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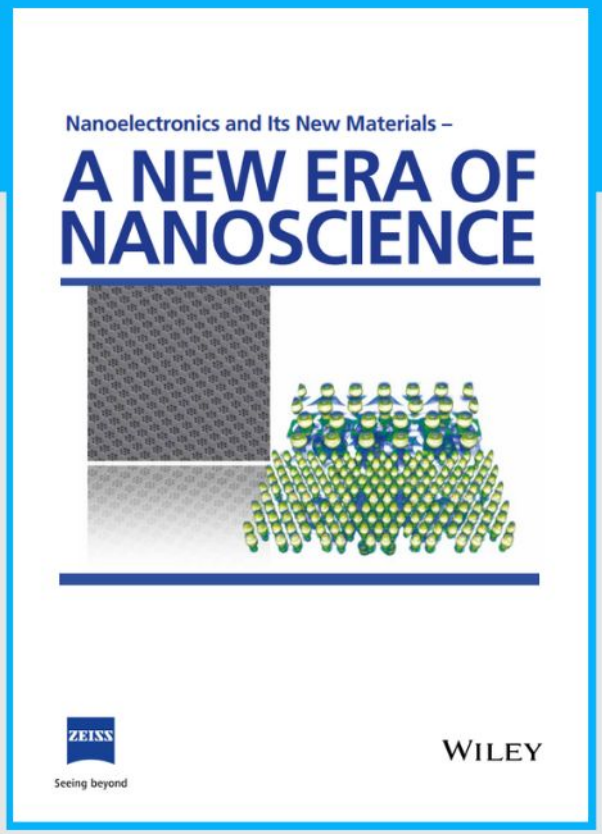

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Pearl-Like Sheen in Soft Capsules: An Unusual Optical Effect that is Reversibly Induced by Temperature

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A pearl-like sheen (i.e., pearlescence) is seen in many natural materials like nacre and in some commercial paints and cosmetics. This phenomenon is attributed to the interaction of light with plate-like particles in the material. Here, for the first time, pearlescence is demonstrated in soft millimeter-scale capsules that contain no plate-like particles. The capsules have a thin (~500 µm) outer shell of *N*-isopropylacrylamide (NIPA) hydrogel, which has a lower critical solution temperature (LCST) of 32 °C. When a transparent NIPA-shelled capsule is heated above this LCST, it turns pearlescent. The effect is reversible, with the transparent state being recovered upon cooling. This is the *first example of reversible pearlescence* in any solid. Specular reflectance measurements show that the pearlescence of the capsules is comparable to that of natural pearls. Pearlescence is not observed in NIPA hydrogels; it arises only in NIPA-shelled capsules, and that too only when the shell is thin. Above its LCST, the NIPA shell shrinks and gets stretched, and nanoscale NIPA-rich domains arise within this shell, which induce the pearlescence. This study sheds fresh insight into the nature of pearlescence, on how it can be tuned, and on how this property can be introduced into various soft materials.

1. Introduction

Pearls are precious gems with a distinctive metallic sheen, the technical name for which is pearlescence.[1–3] This phenomenon, much like its close cousin, iridescence, is an example of *structural* color, i.e., color that arises not from pigments but due to the interaction of light with structures in the material.[4] If either the sizes of these internal structures or the spacing between them is comparable to the wavelength of light (≈200–1000 nm), light is induced to diffract, leading to structural color.[4] In the case of iridescence (which is seen in opals, butterflies, etc.), light is diffracted at distinct wavelengths from ordered particle arrays,[5–7] resulting in bright hues — and the observed hues (reflected light) depend on the viewing angle. In the case of pearlescence, light interacts with structures that are less ordered, resulting in the reflected light being white or metal-like and independent of the viewing angle.[1,4] Pearls are formed naturally inside mollusks, which secrete nacre (mother-of-pearl) around an irritant like a grain of sand.[1,2] Nacre has layers of aragonite ($CaCO_3$) separated by biopolymers, and the spacing between the plate-like layers dictates the pearlescence. Many companies seek to impart a pleasing pearl-like appearance to their products, which include paints, shampoos, sunscreens, and skin creams.[8] To make a product pearlescent, plate or disc-like particles are typically added to it.[9–11] Examples include flakes of titanium dioxide (TiO_2) or mica or surfactant crystals. **Figure 1**A shows a natural pearl while Figure 1B shows a pearlescent shampoo. In the latter, irregular disc-like particles can be seen by microscopy, which are responsible for the pearlescence.

A common theme in all known cases of pearlescence (both in natural pearls as well as pearlescent paints or cosmetics) is that the effect arises due to the plate-like particles present. To our knowledge, there are no examples of pearlescent materials that do not contain such particles. Also, because pearlescence is associated with irregular particles, it is harder to tune the phenomenon — i.e., once these particles are added, the pearlescence is fixed. In contrast, iridescence, which is associated with ordered particle arrays (e.g., monodisperse spheres or other shapes), can be altered by changing the particle size or spacing. An example in this regard is an ordered array (photonic crystal) of spherical polymer microgels, such as those of *N*-isopropyl-acrylamide (NIPA) (also abbreviated in some papers as NIPAM or NIPAAm).[12,13] Gels (i.e., crosslinked networks) of NIPA are known to shrink when heated above their lower critical solution temperature (LCST).[14,15] As NIPA microgels shrink, the spacing between these microgels in an array gets altered, thereby changing the iridescence from the array.[13] Thus, iridescence can be modulated by external stimuli such as temperature or even by the addition of analytes.[12,13] For these reasons, iridescent arrays have been used as chemical

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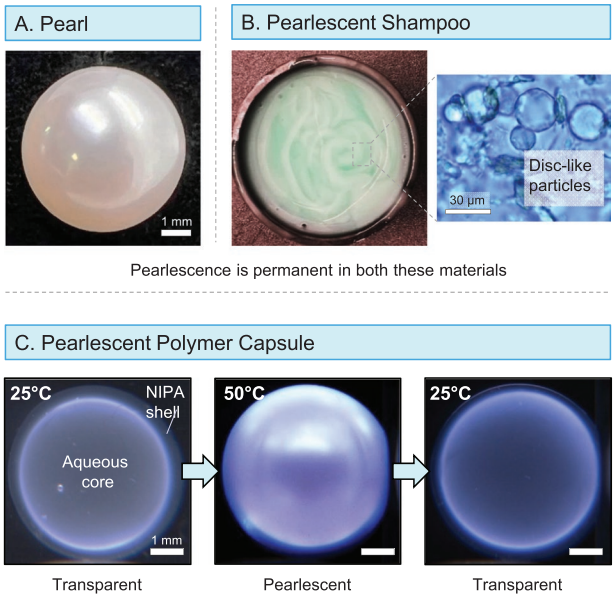

Figure 1. Examples of pearlescence. A) A natural pearl exhibiting its metallic sheen. B) A pearlescent shampoo that contains disc-like particles (seen in the optical micrograph, inset). C) Capsules with an *N*-isopropylacrylamide (NIPA) outer shell turn pearlescent when heated to 50 °C (this study). The transparent state is recovered on cooling. Pearlescence in (C) is thus tunable and reversible while in (A) and (B), it is permanent and cannot be altered.

sensors[12] or as active camouflage.[16,17] Pearlescence, on the other hand, is not tunable by stimuli, and there are no examples of a solid being switchable between a pearlescent and a non-pearlescent state.

In this paper, we report our discovery that pearlescence can arise spontaneously in certain capsules that have an aqueous core and polymer shell(s). Importantly, there are no micro- or nanoparticles in the capsule, and yet we observe pearlescence. The outer shell of the capsules is a hydrogel made of NIPA (≈500 µm thick), which we create by an inside-out polymerization technique.[18–20] When the capsules are heated above the LCST of NIPA, the transparent capsules spontaneously turn pearlescent (Figure 1C). The effect is reversible, with the transparent state being recovered upon cooling. We have used reflectance measurements and optical microscopy to study the transition to pearlescence in real time. Once the transition is complete, the pearlescence of the capsules is found to be comparable to that of natural pearls. The onset temperature for pearlescence can be tuned by adding salts to the system. Thus, this is the first example of solid pearlescence that can be reversibly tuned by external stimuli. Regarding the origin of this effect, we find no pearlescence in bulk NIPA gels or thin sheets — all these materials simply turn turbid upon heating.[14] Pearlescence is only observed when a sufficiently thin NIPA shell encloses an aqueous core. In such cases, above the LCST, we expect NIPA-rich domains to be formed within the thin shell due to the phase transition. The size or spacing of these domains is likely to be responsible for the pearlescence. Our work sheds fresh insight into the nature of pearlescence and its tunability. Responsive pearlescent capsules could be used in materials for camouflage[16,17] or in new dye and pigment-free consumer products.[21,22]

2. Results and Discussion

2.1. Synthesis of Capsules

The capsules described in this paper were synthesized by growing polymer shell(s) around a core (**Figure 2**). We focus on two types of capsules: one with a liquid core (Figure 2A) and one where the core is a physical gel (Figure 2B). The routes for synthesizing these capsules have been reported previously by our lab.[18,19] In both cases, we use the well-known anionic biopolymer, sodium alginate (Alg). A sol of Alg is known to

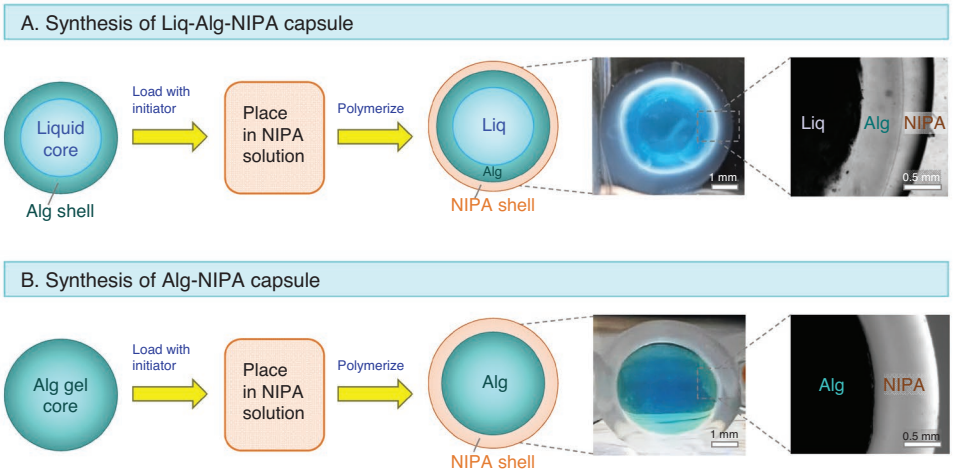

Figure 2. Synthesis of liquid-core (Liq-Alg-NIPA) and gel-core (Alg-NIPA) capsules. A) To make the former, thickened Ca^{2+} is dropped into an Alg solution to form an Alg gel around a liquid core. This capsule is then loaded with initiator and placed in NIPA, and upon polymerization, an outer NIPA shell is formed. B) To make the latter, an Alg gel is first made by dropping an Alg solution into Ca^{2+}. This gel is then loaded with initiator and placed in NIPA to form an outer NIPA shell. Photos and optical micrographs of the final capsules are shown for each case (for the latter, the cores are loaded with carbon black (CB) nanoparticles to clearly distinguish the cores from the shells).

transform into a physical gel when combined with divalent cations such as calcium (Ca^{2+}).[18] In our gel-core capsules, the core is an Alg gel synthesized by dropping a 2% Alg solution into a reservoir of 5% $CaCl_2$. In our liquid-core capsules,[19] we reverse the order and introduce a viscous 1.5% $CaCl_2$ solution into a reservoir of 0.5% Alg (the feed is made viscous by using an 80–20 mixture of glycerol-water). In both cases, once the feed droplet contacts the reservoir, it is converted into a soft solid. By using needles or pipettes of different diameters, we can control the droplet size (and thereby the capsule size).

We then use the "*inside-out polymerization*" technique developed by our lab to grow a shell of NIPA gel around each of the above structures.[18–20] The idea behind this technique is that one of the components required for a free-radical polymerization (the initiator) is present only in the core while the others are only present in the surrounding solution.[18] Specifically, we load the cores with ammonium persulfate (APS, a thermal initiator) and then place them in a solution containing the NIPA monomer as well as other components (see Experimental Section for details). APS diffuses out of the core and polymerizes the NIPA into a shell around the core. The reaction goes to completion within 10 min at room temperature. Photos and optical micrographs of typical capsules are shown in Figure 2. The gel-core capsule, denoted as Alg-NIPA, has an overall diameter of 5 mm and the NIPA shell thickness is 1 mm. The liquid-core capsule, denoted as Liq-Alg-NIPA, has an overall diameter of 5 mm as well, and in this case, there are two shells: an inner Alg (≈600 μm) and an outer NIPA (≈350 μm). For the optical micrographs in Figure 2, carbon black (CB) nanoparticles were added to the cores to provide contrast with the shells and thus clearly resolve the two.

2.2. Pearlescence of Liq-Alg-NIPA Capsules

Both the Liq-Alg-NIPA and the Alg-NIPA capsules are transparent and show no trace of pearlescence at room temperature. We will first show the emergence of pearlescence in the former, which is induced by heating it above the LCST of NIPA (≈32 °C). In **Figure 3**A, at $t = 0$, a Liq-Alg-NIPA capsule of ≈5 mm diameter is immersed in warm water (50 °C) and observed over time by optical microscopy. Images at discrete time points are shown (A1 to A4). Initially (A1), the capsule is clear because NIPA has not undergone phase-separation. Within a few seconds, the capsule turns turbid as NIPA crosses its phase boundary (A2, A3). But by the 20 s mark (A4), the turbid capsule becomes strongly pearlescent, as can be seen from its metallic sheen. Figure 3B shows that this pearlescence is reversible. When the hot capsule is immersed in cool water (20 °C), it becomes clear and loses its pearlescence over a period of 20 s. Movie S1 (Supporting Information) reveals the above behavior in real-time.

The pearlescent appearance of Liq-Alg-NIPA capsules (above the LCST of NIPA) is clearly unusual. Although we and others have previously studied NIPA gels as well as NIPA-shelled capsules, we had never observed such optical properties previously. To underscore this difference, we repeated studies on the optical behavior of NIPA gels and capsules — and confirmed that none of them are pearlescent, either at room temperature or upon heating. First, Figure S1 (Supporting Information) reports the temperature-dependent response of a fresh Alg-NIPA capsule (note that the core of this capsule is an Alg gel while the shell is a NIPA gel). When immersed in warm water (50 °C), this capsule turns turbid (Figure S1A, Supporting

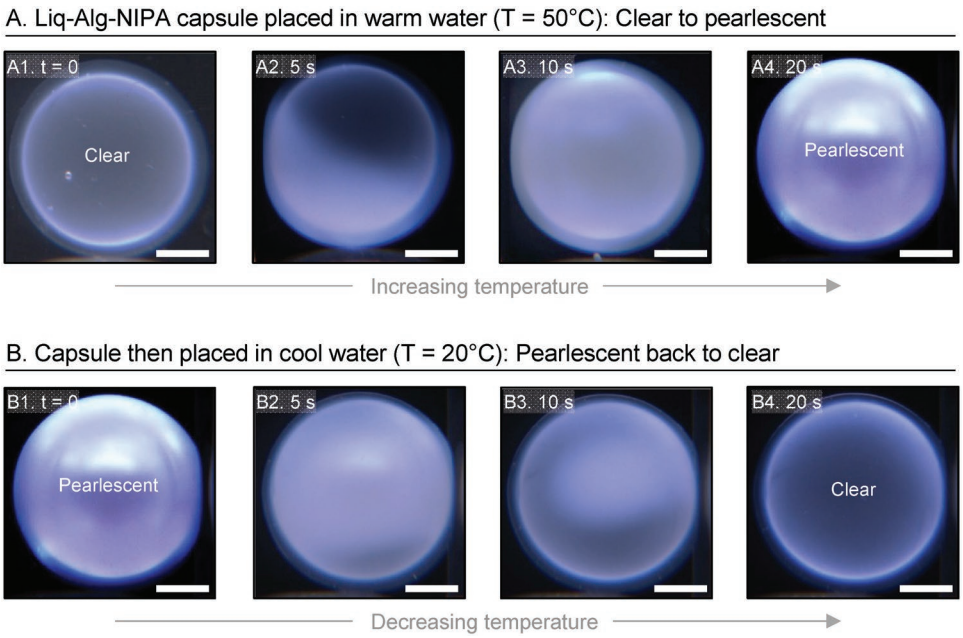

Figure 3. Reversible pearlescence of a Liq-Alg-NIPA capsule with temperature. A) The clear capsule is placed in warm (50 °C) water and observed. Images A1 to A4 show that it becomes pearlescent over 20 s. B) The pearlescent capsule is then placed in cool (20 °C) water. Images B1 to B4 show that it reverts to its clear state in 20 s. Scale bars: 2 mm. The above sequence of reversible pearlescence is also revealed in real time by Movie S1 (Supporting Information).

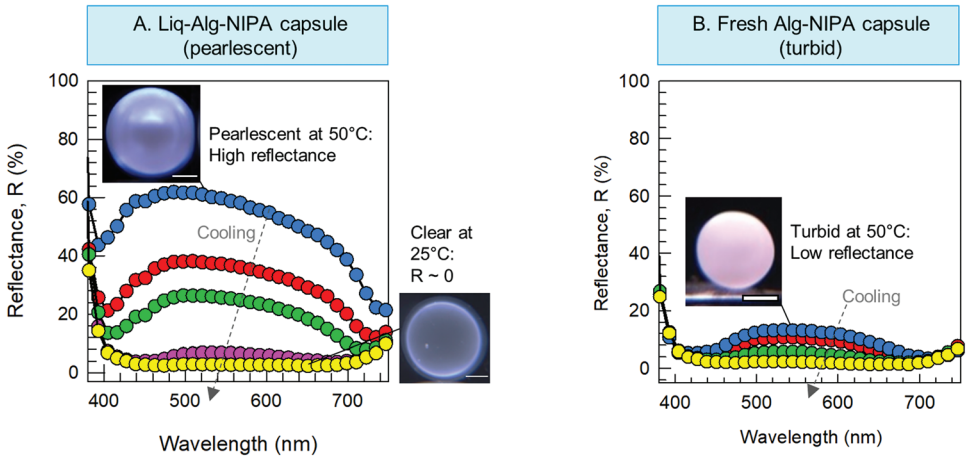

Figure 4. Specular reflectance spectra of a Liq-Alg-NIPA capsule and a fresh Alg-NIPA capsule at various temperatures. The capsules are taken out of water at 50 °C and successive spectra are measured as they cool. A) The Liq-Alg-NIPA capsule is pearlescent and has high specular reflectance (R) at 50 °C, but becomes clear and non-reflective (R ~ 0) at room temperature. B) The fresh Alg-NIPA capsule is turbid with low R at 50 °C and becomes clear and non-reflective (R ~ 0) at room temperature. Scale bars: 2 mm.

Information) and when the hot capsule is immersed in cool water (20 °C), it reverts to clear (Figure S1B, Supporting Information). The dull turbidity of this capsule contrasts with the glossy sheen of the pearlescent capsule in Figure 3. Similarly, NIPA gels also become turbid above their LCST,[14] regardless of their geometry (cylinder, sphere, thin sheet) (Figure S2, Supporting Information). Turbidity arises because, as NIPA gels phase-separate above their LCST, chain segments aggregate into nano- or micro-scale domains that scatter light.[23–26] Thus, turbidity is to be expected upon heating in NIPA-based gels, but pearlescence is not.

From visual observation, the pearlescence of Liq-Alg-NIPA capsules is striking, and it is very distinct from simple turbidity. But can we quantify these differences? For this purpose, we resorted to reflectance measurements (see Experimental Section for details). Capsules were illuminated with white light and the reflected light was measured. We ensured that the reflected light mainly corresponded to *specular* reflection,[3] i.e., reflection at the same angle as the incident light, and this reflectance was normalized to that of a white standard. **Figure 4**A plots the normalized specular reflectance (R) versus wavelength for the Liq-Alg-NIPA capsule as it is cooled from 50 °C to room temperature. At 50 °C, when the capsule is pearlescent, R is at its highest (≈60%). As the capsule cools, it is no longer pearlescent and R drops. When the capsule finally becomes transparent, R falls to nearly zero. For comparison, Figure 4B shows the reflectance spectra for an Alg-NIPA capsule as it is cooled from 50 °C. This capsule is turbid, not pearlescent, at 50 °C, and its R is at most 20%, which is 3× lower than that of the Liq-Alg-NIPA capsule. R again decreases to zero as the turbid capsule transforms to clear.

Figure 4A and B reveal that: (a) the pearlescent state is characterized by its high R; and (b) R is much higher for a pearlescent than a turbid capsule. Also, consistent with our observations from optical microscopy (Figure 3), we find a transition from clear (R ~ 0) to pearlescent (R ~ 60%) for the Liq-Alg-NIPA capsule as it is heated above its LCST. We were curious how the pearlescence of this soft capsule compared to that of a real (natural) pearl. **Figure 5** shows the specular reflectance spectra for a natural white pearl (AA grade) and a white polystyrene bead, both with diameters ≈6 mm. For comparison, we also studied a Liq-Alg-NIPA capsule with the same diameter, and the specular reflectance of this capsule at 50 °C (well above its LCST) is also plotted in Figure 5. Both the pearlescent capsule and the natural pearl exhibit a high R (60% and above), which is consistent with their shiny appearance.[1–3] The natural pearl shown in Figure 5 has an R ≈80%, but other natural pearls we tested had R ~ 60%. In the literature, natural pearls with R between 60 and 80% have been reported.[3] In comparison, the white bead has an R below 20%, which is similar to that of a turbid capsule.

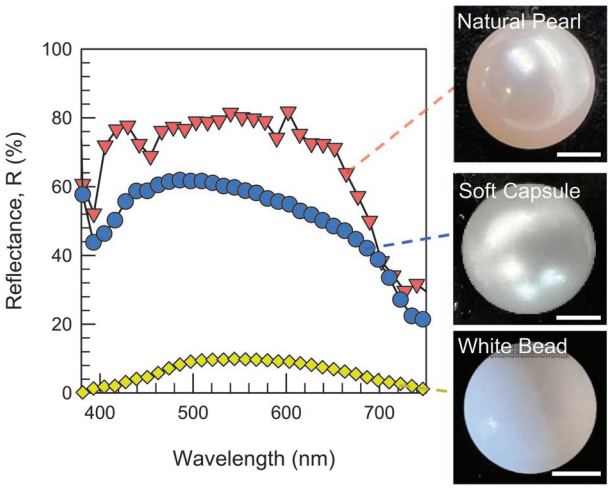

Figure 5. Specular reflectance spectra for pearlescent vs non-glossy objects. A natural pearl (AA grade) and a Liq-Alg-NIPA capsule in its pearlescent state (at 50 °C) both show high specular reflectance and a similar glossy sheen. In contrast, a white bead of polystyrene does not have a sheen and its spectrum shows a much lower reflectance. Scale bars: 2 mm.

The counterpart to specular reflection is *diffuse* reflection, which refers to reflection of light at angles different from that of the incident light. Figure S3 (Supporting Information) shows the normalized diffuse reflectance from the same three materials studied in Figure 5. The top panel (Figure S3A, Supporting Information) clarifies the distinction between specular and diffuse reflectance. Shiny materials like metals or pearls are expected to show high specular and low diffuse reflectance, whereas the opposite will be true for non-shiny materials like surfaces with a matte finish. This is indeed borne out by the data in Figure S3B (Supporting Information): both the pearl and the pearlescent Liq-Alg-NIPA capsule have low diffuse reflectances whereas the white polystyrene bead has a high diffuse reflectance.

2.3. Factors that Affect Pearlescence

The data thus far have shown the onset of pearlescence in Liq-Alg-NIPA capsules upon heating. We confirmed that the pearlescence was not simply a property of NIPA gels (Figure S1, Supporting Information). We also noted that fresh Alg-NIPA capsules become turbid, but not pearlescent, upon heating (Figure 4B; Figure S1, Supporting Information). The same capsules, however, do become pearlescent after they are placed in deionized (DI) water for a day or more (**Figure 6**). During this time, the capsules swell due to the osmotic gradient between the gel core and the surrounding water. As an example, the capsule in Figure 6A has an initial diameter of 5.8 mm (Image A1) whereas after two days, it has swelled to a diameter of 8.0 mm (Image A3). When the swollen capsule is heated to 50 °C, it exhibits pearlescence (Image A6). In contrast, the initial capsule only becomes turbid at this temperature (Image A4). The specular reflectance spectra (Figure 6B) for the hot capsules show a low *R* initially (Day 0) while the *R* increases on Day 1 and then further on Day 2. Note that the *R* on Day 2 is ≈60%, which is comparable to that for the Liq-Alg-NIPA capsule at the same temperature. Why does swelling lead to pearlescence? As the capsule swells, the NIPA shell is stretched out and thereby becomes thinner. Could the thinning of the shell be a contributing factor?

To test if shell thickness plays a role in pearlescence, we made Alg-NIPA capsules with different NIPA shell thicknesses. This was done by varying the initiator (APS) concentration during the synthesis[18,19] — the higher the APS, the thicker the NIPA shell (**Figure 7**A). From the images, the shell thickness varies from ≈0.7 mm for 2% APS to ≈1.1 mm for 5% APS and ≈1.6 mm for 10% APS. After swelling in water, the capsules were tested for pearlescence on Day 2 by heating to 50 °C. As the NIPA shell becomes thicker, the pearlescence decreases. The lack of pearlescence in the case of the thickest NIPA shell can be seen from Image A6 and is also confirmed by its specular reflectance spectra (Figure 7B). The reflectance *R* for this capsule is only ≈20%, which is ≈3× lower than for the capsule with the thinnest NIPA shell.

2.4. Mechanism for Pearlescence

Summarizing our findings thus far, capsules with a NIPA outer shell exhibit pearlescence when heated above the LCST of NIPA. The necessary conditions for pearlescence are a thin NIPA shell surrounding a water-rich core. Liquid-core capsules (Liq-Alg-NIPA) show pearlescence even when freshly prepared. Gel-core capsules (Alg-NIPA) must be swollen in water before they exhibit this phenomenon. This necessity for swelling

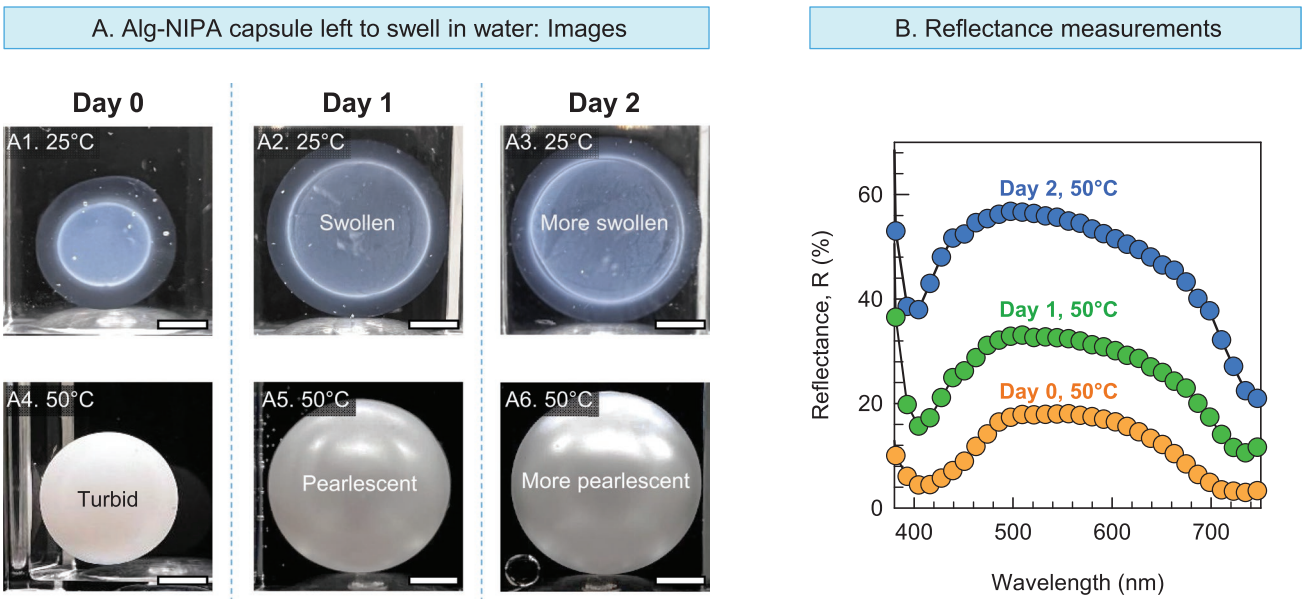

Figure 6. Swollen Alg-NIPA capsules exhibit pearlescence on heating. A) Soon after preparation (Day 0), the fresh capsule (Image A1) becomes turbid upon heating (A4). If left in water, the capsule swells, as seen from the images on Day 1 and 2 (A2, A3). The swollen capsule exhibits pearlescence on heating (A5, A6). Scale bars: 2 mm. B) The pearlescence is also seen from the specular reflectance spectra: while the turbid capsule on Day 0 has low R, the R is significantly higher by Day 2 when the capsule is pearlescent.

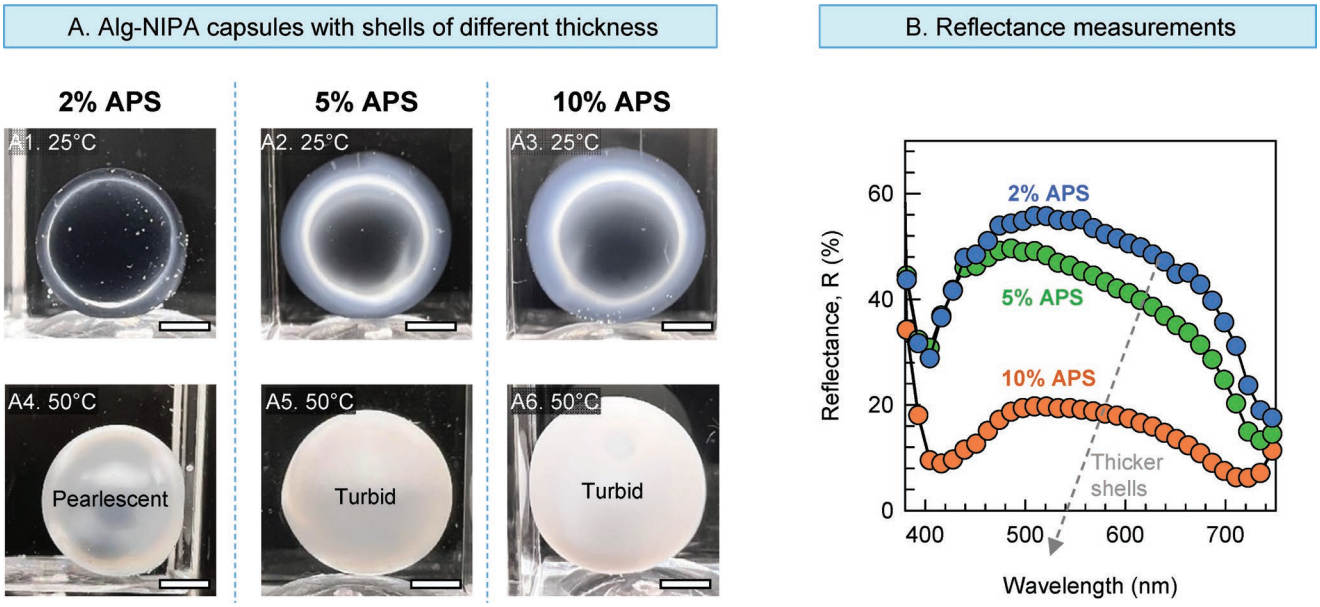

Figure 7. Capsules become pearlescent only if the NIPA shell is thin. A) Alg-NIPA capsules are made with increasing concentrations of APS initiator, which leads to thicker shells (Images A1 to A3). Note that the cores are loaded with CB nanoparticles to contrast with the shells. The capsules are left to swell in water and on Day 2, they are heated to 50 °C. The capsule with the thinnest NIPA shell becomes pearlescent (A4) whereas the capsules with thicker shells only turn turbid (A5, A6). Scale bars: 2 mm. B) Specular reflectance spectra at 50 °C are consistent with the images in (A): R is high for the pearlescent capsule and low for the turbid capsule.

implies that the NIPA shell should be sufficiently stretched (and thereby thinned) around the core. Another striking observation in this regard is shown in Figure S4 (Supporting Information). Here, we study an Alg-NIPA capsule that is pearlescent at 50 °C (Figure S4A, Supporting Information and Image A1) — as expected, it has a high specular reflectance ($R \sim 60\%$) (Figure S4B, Supporting Information). While at 50 °C, we use a needle to puncture the capsule (Image A2). Within seconds, the pearlescence vanishes and the capsule shrinks and transforms to turbid (Images A3, A4). The NIPA shell, which was tautly stretched around the core, is now deflated, and eventually slips off the core into the water; note that the shell on its own is turbid. Also, the punctured capsule shows a low specular reflectance ($R \sim 20\%$) (Figure S4B, Supporting Information). Thus, for a capsule to exhibit pearlescence, the NIPA shell must be *intact and stretched* around the core.

Figure 8 reveals the dramatic extent to which the NIPA shell is shrunk by heating. Previously, in the capsules in Figures 3, 6, and 7, the NIPA outer shell was thick enough to be clearly resolved at room temperature. However, when the capsule was heated, the shell could not be resolved any more because it had shrunk (and moreover it was turbid). But by *how much* had the shell shrunk? To quantify this, we made a Liq-Alg-NIPA capsule in which the NIPA was fluorescently labeled with fluorescein isothiocyanate (FITC) (see Experimental Section for details).[27] Figure 8 shows images of this capsule from confocal microscopy, focusing on the interface between Alg (no fluorescence) and NIPA (green fluorescence). At 25 °C, the NIPA shell has a thickness of 680 ± 5 µm (Figure 8A). When the temperature is increased to 50 °C, the NIPA shell dramatically shrinks to a thickness of 25 ± 3 µm (Figure 8B). This corresponds to a 27-fold thinning of the shell. It occurs because NIPA becomes hydrophobic above its LCST and hence the shell expels water.[14,15]

To explain pearlescence, we need to discuss phase transitions in NIPA solutions and gels. When a solution of *linear NIPA* in water is heated above the LCST, the onset of phase separation is marked by *spinodal decomposition* (SD).[23–26] During SD, hydrophobic NIPA chains aggregate into NIPA-rich domains within the aqueous phase. These domains grow across the sample volume. Eventually, the domains coalesce and the sample separates into a NIPA-rich and a water-rich phase. As the NIPA-rich domains form, the sample will appear turbid because light will scatter from the domains.[23–26] Light scattering arises due to the refractive index (RI) of the domains being higher than that of the surrounding solvent (due to the higher NIPA concentration). As the domains grow, they become large compared to the

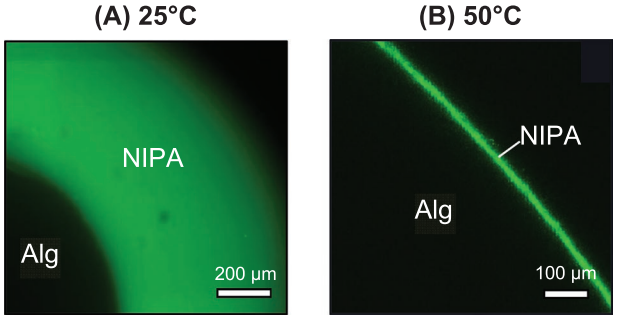

Figure 8. Confocal microscopy of a Liq-Alg-NIPA capsule. The NIPA is fluorescently labeled with FITC to enable visualization. A) At 25 °C, the outer NIPA shell is 680 µm thick and in this state the capsule is clear. B) When heated to 50 °C, the NIPA shell shrinks to 25 µm (i.e., by 27-fold). The thinning of the NIPA shell is key to the pearlescence of the capsule.

wavelength of light (i.e., > 100 nm), and this increases the light scattering and hence the turbidity.

In comparison to a NIPA solution, when a *NIPA gel* in water is heated above the LCST, it becomes turbid and stays that way (as shown experimentally in Figure S2, Supporting Information). In a NIPA gel, the polymer chains are constrained at cross-links and hence cannot freely diffuse and aggregate. Instead, aggregation into domains during SD will occur locally at the nanoscale,[23–26] i.e., the only moieties that can aggregate will be NIPA chain segments between adjacent cross-links. In the literature, this process is termed *microphase separation* (see the work of Bansil et al.[24,25]) and it implies that nano- or microscale domains will be "trapped" in the gel. Because NIPA is hydrophobic above its LCST, the gel will also expel water and thus shrink in volume. This is the scenario relevant to our observations.

We now put forward a mechanism to explain why our capsules become pearlescent upon heating above the LCST of NIPA. Images of a Liq-Alg-NIPA capsule before, during, and after the onset of pearlescence are shown in **Figure 9**, along with schematics that home in on the NIPA outer shell. Initially, i.e., at low temperatures (Figure 9A), the capsule is transparent, and the NIPA shell is thick. When heated above its LCST, NIPA-rich domains will form in the shell by SD (Figure 9B). The domains will grow over time, while the shell will also become thinner due to expulsion of water (Figure 9C). At this stage, we suggest that the capsule will exhibit pearlescence. The key is that the domains are trapped within a *thin and stretched shell*. Figure 8 showed how the shell will become much thinner upon heating. We expect that the reflected light interacts (via interference and/or diffraction[1,3]) with the NIPA domains in this thin shell. Just as in natural pearls, the domains will not be uniform in size, nor will they be in an ordered arrangement. As a result, the reflected light will have a metallic sheen, independent of viewing angle.[28]

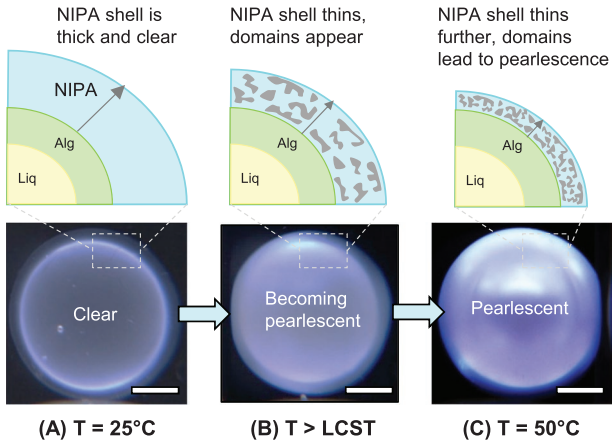

Figure 9. Mechanism for onset of pearlescence in a Liq-Alg-NIPA capsule. Pearlescence arises when the capsule is heated above the LCST of NIPA (images from Figure 3). Initially A), the capsule is clear, and the NIPA shell is thick. Upon heating B), NIPA-rich domains form in the shell and the shell thins as it expels water. With further heating C), the shell thins further and the domains grow. In turn, the interaction of light with these domains leads to pearlescence.

Domains formed during "microphase separation" in NIPA gels above the LCST have been discussed in the literature,[23–26] but have never been directly visualized. We tried to use confocal microscopy to see the domains in situ. Previously, in Figure 8, a fluorescently-labeled NIPA shell was shown, but no domains were visible at higher magnification in this shell above the LCST. We tried an alternative approach using Nile Red (NR) as a fluorescent probe. NR is insoluble in water, but fluoresces red in a nonpolar environment.[29] As shown in Figure S5A (Supporting Information), we place a Liq-Alg-NIPA capsule in an NR solution in DMSO/water (Image A1). At 25 °C, the capsule does not take up NR and thus no fluorescence is seen (Image A2). At 50 °C (above the LCST), NIPA becomes hydrophobic and the NIPA shell then imbibes NR from the solution.[29] The shell thus fluoresces red (Image B2), but here again domains cannot be resolved at higher magnification. Note that the capsule at this temperature has a pink pearlescence due to the NR (Image B1). When the hot capsule is cooled back to 25 °C, it turns clear, but the shell retains some pink color (Image C1). In confocal microscopy, specks of fluorescence from NR can be seen in the shell (Image C2). These arise because the NIPA is now hydrophilic, and the NR is no longer solubilized in the NIPA domains. We believe the NR specks are *indirect evidence* for the existence of hydrophobic NIPA domains in the shell above the LCST.

One point worth clarifying is that the NIPA domains mentioned above are unrelated to the mesh sizes of NIPA gels. The mesh sizes of chemically cross-linked gels such as NIPA have been reported to be ≈10–40 nm in the literature.[30,31] One way to estimate the mesh size ξ of a gel is from dynamic rheological data. ξ can be calculated from the following equation:[31,32]

$$\xi = \left(\frac{k_B T}{G_0}\right)^{1/3} \quad (1)$$

where k_B is Boltzmann's constant, T the absolute temperature and G_0 the gel modulus. We ran dynamic rheology on a NIPA gel with the same composition as the shell in a Liq-Alg-NIPA capsule. From the frequency spectra, G_0 at 25 °C is 3.5 kPa (see Figure S6, Supporting Information), which gives a value of 10.5 nm for ξ by equation 1. When the NIPA gel is heated to 50 °C, G_0 increases to 19.4 kPa. This implies a decrease in ξ to 6.0 nm by equation 1, which is to be expected due to the higher NIPA concentration in the shrunken gel. Both mesh sizes are much smaller than the wavelength of light — and hence are unrelated to the turbidity of NIPA gels above the LCST or the pearlescence of our capsules.

The mechanism shown by Figure 9 is consistent with other experiments that we have reported in the paper. Figure 7 showed the necessity of having a thin NIPA shell for pearlescence. If the shell is too thick, the capsule simply appears turbid upon heating, presumably because multiple scattering from the NIPA domains attenuates the reflected light. Figure 6 revealed pearlescence in Alg-NIPA capsules after swelling for a couple of days. In that time, the swelling of the Alg core thins and stretches the NIPA shell, which is key for pearlescence. Also, Figure S4 (Supporting Information) showed that puncturing a pearlescent capsule at 50 °C eliminates the pearlescence. The NIPA shell gets deflated and wrinkled when punctured

— and in this state it appears turbid. Thus, it is not enough to have a thin NIPA shell — the shell must also be stretched tautly around the core. In other words, the role of the core is to ensure that the shell remains stretched.

An interesting corollary to the above points is that the core does not have to be transparent; in fact, pearlescence is still seen when the core is opaque. This is shown by Figure S7 (Supporting Information), where we report pearlescent capsules with *different colors*, including orange, pink and black, by simply embedding colored nanoparticles in the core of Alg-NIPA capsules. For example, when carbon black (CB) nanoparticles are present in the Alg core, the core is black and opaque, but the capsule shows a shiny black pearlescence when heated to 50 °C. This means that some light must pass through the thin NIPA shell at 50 °C, i.e., it must be translucent. Still, most of the light incident on the capsule is reflected, and thus the reflected light captures the color of the core. Figure S7D (Supporting Information) shows another way to impart color to a pearlescent capsule, and that is by using copper (Cu^{2+}) as the cross-linking cation for Alg in the core (instead of Ca^{2+}). In that case, the core Alg gel is translucent, but with a pleasing blue tinge. In turn, the Alg-NIPA capsule shows a blue pearlescence at 50 °C.

Figure S8 (Supporting Information) describes a further way to tune the pearlescence of our capsules. Thus far, we have induced pearlescence by heating capsules to a temperature above the LCST of NIPA. It is well-known that the LCST can be altered by various additives, such as salts.[33–35] For example, adding a chloride (Cl^-) or sulfate (SO_4^{2-}) salt to water decreases the LCST whereas salts of anions like thiocyanate (SCN^-) increase the LCST.[35] The differences between the anions stem from their different effects on the hydrogen-bonded structure of water, i.e., their position in the Hofmeister series.[33–35] Sulfates are kosmotropes and they stabilize the water structure whereas thiocyanates are chaotropes and they break the structure of water. We experimented with a kosmotropic salt, ammonium sulfate, i.e., $(NH_4)_2SO_4$, which is known to lower the LCST of NIPA,[35] and the results are shown in Figure S5 (Supporting Information). A swollen Alg-NIPA capsule in DI water turns pearlescent only when heated above 32 °C. When this capsule is placed in a 1 M $(NH_4)_2SO_4$ solution at room temperature (25 °C), within 15 min, the capsule becomes pearlescent. Note that the NIPA shell around the core is evident at the outset, but it is shrunk and not visible when the capsule has turned pearlescent. This means that the LCST of NIPA has been lowered *below room temperature* by the salt. We have thus demonstrated how pearlescence in capsules can be engineered to occur under ambient conditions by exploiting the well-known principles of polymer phase behavior. Incidentally, the capsule does not have to be immersed in water for pearlescence to be observed. Figure S9 (Supporting Information) shows that a Liq-Alg-NIPA capsule becomes pearlescent even when taken out of water and heated on a hot plate.

3. Conclusion

In conclusion, the spontaneous appearance of pearlescence in soft solids is reported for the first time. Aqueous capsules with a NIPA shell are colorless and transparent at room temperature but become pearlescent when heated above the LCST of NIPA. The effect is reversible, and the capsules revert to a transparent state upon cooling. Pearlescence in these capsules is achieved without the need for plate-like particles or other additives. Reflectance measurements confirm that the capsules show high specular reflection ($R > 60\%$) in the pearlescent state, and they compare well with natural pearls in this regard. While a NIPA shell is necessary for pearlescence, it is not sufficient. The shell must be sufficiently thin, and upon heating above the LCST, it further thins and gets stretched. NIPA-rich domains form in the shell by spinodal decomposition, and the size and/or spacing of these domains are expected to be on the order of the wavelength of light. Reflected light then undergoes interference and/or diffraction with the domains in the thin shell, leading to pearlescence. Overall, this work demonstrates that pearlescence in soft materials is a tunable property, much like iridescence from photonic crystals. For example, capsules can be induced to become pearlescent at room temperature (without the need for heating), by tuning the LCST of NIPA with additives. Similarly, pearlescence in different colors can be achieved by altering the contents of the capsule core.

4. Experimental Section

Materials: Most chemicals were purchased from Sigma–Aldrich. These included the biopolymers alginate (Alg), which was a medium viscosity alginic acid, sodium salt from brown algae, and xanthan gum (XG). Chemicals used for forming the polymer shell were the crosslinker N,N′-methylene-bis(acrylamide) (BIS), the initiator ammonium persulfate (APS), and the accelerant tetramethylethylene diamine (TEMED). Salts used in this study were calcium chloride dihydrate ($CaCl_2$), copper chloride ($CuCl_2$), and ammonium sulfate ($(NH_4)_2SO_4$). Other chemicals included glycerol, allylamine, dimethyl sulfoxide (DMSO), and the fluorescent dyes fluorescein isothiocyanate (FITC) and Nile Red (NR). *N*-isopropylacrylamide (NIPA) was purchased from TCI America. Deionized (DI) water was used in all experiments.

Synthesis of Alg-NIPA Capsules: A feed solution was first made with 2% Alg in DI water. This was dropped into a 1.7% (150 mM) $CaCl_2$ solution using a syringe or transfer pipette. The Alg droplets were allowed to incubate in the salt solution typically for 5 min, whereupon the droplets were converted into Alg/Ca^{2+} gels with diameters ≈4 mm. The gels were then soaked in a 2% solution of the initiator APS for 10 min. The APS-loaded gels were then suspended in a monomer solution made by dissolving 11% (1 M) NIPA, 0.34% of the crosslinker (BIS) (this was 2.2 mol.% with respect to the monomer), 1.5% accelerant (TEMED), and 0.75% thickener (XG). Polymerization was conducted at room temperature for 10 min, whereupon a 1-mm thick NIPA shell formed around the Alg gels, as shown by the schematic in Figure 2. The resulting structures were washed three times with DI water and then stored in DI water.

Synthesis of Liq-Alg-NIPA Capsules: A feed solution was made by dissolving 1.7% $CaCl_2$ in an 80/20 (v/v) mixture of glycerol and DI water. A reservoir solution was prepared by dissolving 0.5% Alg in DI water. The feed was loaded into a syringe and dropped into the reservoir, where they incubated for 5 min. Thereby, the droplets were converted into capsules with a liquid core and an Alg shell (overall diameter ≈4 mm). The capsules were then soaked in a 2% APS solution for 10 min and then taken out and suspended in the same monomer solution as above (11% NIPA, 0.34% BIS, 1.5% TEMED and 0.75% XG). Polymerization was conducted at room temperature for 10 min, whereupon a ≈0.5-mm thick NIPA shell formed on the outside, as shown by the schematic in Figure 2. The resulting structures were washed three times with DI water and then stored in DI water.

Synthesis of Fluorescent Capsule: The NIPA layer in a Liq-Alg-NIPA capsule was functionalized with fluorescein isothiocyanate (FITC) during polymerization. The procedure followed was the one reported by Fussell et al.[27] Briefly, 15 mg of FITC was added to a 100 µM solution of NaOH along with 15 µL of allylamine. This solution was allowed to stir for 4 h. Later, 100 µL of this solution was added to the monomer solution before polymerization. Thereafter, as above, the capsule with a liquid core and an Alg shell was suspended in the monomer solution and allowed to polymerize for 10 min. The result is that the NIPA shell becomes fluorescently labeled with FITC, which we characterized by confocal microscopy.

Fluorescence Experiments with Nile Red: A solution of NR in DMSO was diluted in DI water such that the final NR concentration was 3 µM. A Liq-Alg-NIPA capsule was placed in this NR solution at 25 °C and imaged by confocal microscopy. The sample was then heated to 50 °C and left overnight. Thereafter, it was imaged again. Finally, the sample was cooled down to 25 °C and imaged once more.

Optical and Confocal Microscopy: Brightfield images of the capsules were taken with an inverted optical microscope (Zeiss Axio-Observer 7) using a 2.5× or 10× objective. Confocal microscopy was done with a Fluoview FV3000 confocal microscope using several objectives. In the case of NIPA with FITC, the sample was excited at 488 nm and the emission filter at 517 nm (10 nm bandwidth) was selected. In the case of the NR experiments, excitation was done at 560 nm and emission was collected through a filter at 610 nm (10 nm bandwidth).

Reflectance Spectroscopy: Reflectance spectra were collected using a ThorLabs CCS-200 compact UV-vis spectrometer, which was connected to a reflectance probe (RP20, Thorlabs). For measurements of specular reflectance, a halogen fiber light source (Hamamatsu L10290) was connected to the above reflectance probe, which was fixed on a probe stand (RPS-SMA, Thorlabs). Light was shining normal to the capsule of interest, and the reflected light was then detected at the same angle. For diffuse reflectance measurements, the sample was illuminated evenly by a halogen light source (QTH10, Thorlabs) and the reflected light was collected at an angle different from the angle of illumination. (Measurements of diffuse reflectance typically use an integrating sphere, which averages over all angles of reflected light, but such a sphere was not available for our purpose.) For both specular and diffuse reflectance, collected values were normalized to those of a white reference standard (flat disc, from Ocean Optics).

Rheology: A NIPA gel was made by polymerizing a mixture of 11% NIPA, 0.34% BIS, 1.5% TEMED, and 2% APS in a vial. This composition of the gel corresponded to the shell in Liq-Alg-NIPA and Alg-NIPA capsules. The gel was cut into a disc with a diameter of 20 mm and thickness 2 mm. Experiments on this gel were performed at 25 and 50 °C on an AR2000 stress-controlled rheometer (TA Instruments) using 20-mm parallel plates. Dynamic stress-sweeps were first performed to identify the linear viscoelastic (LVE) region of the sample. Dynamic frequency sweeps were then conducted at a constant strain amplitude within the LVE region.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

glossy sheen, lustrous sheen, pearl-like appearance, stimuli-responsive capsules, thermoresponsive capsules

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