

(11) Sauer, R.; Froimowicz, P.; Schöller, K.; Cramer, J.-M.; Ritz, S.; Mailänder, V.; Landfester, K. *Chem.−Eur. J.* **2012**, *18*, 5201−5212.

(12) Fischer, V.; Landfester, K.; Muñoz-Espí, R. *ACS Macro Lett.* **2012**, *1*, 1371−1374.

(13) Sawaryn, C.; Landfester, K.; Taden, A. *Macromolecules* **2010**, *43*, 8933−8941.

(14) Rosenbauer, E.-M.; Landfester, K.; Musyanovych, A. *Langmuir* **2009**, *25*, 12084−12091.

(15) Antonietti, M.; Landfester, K. *Prog. Polym. Sci.* **2002**, *27*, 689−757.

(16) Griffin, W. C. *J. Cosmet. Sci.* **1949**, *1*, 311−326.

(17) Zhang, Y.; Foos, R.; Landfester, K.; Taden, A. *Polymer* **2014**, *55*, 2305−2315.

(18) Beckert, H.; Fanghänel, E.; Habicher, W. D.; Metz, P.; Pavel, D.; Schwetlick, K. In *Organikum*, 22nd ed.; Wiley-VCH: Weinheim, 2004; p 303.

(19) Rotureau, E.; Leonard, M.; Marie, E.; Dellacherie, E.; Camesano, T. A.; Durand, A. *Colloids Surf., A* **2006**, *288*, 131−137.

(20) Durand, A.; Marie, E. *Adv. Colloid Interface Sci.* **2009**, *150*, 90−105.

(21) Fleer, G. J. *Adv. Colloid Interface Sci.* **2010**, *159*, 99−116.

(22) Chanamai, R.; McClements, D. J. *Colloids Surf., A* **2001**, *181*, 261−269.

(23) Blandamer, M. J.; Cullis, P. M.; Engberts, J. B. F. N. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2261−2267.

(24) Kevelam, J.; van Breemen, J. F. L.; Blokzijl, W.; Engberts, J. B. F. N. *Langmuir* **1996**, *12*, 4709−4717.

(25) Wang, G.; Olofsson, G. *J. Phys. Chem. B* **1998**, *102*, 9276−9283.

(26) Hamberger, A.; Landfester, K. *Colloid Polym. Sci.* **2011**, *289*, 3−14.

(27) Freire, E.; Mayorga, O. L.; Straume, M. *Anal. Chem.* **1990**, *62*, 950A−959A.

(28) Lewis, E.; Murphy, K. In *Protein-Ligand Interactions*; Ulrich Nienhaus, G., Ed.; Humana Press: Totowa, NJ, 2005; Vol. *305*, pp 1−15.