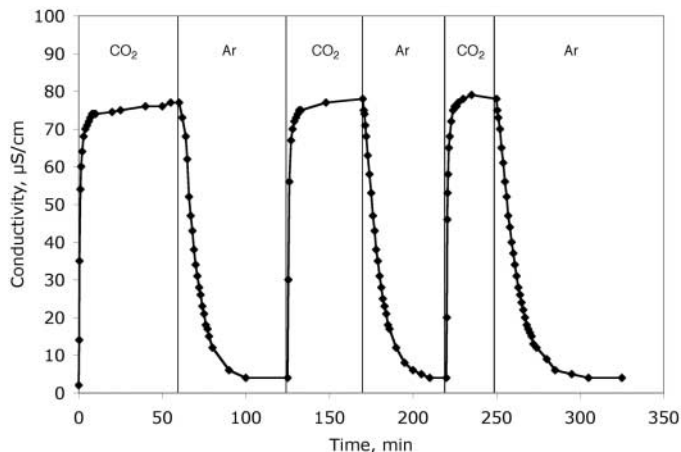
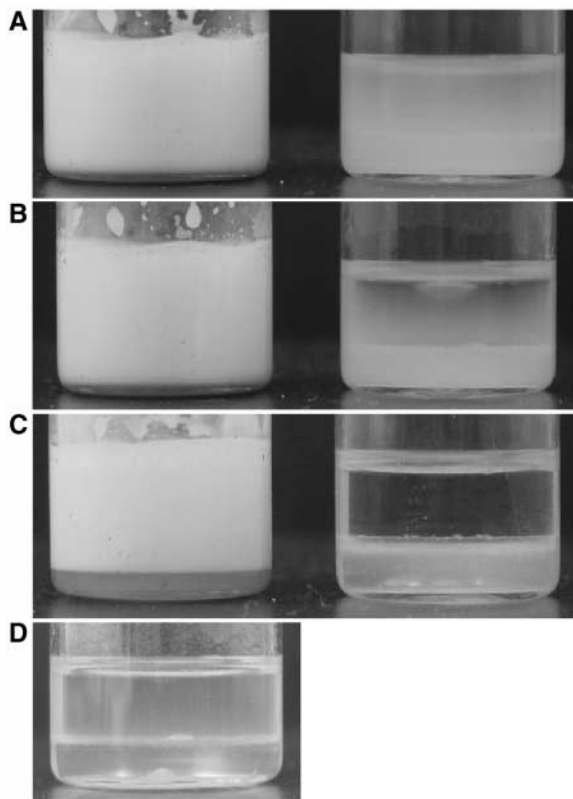




**Fig. 1.** The conductivity of a DMSO solution of **1a** at 23°C as a function of time during three cycles of treatment with CO<sub>2</sub> followed by argon.



**Fig. 2.** Photographs of 2:1 (v/v) hexadecane/water mixtures containing **1a** and either CO<sub>2</sub> (left) or argon (right) after 10 min of shaking followed by a waiting period of (A) 5 min, (B) 30 min, and (C) 24 hours. (D) Photograph of the CO<sub>2</sub>-induced emulsion after treatment with argon at 65 to 70°C for 2 hours (26).



solution, and it dropped upon argon addition. Air was found to have the same effect as argon.

The capacity of the amidines for stabilizing an emulsion was evaluated by automated shaking of mixtures of hexadecane and water containing **1a** (90 mg). Although an emulsion formed, it clearly separated into two layers within 5 min after the cessation of shaking (Fig. 2). However, if the solution was treated with CO<sub>2</sub> for an hour before the shaking, the emulsion was much more stable. It showed no evidence of separation for 3 hours, at which point a very thin layer of cloudy liquid began to appear at the bottom of the flask. After one day, the emulsion still

occupied 82% of the liquid volume (Fig. 2C). Bubbling argon through the emulsion at 65°C resulted in a complete separation of the hexadecane and water into two clear layers.

Similar experiments were performed with crude oil, but with notably different results (Fig. 3). Light crude oil, when shaken with water but without any additive, was able to form a fairly stable emulsion, presumably as a result of naturally occurring surfactants in the oil (18, 19). A stable emulsion also resulted from treatment of the same oil/water mixture with compound **1a** and CO<sub>2</sub>. However, addition of compound **1a** under argon does not lead to a stable emulsion; the mixture separates into two layers within 30 min,

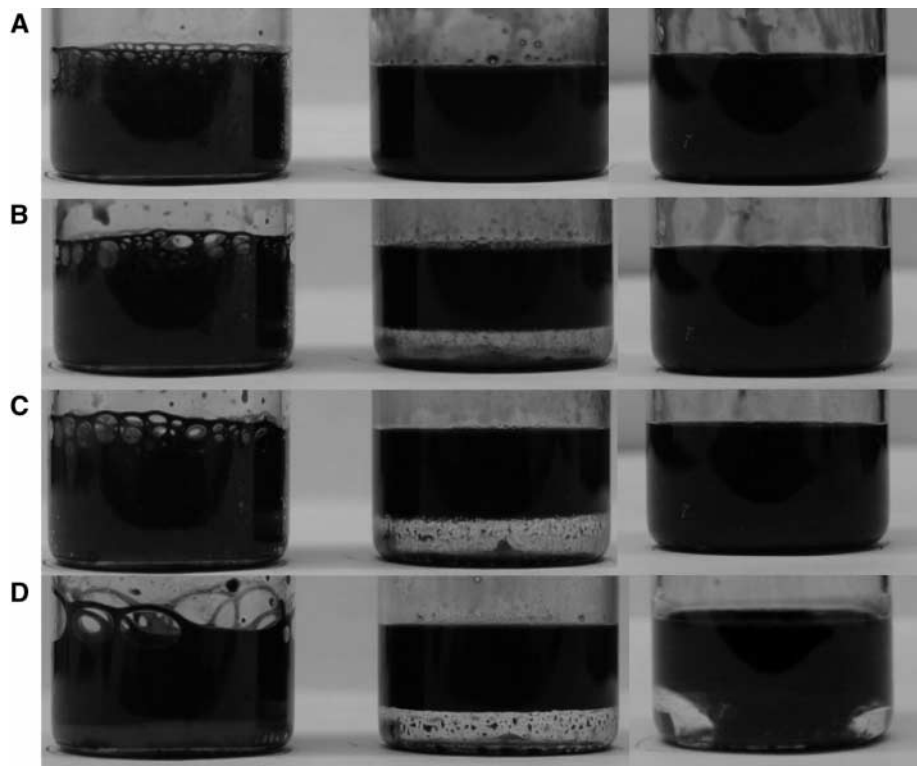
revealing that the uncharged amidine functions as a demulsifier (20). This demulsifying effect suggests that variations of these switchable surfactants may be useful in oil production for such applications as the breaking emulsions after EOR, oil-sands separations, and even cleaning of equipment. Although demulsifiers are known, including some that contain closely related head groups such as cyclic amidines (21), reversible switching between surfactant and demulsifier is, to our knowledge, unprecedented. Application of this technology to oil industry operations may depend on modifying the structure of the switchable demulsifier so that it will demulsify emulsions of heavy crudes.

Surfactants are also used to protect the surfaces of nanoparticles, colloids, latexes, and other particulates during their synthesis; in the absence of a coating of surfactant, these particles tend to agglomerate into undesirably large particles. In many cases, once the synthesis is complete, protection by the surfactant is no longer needed. For some applications, such as the preparation of supported metal catalysts, the complete removal of the surfactant is desired but difficult because the surfactant binds too strongly to the surface. For other applications, mere deactivation of the surfactant is desired and not necessarily removal. In either case, a switchable surfactant would be advantageous. As a preliminary demonstration that the amidine-based switchable surfactants can be used to protect growing particles during synthesis and then can be switched off, we tested their use in a microsuspension polymerization (Reaction 2) (22, 23). Microsuspension and emulsion polymerizations, techniques very commonly used for polymerizations involving radical mechanisms, require surfactants to protect the growing polymer particles during the synthesis. The product is a latex, meaning a surfactant-stabilized dispersion of polymeric particles in water. Isolation of the polymer from the suspension is facilitated if the surfactant can be switched off. The current industrial method to isolate the polymeric product is the addition of salts to coagulate the dispersion, followed by filtration and removal of the surfactant and added salts by washing (24). The washing step is often ineffective in removing the surfactants, resulting in polymers that are unnecessarily hydrophilic, which can be undesirable in many applications. An alternative route is to perform the polymerization in an organic solvent, but this approach is undesirable for two reasons. First, the removal of the solvent from the product is hindered by the high viscosity of the product mixture. More important, the use of the solvent increases emissions of volatile organic compounds (25). Although many polymers are made by surfactant-stabilized

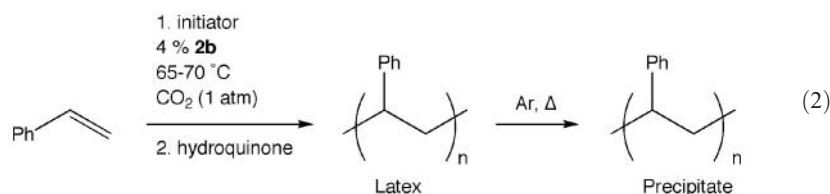
methods, styrene polymerization was chosen as a test example. The radical polymerization of styrene, initiated by thermal decomposition of an azo-based free radical initiator, was performed in a styrene-in-water emulsion stabilized by **2b** under CO<sub>2</sub>. Switching the surfactant off by bubbling argon or nitrogen through the system at 65°C and then cooling to room temperature and adding more water allows the polymer to settle. The settling is accelerated if the sample is

centrifuged. However, without the argon/nitrogen treatment, the polymer failed to settle within an observation period of 3 days or with centrifuging (Fig. 4).

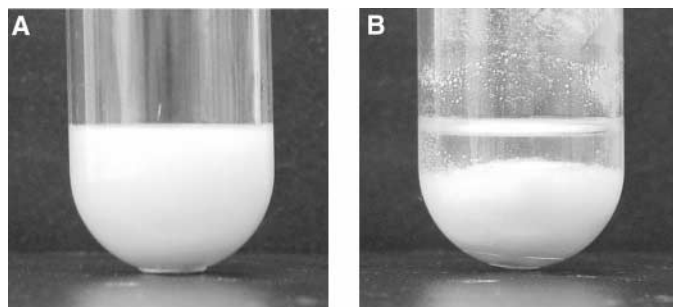
Future work in this area will include quantitative measurement and improvement of the rate of surfactant switching and optimization of the surfactant designs for specific applications, especially in nanoparticle synthesis, polymerization, and the oil industry applications that we have described.



**Fig. 3.** Photographs of 2:1 (v/v) crude oil/water mixtures containing either **1a** and CO<sub>2</sub> (left), **1a** and argon (center), or only argon (right) after 10 min of shaking followed by a waiting period of (A) 5 min, (B) 30 min, (C) 60 min, and (D) 15.5 hours.



**Fig. 4.** Photographs of a latex suspension of polystyrene particles after polymerization in the presence of **2b** and (A) after centrifugation or (B) after argon treatment followed by centrifugation.



## References and Notes

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- The rates of, and minimum times required for, the conversion of **1** to **2**, the conversion of **2** to **1**, and the transport of the surfactant to the liquid-liquid interface have not yet been quantified.
- We thank Shell and Imperial Oil for gifts of crude oil, and the Canada Research Chair program and the Natural Sciences and Engineering Research Council of Canada for funding the work.

## Supporting Online Material

www.sciencemag.org/cgi/content/full/313/5789/958/DC1  
Materials and Methods

SOM Text

Figs. S1 to S3

Table S1

References

30 March 2006; accepted 6 July 2006

10.1126/science.1128142