

Crystal Comets: Dewetting During Emulsion Droplet Crystallization

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Liquid oil emulsion droplets can violently dewet their own solid crystals during crystallization as a result of surfactant adsorption. The crystal shape formed is a function of the relative rates of dewetting and crystallization as controlled by surfactant adsorption, cooling rate, and lipid purity. For negligible dewetting rates, crystals nucleate and grow within the droplet. At similar crystallization and dewetting rates, the droplet is propelled around the continuous phase on a crystalline ‘comet tail’ much larger than the original droplet. Rapid dewetting causes the ejection of small discrete crystals across the droplet’s oil–water interface.

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Oil-in-water emulsions are excellent substrates for synthesizing biomimetic,^[1] photonic,^[2] encapsulation,^[3] and interesting colloidal^[4] materials, while crystallization of emulsions is used to create consumer product microstructure,^[5] and to purify small molecules^[6] and proteins.^[7] Crystals formed within an emulsion can partition at the oil–water interface and stabilize an emulsion against coalescence,^[8,9] destabilize it by partial coalescence,^[10] or even leave the droplet entirely,^[10,11] depending on their wettability. Previous work on crystal wettability in emulsions only examines partially crystallizing emulsions with a focus on equilibrium crystal partitioning and long-time instability,^[12,13] while the dynamics of crystal wetting receive little attention. An unstudied case is when the entire droplet crystallizes while simultaneous rapid dewetting occurs on the same time scale. Such a case offers a new approach to controlling the morphology of particles formed from emulsion droplets.

Here the surfactant molecular packing geometry^[14] is tuned to induce crystal dewetting during crystallization of molten polar lipid emulsions. Addition of cosurfactant to a surfactant solution increases surfactant packing efficiency and lowers the curvature of the monolayer adsorbed at the oil–water interface.^[15,16] As a result, vigorous dewetting of solid lipid crystals occurs as their own liquid phase is ‘washed off’ during crystallization. The resulting solid morphology can vary widely and is a function of the relative dewetting and crystallization rates as controlled by changes in surfactant packing, cooling rate, and lipid purity. When dewetting and crystallization rates are similar the emulsion droplet is violently propelled around the continuous phase on a crystalline ‘comet tail’. When dewetting dominates, discrete crystals are ejected across the oil–water interface, creating crystals smaller than the parent droplet.

The crystallization of three lipids was studied in an aqueous surfactant environment. The lipids, tristearin (99%, Sigma), tripalmitin (99%, Aldrich), and trihydroxystearin (90%, Rheox) were used as received and were chosen for their relative purities and high melt temperatures (75°C, 66°C, and 90°C, respectively). Two surfactants were used, sodium dodecyl sulfate (SDS) (99%, Fluka) and C₁₄-dimethyl amine oxide (C₁₄DMAO) (37% C₁₂, 47% C₁₄, 8% C₁₆, Lonza Barlox 14). Decanol (99%, Aldrich) was used as a cosurfactant. A sample cell made of two round 16 mm glass coverslips and a 16 mm outside diameter, 14 mm internal diameter, stainless steel spacer was used for all experiments to prevent water evaporation. The solid lipid and surfactant solution were placed between the coverslips with the spacer to provide a 0.5 mm gap and the system sealed tightly by coating the spacer with high-vacuum silicone grease (Dow Corning). The assembly was placed inside a larger stainless steel ring 16.2 mm in diameter and 3 mm tall to allow positioning on the microscope stage. Contact between the lipid–surfactant system and the silicone grease was avoided. Experiments were carried out on a Linkam THMS 600 controlled-temperature stage on a Zeiss Axioplan 2 optical microscope by heating the sample above the lipid melting temperature, holding for 1 min, then cooling at a constant rate to 25°C. Time-lapse images were digitized using a Coolsnap CF camera (Photometrics) and *MetaMorph* software (ver. 6.1, Universal Imaging).

The traditional picture of emulsion droplet crystallization is the nucleation and growth of crystals bounded by the oil–water interface to produce a solid particle similar in size to the parent droplet.^[17] Such a sequence is shown in Fig. 1*a* for a pure biological lipid, the saturated C₁₈ triglyceride tristearin, crystallizing in aqueous 25% w/w SDS solution. In Fig. 1*a*, the initially molten droplet solidifies rapidly as nucleation

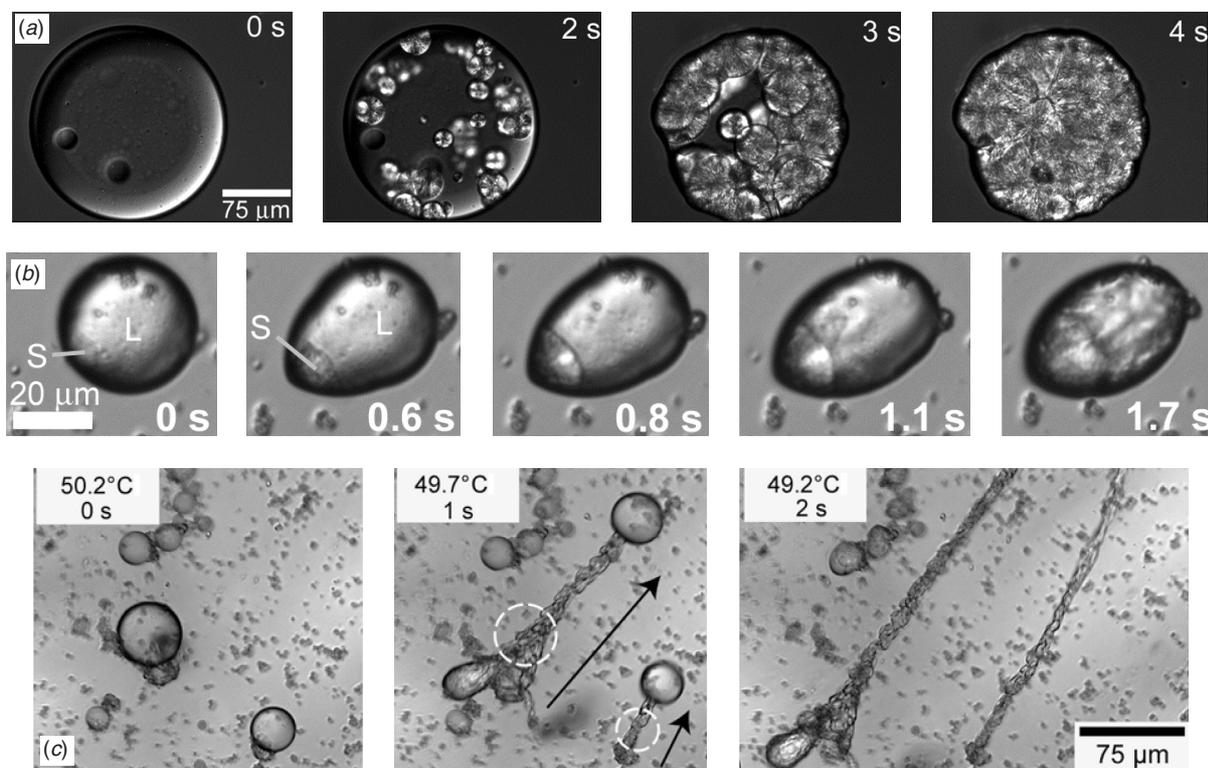


Fig. 1. (a) Time-lapse polarized light optical micrographs of tristearin crystallizing during cooling at $10^{\circ}\text{C min}^{-1}$. (b) Pure tristearin crystallizing in aqueous 6 wt% SDS and 0.6% decanol during cooling at $6^{\circ}\text{C min}^{-1}$. (c) Pure tristearin crystallizing with 4 wt% SDS and 0.4% decanol in water cooled at $30^{\circ}\text{C min}^{-1}$.

and growth occur in circular bright regions in the droplet. The crystal grains grow to adjoin and fill the droplet boundary, producing a solid the same size as the starting droplet. Tristearin behaves similarly in air, pure water, and in aqueous solutions of SDS above and below the critical micelle concentration (CMC) of 0.24% w/w.^[18] Crystal growth is bounded by the droplet interface because crystal dewetting is negligible relative to the crystallization rate.

Adding salt or cosurfactant like decanol to an SDS solution allows the surfactant to pack more efficiently at interfaces by effectively rendering the surfactant less hydrophilic,^[15,16] as seen in the schematic in Fig. 2. Sufficient surfactant adsorption at the oil–water interface causes dewetting of the crystal by its own liquid oil phase, likely by modification of the newly formed crystal’s wettability. Surfactant micelles in the aqueous phase exert a pressure on the liquid oil phase that forces it off of the growing crystal, which is a process of detergency-induced dewetting.^[19] A mass ratio of 10:1 SDS:decanol is effective here, consistent with work on polar lipid removal from solids by detergency.^[16] The small amount of decanol added to aqueous SDS causes crystallization of tristearin emulsion droplets to significantly deviate from that seen in Fig. 1a. Fig. 1b shows the progression of a typical droplet during crystallization—in two seconds the initially spherical droplet dewets its own solid phase as crystallization occurs, elongating into an almost ellipsoidal solid. First a solid grain (S) forms within the lower left boundary of a liquid droplet (L). In later frames the liquid oil phase dewets the continuously growing solid while maintaining a hemispheric profile.

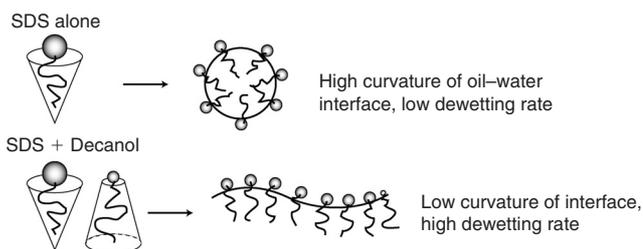


Fig. 2. Schematic of the hypothesized change in interfacial packing of SDS upon addition of decanol. Decanol is expected to increase the surfactant molecular packing density at the oil–water interface, lowering the curvature of the surfactant monolayer and inducing the observed dewetting.

The last frame shows a solid ellipsoidal particle resembling shapes formed in extensional flow,^[20] although here the elongating force is the interfacial energy gradient. The addition of decanol is the only difference between Figs 1b and 1a. The dewetting-induced elongation occurs only above the ternary system’s CMC (0.06% SDS) for a constant SDS:decanol mass ratio of 10:1.

A more extreme example in the same system is shown in Fig. 1c as two tristearin droplets dewet their own solid phase so rapidly that they are propelled far away from their original positions. Left behind is a crystalline ‘comet tail’ tracing the droplet trajectory. The larger droplet travels $100\ \mu\text{m}$, more than twice its initial diameter, in 1 s. The dashed circles indicate the initial positions of the droplets prior to crystallization. Although dewetting is at work here as in (Fig. 1b), the

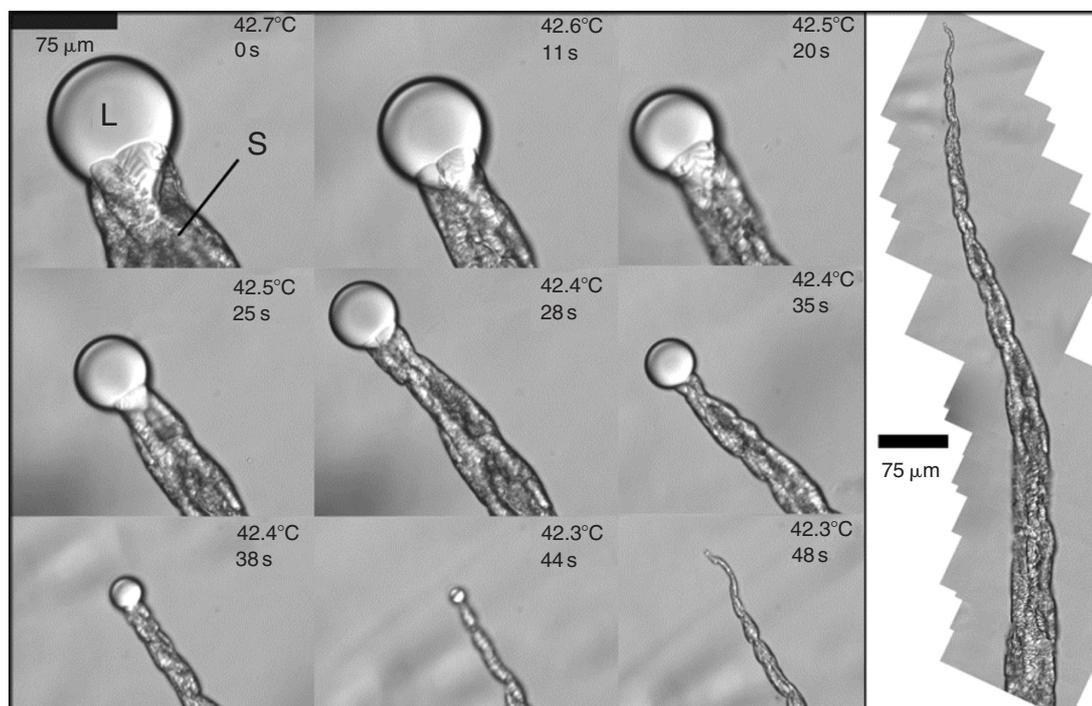


Fig. 3. Time-lapse sequence of polarized-light images of a liquid droplet (L) of tristearin (20 wt%) and tripalmitin (80 wt%) mixture crystallizing in aqueous 25% SDS and 2.5% decanol. See also movie 1 in the Accessory Materials. The final solid particle formed is shown to the right in a panoramic view.

resultant solid particle is different. The behaviour in Fig. 1c is more rare in this system than the slight elongation in Fig. 1b but both occur by liquid dewetting its own solid phase, where the more extreme dewetting occurs in droplets with a greater degree of supercooling. Similar elongated structures appear in Boode and Walstra^[10] (fig. 7), but the dynamics that form such structures were not studied. Experiments here showed the dewetting driving force can move the droplet or the solid tail depending on any adhesion to the coverslip. When no adhesion occurs, the object's centre of mass is stationary and droplet and tail move away from each other in opposite directions.

The radical dewetting behaviour in Fig. 1c is difficult to study because it is rare in the tristearin–SDS–decanol–water system. Crystallization of a lipid mixture, 20% tristearin and 80% tripalmitin (C_{16} saturated triglyceride) was then examined in the aqueous 10:1 SDS:decanol system. In Fig. 3 the time-lapse sequence shows that the mixed lipids exhibit even more dramatic propulsion and elongation than in Fig. 1c for pure tristearin, and here the phenomenon occurs in all droplets. The first three frames of Fig. 3 show a distended portion of the liquid drop (L) within or under the tail as if the solid region (S) were hollow and exerted a stress on the droplet. The droplet remains hemispherical throughout crystallization, even when mass depletion reduces it to sub-micron size. A panoramic view of the final solid particle is also shown in Fig. 3 to contrast its size with that of the original droplet. Droplet velocity correlates well with the applied cooling rate—faster cooling accelerates crystallization and droplet motion. As droplet motion is driven by the oil–crystal interfacial energy gradient, the movement seen here is

analogous to droplet movement on a surface with a chemical wettability gradient,^[21] although here crystallization steadily provides new surface not preferentially wetted by the oil. We observe droplet velocities on the order of $1 \mu\text{m s}^{-1}$, slower than droplets moving in air^[21] due to higher fluid drag.

In Figs 1 and 3 no discrete crystals emerge from emulsion droplets during crystallization as previously suggested,^[10] likely because the crystallization rate of pure lipids is too high relative to the dewetting rate. Crystallization of a commercial wax mixture, trihydroxystearin (THS) with a broad crystallization transition between 65 and 90°C, was next examined. A commercial surfactant, C_{14} DMAO, was used to tune interfacial packing conditions during THS crystallization. Surface-active impurities in THS required the use of a different surfactant from SDS. Fig. 4 documents a continuous progression from dewetting dominance to crystallization dominance as droplet supercooling increases. In the first frame of Fig. 4, four crystals (S) have just crossed the oil–water interface and surrounded a liquid droplet (L). The emergence of discrete crystals occurs at this early stage of crystallization when the dewetting rate exceeds the crystallization rate. Next two crystals (x, y) emerge from the droplet over ten seconds. The crystals ejected later are more elongated as crystallization rates approach the dewetting rate. After 22 s, crystallization rate balances dewetting and continues feeding the ejected crystal, forming a comet tail. The last frame of Fig. 4 shows that numerous other comets have formed. Although shown in two dimensions here, the dewetting effect is three dimensional, as evident from the out-of-focus sections of the comets in Fig. 4, and occurs in the bulk fluid of both static and stirred systems. A panoramic view of the final

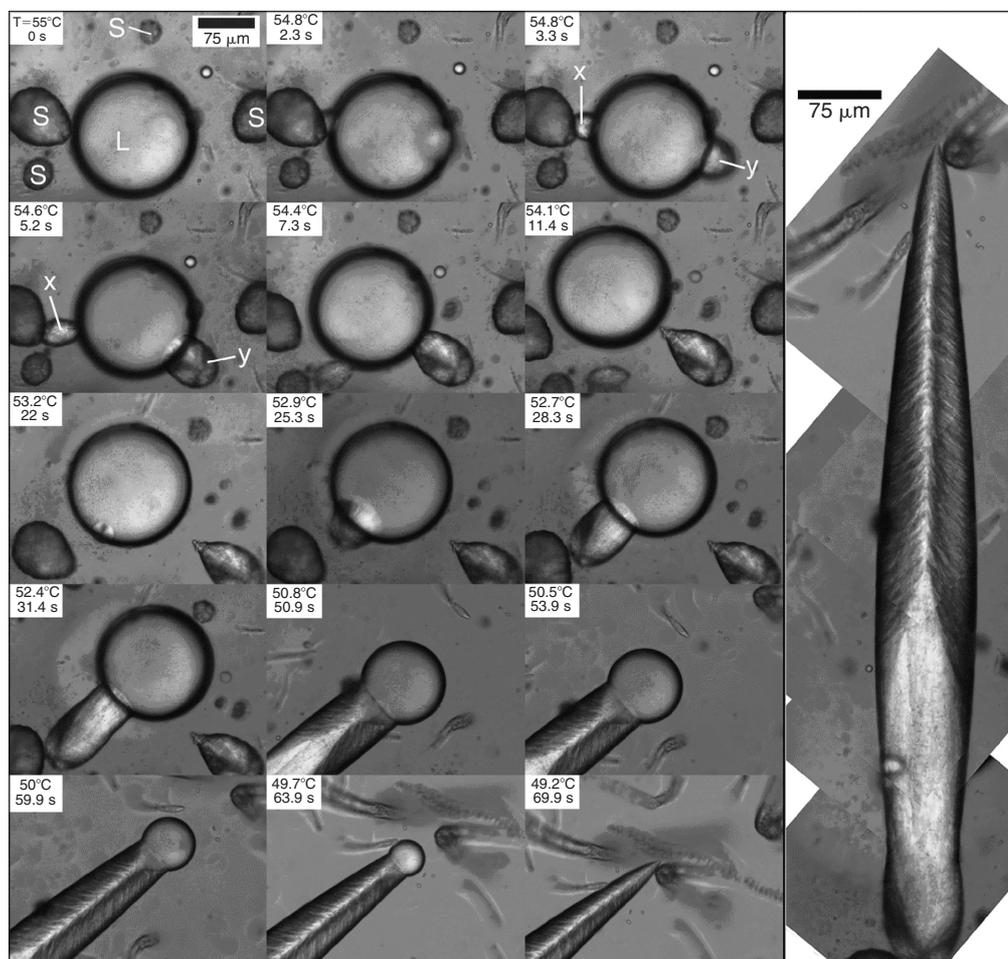


Fig. 4. Time evolution of a molten trihydroxystearin droplet crystallizing in aqueous 0.6 wt% C_{14} DMAO surfactant solution. See also movie 2 in the Accessory Materials. The full view of the final particle on the right shows the symmetric dagger-like structure.

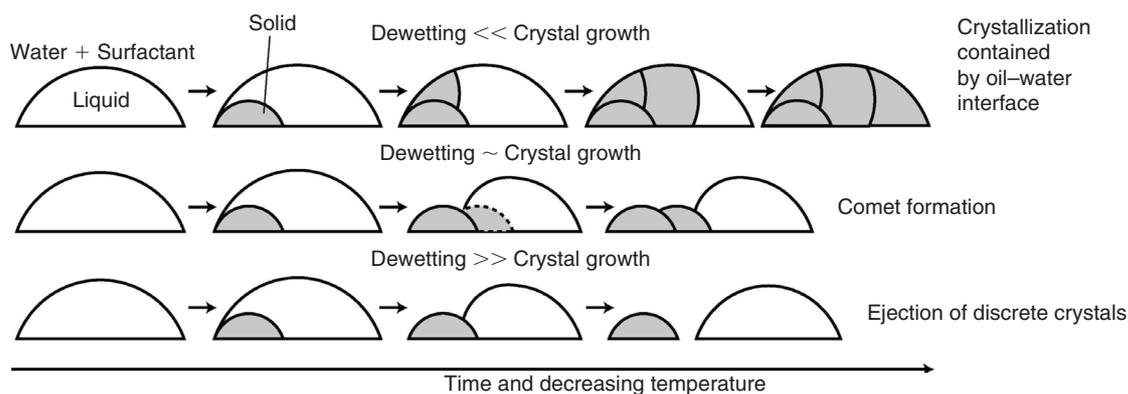


Fig. 5. Schematic of the three types of dewetting possible during emulsion crystallization. As dewetting becomes increasingly dominant the oil–water interface becomes less of a boundary for crystal growth.

solid particle in Fig. 4 indicates the more symmetric morphology formed here relative to Fig. 3. A schematic overview of the different types of crystallization observed here is shown in Fig. 5 with each case labeled by the relative significance of dewetting and crystal growth rates.

In any surfactant–lipid system, dewetting during crystallization only occurs at surfactant concentrations above the

CMC, near maximum adsorption. So, surfactant adsorption provides the critical trigger and driving force for dewetting. Crystal dewetting by the liquid oil is energetically favoured if the difference of the interfacial energy between the solid and the water phase (γ_{sw}) and between the solid and the oil (γ_{so}) is negative. Thus, dewetting is favourable when $(\gamma_{sw} - \gamma_{so}) < 0$, or, using Young's equation: $\gamma_{ow} \cos \theta < 0$,

where γ_{OW} is the oil–water interfacial tension and θ is the oil–crystal contact angle.^[22] For most surfactant–lipid systems, tuning of the surfactant packing is necessary to cause dewetting by increasing the value of θ above 90°. In our systems γ_{OW} is easily measured, but droplet motion impedes measurement of θ , so surfactant packing was tuned using the molecular geometric parameters that guide detergency optimization.^[16] Therefore, although aqueous SDS alone does not cause tristearin to dewet during crystallization, SDS with added decanol cosurfactant does. Adding decanol produces a more efficient surfactant packing that washes liquid oil from the crystal during growth, just as polar soils are best cleaned by a mixture with the same SDS:decanol ratio.^[16] Even small amounts of amphiphilic natural impurities determine whether crystal dewetting occurs.

Vigorous dewetting adds another level of complexity to conventional emulsion crystallization but produces a broader range of crystal shapes. For example, discrete crystals can be produced by cooling to, and holding at, the crystallization onset temperature, while high-aspect ratio particles are made by cooling rapidly through the crystallization transition. Dewetting can be prevented, for example when it causes instabilities, by adding hydrophilic surfactants or cosurfactants. It is likely that purification of the solids produced occurs, both during comet formation at moderate dewetting rates and during discrete crystal ejection at high dewetting rates. The relative purity of the ejected crystals, and how the comets vary spatially in composition, are not yet known. However, these questions are the subject of present work. It is also possible that some lipid is solubilized by surfactant micelles during these experiments and it is not clear how that might affect the observed crystallization behaviour. Although not observed in these experiments, when significant solubilization does occur, small crystals nucleate around the emulsion droplet during cooling but dewetting behaviour seems unaffected.

Unusual, dewetting-dominated crystallization dynamics occur in both pure and commercial-grade oil-in-water emulsions when surfactant packing efficiency at the oil–water interface is increased. Small amounts of additive can cause large variation in particle morphology, consistent with theories of wetting effects on melt solidification in air.^[23,24] Surfactant adsorption decreases wettability of the crystals by their own melt, and crystal shape is controlled by the competition between dewetting and crystallization rates. The process is usually observed for polar solutes and has the potential to enhance protein crystallization,^[25] and add a hydrodynamic component to existing techniques of controlling crystallization at interfaces.^[26] Further study of crystal dewetting could illuminate the dynamics of adsorbed particles in emulsions when interface crossing occurs^[27] and when particle adsorption is normally irreversible.^[8]

Accessory Materials 1 & 2

Movies of the crystallization processes are available from the authors or, until September 2010, the *Australian Journal of Chemistry*.

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