

## Sugar-Based Microemulsion Glass Templates

Feng Gao, Chia-Chi Ho, and Carlos C. Co\*

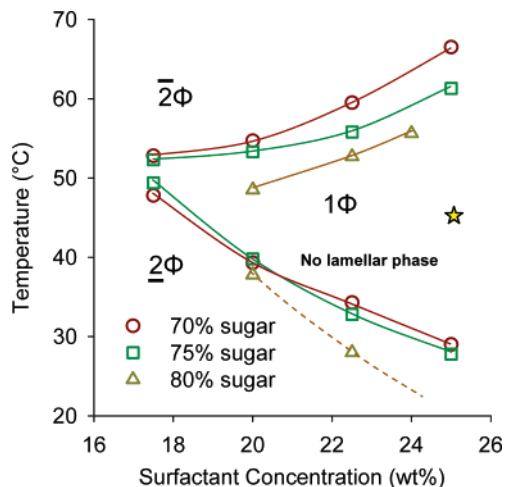
Department of Chemical and Materials Engineering, 497 Rhodes Hall,  
University of Cincinnati, Cincinnati, Ohio 45221

Received June 4, 2004; E-mail: carlos.co@uc.edu

Usually when one hears of microemulsions and complex fluids, the picture that comes to mind is a fluid-like mixture comprising surfactant, water, and/or oil that self-assemble to form various structures, ranging from spherical swollen-micelles, viscous rod-like micelles, and bicontinuous microemulsions to ordered liquid crystalline phases. Here, we report a new class of microemulsions that comprise surfactant, oil, and sugar, containing no water. These sugar-based microemulsions form amorphous solid glasses and resemble transparent brittle pieces of candy that nonetheless contain up to 50 vol % liquid oil. As such, they have great utility in encapsulation and controlled-release applications.

The principal motivation for this research, however, came from the observation that complex fluid structures are extensively used as templates for nanomaterials synthesis. In practically all such reports, however, the structures of the final materials formed are not exact complementary replicas of the template structure. These results, while negative, do convincingly demonstrate that the principal challenge in forming one-to-one polymerized copies of the surfactant nanostructures is avoiding “breakthrough” of the surfactant templates, which typically rearrange on a time scale faster than the templating reaction. Reactions inevitably result in compositional changes that, in most cases, significantly change the thermodynamics of self-assembly. As a result, the template, instead of imposing its structure on the reaction, rearranges to best accommodate the macromolecules that result. Our idea, therefore, is to replace water in these complex fluids with sugars to form solid complex glasses whose robust nanostructures can hold up against the forces that result from polymerization. In effect, liquid monomers will be polymerized within a solid template, which after reaction can be dissolved in water. As a first demonstration of this principle, we apply it to bicontinuous microemulsions, which are possibly the most challenging structures to template because of their rapid rearrangement dynamics and sensitivity to compositional changes.

To form microemulsion glasses, we start with sugar-rich microemulsions wherein water in traditional microemulsions is replaced with highly concentrated equimolar mixtures of sucrose and trehalose. Systematic phase behavior studies revealed that one-phase microemulsions, containing equal masses of sugar and isobutylacrylate oil, can be formed over a wide temperature range by carefully tuning the interfacial properties through the relative amounts of octyl and dodecyl glucoside surfactants ( $C_8G_1$  and  $C_{12}G_1$ , respectively) and 1,2-octanediol cosurfactant.<sup>3,4</sup> Key results from these studies are summarized in Figure 1, which reveals a large common one-phase region for microemulsions with increasing concentrations of sugar in their “aqueous” phase—simulating the effect of desiccation. Theoretical<sup>5</sup> and experimental considerations from the voluminous body of phase behavior studies of non-ionic microemulsions<sup>6</sup> initially led to great concern that mono- and multiphase lamellar regions would spoil the quest in locating suitable conditions for desiccating sugar-rich microemulsions to the glassy

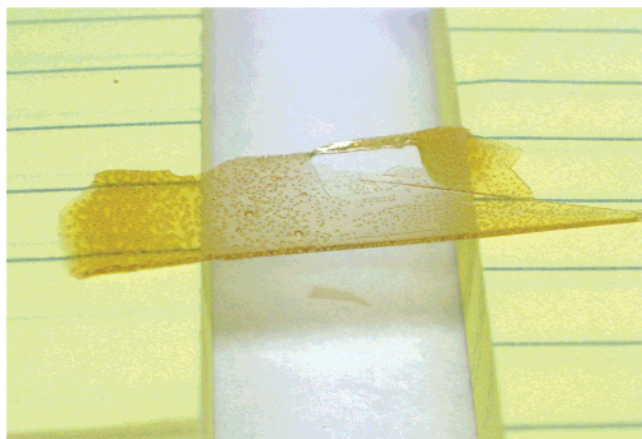


**Figure 1.** Phase diagram of sugar-based microemulsions containing equal masses of sugar (equimolar mixture of sucrose and trehalose to prevent crystallization during desiccation) and isobutylacrylate oil. Water used in traditional microemulsions is replaced with supersaturated 70, 75, and 80 wt % aqueous sugar solutions. The concentration axis represents the overall concentration of a 35:65 weight ratio of  $C_8G_1$  and  $C_{12}G_1$  surfactants, with 9 wt % (relative to the two surfactants) of octanediol cosurfactant, in the entire microemulsion sample. Phase boundaries delineate two-phase emulsion regions from one-phase microemulsion regions. Microemulsions with 80% sugar in their “aqueous” phase are highly viscous and require several hours to noticeably phase separate, making it impractical to locate the lower phase boundary accurately. The composition and temperature of the 75% sugar microemulsion desiccated to the complex glass shown in Figure 2 is marked by the star.

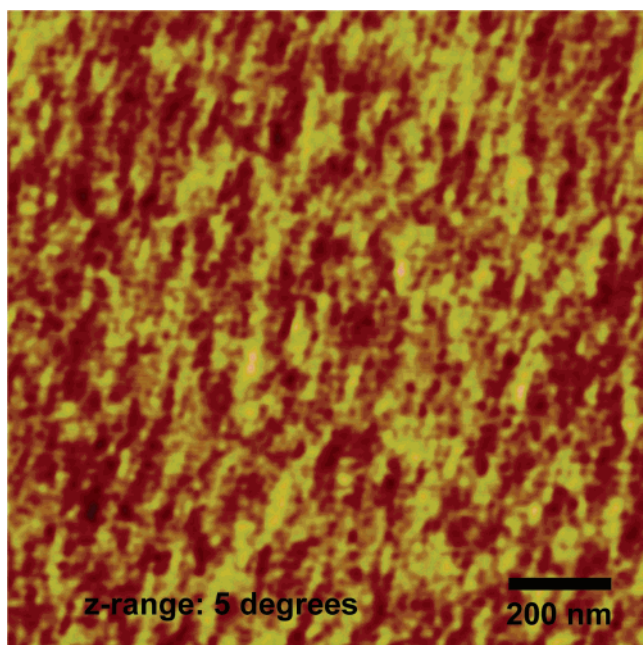
state. Nonetheless, systematic fine-tuning of the curvature and stiffness of the interfacial film allow effective suppression of lamellar phases (Figure 1). Liquid crystalline phases are still observed at higher surfactant concentrations (>30 wt % surfactant), and work is in progress to map out their phase behavior and desiccate them to the glassy state.

Controlled desiccation of the 75% sugar microemulsion, designated with a star in Figure 1, within a thermostated sealed chamber saturated with isobutylacrylate vapor yields optically clear glasses that are surprisingly brittle, considering that they contain equal masses of liquid oil and sugar (Figure 2). No visible phase separation can be observed when samples containing thermally stable UV-activated initiator are polymerized at temperatures below the glass transition temperature of the sugar domains. However, when the polymerization is performed on samples that have not been thoroughly desiccated, or at temperatures above the glass transition temperature of the sugar matrix, phase separation, as evidenced by the samples turning opaque, occurs after ~15 min of UV exposure.

Phase-lag AFM imaging of the fracture cross-section of the polymerized films (Figure 3) reveals bicontinuous ~70 nm size domains of sugar and polymer. The noticeable alignment of the



**Figure 2.** Optically clear and brittle complex glass, containing equal masses of sugar and liquid isobutylacrylate oil, resulting from the controlled desiccation of the sample described in Figure 1. Samples polymerized by UV irradiation at temperatures below the glass transition of the sugar domains remain optically clear and visually indistinguishable from the original unpolymerized microemulsion glass.



**Figure 3.** Phase-lag AFM image of the fracture cross section of the polymerized complex glass shown in Figure 2. Brighter regions of higher phase-lag correspond to soft polyisobutylacrylate ( $T_g \approx -43^\circ\text{C}$ ) domains. Dark regions correspond to hard sugar glass domains.

elongated domains observed in Figure 3 is parallel to the plane of the film and may be due to mechanical stresses that build up during the desiccation process. Phase-lag imaging artifacts due to surface roughness are unlikely because the height profile (Supporting Information Figure S1) exhibits minimal correlation, and phase lag images of control sugar–film samples exhibit uniform surface hardness (Supporting Information Figure S2). Modulated DSC measurements further confirm the existence of glassy sugar domains, which maintain a  $T_g$  of  $\sim 52^\circ\text{C}$  (Supporting Information Figure S3), independent of the amount of liquid oil.

With polymerized isobutylacrylate microemulsion glasses, dissolution of the sugar template with water collapses the porous structure. This is expected due to the low glass transition temperature ( $T_g \approx -43^\circ\text{C}$ ) of polyisobutylacrylate. However, replacement of isobutylacrylate with divinylbenzene does yield polymerized glasses that remain porous after washing with water (Supporting Information Figure S4).

In conclusion, we present here the first example of a complex glass comprising surfactant, oil, and sugar, prepared through controlled desiccation of sugar-rich microemulsions. In contrast to the microliter-size vitrified microemulsions prepared in early studies of microemulsion structure,<sup>1,2</sup> the approach presented here has no intrinsic scale limits, and multigram pieces of microemulsion glasses are routinely prepared in our laboratory. These complex glasses have a broad range of applications in encapsulation, crystallization, and template synthesis. Unlike template polymerizations in classical complex fluids,<sup>7</sup> the robust nanostructure of complex glasses allows polymerization of hydrophobic monomers without phase separation. Yet after polymerization, the sugar and surfactant template can be easily removed by dissolution in water.

This initial discovery raises many questions concerning the universality of glass formation in complex fluids, and work is in progress to understand the relationships between the phase behavior and structure of complex fluids in the liquid, glass, and polymerized states. The desiccation process reported here was intended to mimic, in a controlled manner, spray-drying processes that can be used to prepare commercial quantities of complex glasses for encapsulation and controlled-release applications. However, diffusive removal of water from complex glasses is not always practical, and molten complex glasses that can be directly injected into moulds and cooled to the glassy state without phase separation are being investigated.

**Acknowledgment.** We thank Eric Rufe and Shaun Howard for assistance with the AFM imaging, and Kimberley Ortiz (NSF REU program) with the phase behavior measurements. The graphic used for the table of contents entry was adapted from Reinhard Strey, Habilitationsschrift (1992).

**Supporting Information Available:** Materials and methods; height profile of AFM phase lag image corresponding to Figure 3; AFM phase lag image of a control film of pure sugar; heat capacity traces and glass transitions of microemulsion glasses containing varying liquid oil loadings by modulated differential scanning calorimetry (MDSC); SEM image of a polymerized divinylbenzene microemulsion glass after dissolution of the sugar template in water. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Jahn, W.; Strey, R. *J. Phys. Chem.* **1988**, *92*, 2294–2301.
- (2) Dubochet, J.; Alba, C. M.; MacFarlane, D. R.; Angell, C. A.; Kadiyala, R. K.; Adrian, M.; Teixeira, J. *J. Phys. Chem.* **1984**, *88*, 6727–6732.
- (3) Kahlweit, M.; Busse, G.; Faulhaber, B. *Langmuir* **1997**, *13*, 5249–5251.
- (4) Strey, R. *Colloid Polym. Sci.* **1994**, *272*, 1005–1019.
- (5) Kegel, W. K.; Lekkerkerker, H. N. W. *J. Phys. Chem.* **1993**, *97*, 11124–11133.
- (6) Schubert, K. V.; Kaler, E. W. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1996**, *100*, 190–205.
- (7) Antonietti, M.; Caruso, R. A.; Goltner, C. G.; Weissenberger, M. C. *Macromolecules* **1999**, *32*, 1383–1389.

JA0467115