

Osmotically Driven Formation of Double Emulsions Stabilized by Amphiphilic Block Copolymers**

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Abstract: Double emulsions are valuable for the formation of multi-compartmental structures. A variety of pathways to prepare double emulsions have been developed, but high-throughput routes to droplets of controlled size and architecture remain scarce. A new single-step process is introduced for preparation of water-in-oil-in-water double emulsions by a previously unexplained process of self-emulsification. We show that the origin of this process is the osmotic stress resulting from the presence of salt impurities within the amphiphilic block copolymers used for emulsion stabilization. Further, we utilize osmotically driven emulsification to tailor the structures of multiple emulsions, which upon solvent evaporation can yield multi-compartmental capsules or hierarchically structured porous films.

Double emulsions consisting of water-in-oil-in-water (w/o/w) or oil-in-water-in-oil (o/w/o) droplets are of significant interest for pharmaceuticals,^[1–6] cosmetics,^[7,8] separation technologies,^[9] and microreactors.^[10–12] Most commonly, double emulsions are formed through a two-step emulsification process using a combination of oil-soluble and water-soluble surfactants to stabilize the o/w and w/o interfaces, respectively. However, this approach generally yields a broad distribution of droplet sizes, and the second emulsification step introduces the possibility of destabilization through rupturing of the inner droplets.^[13–19] Very recently, Hong et al.^[20] and Besnard et al.^[21] have reported one-step methods for the preparation of double emulsions stabilized by amphiphilic block copolymers as a result of phase inversion processes. However, control over the structures of double emulsions obtained by one-step processes remains challenging. Alternatively, the use of microfluidic techniques enables precise control over droplet size and number at each level within multiple emulsions, but the throughput of these methods is low.^[22–26]

For w/o/w emulsions in particular, osmotic pressure differences between the inner and outer aqueous phases have played a central role in efforts to control droplet

stability.^[15,16,27–34] In particular, the addition of osmolytes to the internal phase is commonly used to prevent instability that is due to transport of water to the external phase driven by differences in Laplace pressure (that is, Ostwald ripening). However, such osmotically stabilized double emulsions have previously been prepared only by two-step processes because the inner water droplets must contain a different concentration of water-soluble species than the continuous phase.

Herein, we introduce a new single-step method that takes advantage of osmotic pressure differences to yield formation of highly stable w/o/w double emulsions with tailored inner droplet characteristics. Our approach is inspired by the observation that an organic solvent containing amphiphilic block copolymers placed in contact with water will often spontaneously develop a cloudy appearance, for example as shown in Figure 1 for polystyrene-*block*-poly(*N*-isopropyla-

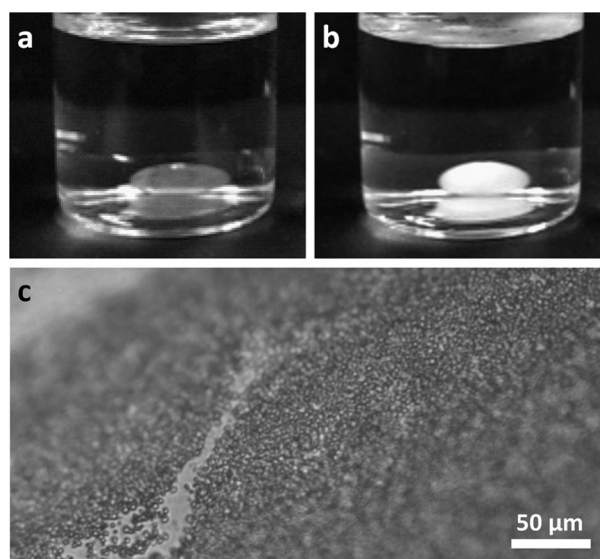


Figure 1. Photographs taken a) 15 s and b) 25 min after placing a large drop of chloroform containing 10 mg mL^{−1} of as received PS-PNIPAM into deionized water. c) Optical micrograph of the μm-scale w/o emulsion droplets spontaneously formed at the macroscopic o/w interface, which account for the increase in cloudiness seen from (a) and (b).

crylamide) (PS-PNIPAM) diblock copolymers dissolved in chloroform (see also the Supporting Information, Movie S1). As revealed by optical microscopy, the cloudiness arises from the spontaneous formation of micrometer-sized water droplets within the solvent phase near the interface with water. In this case, the droplets show a fairly narrow size distribution with an average diameter of 2.8 μm and standard deviation of

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0.4 μm . This phenomenon has been described several times previously,^[35–37] but its origin is not well understood. Indeed, the spontaneous transport of water from the bulk into micrometer-sized droplets, which experience a Laplace pressure of about 10 kPa owing to the solvent/water interfacial tension, seems at first to contradict basic thermodynamic principles. However, we hypothesized that droplet formation was driven by water-soluble impurities present in the copolymer that would be preferentially solvated in the forming droplets, thus providing an osmotic driving force to counterbalance Laplace pressure. Specifically, we suspected this behavior to arise from residual salt species originating from the organometallic initiators used in polymer synthesis, which have previously been shown to play an important role in facilitating electric-field alignment within block copolymer thin films.^[38–40]

We first verified the presence of impurities remaining from the organolithium and organopotassium initiator species using inductively coupled plasma mass spectrometry (ICP-MS) to characterize three commercial amphiphilic block copolymers (Table 1): PS_{16k}-PNIPAM_{5.2k} and two polystyrene-

Table 1: Salt impurity content for three commercial amphiphilic block copolymers.^[a]

Cations/polymer chain	As received	Purified
Li ⁺ /PS _{16k} -PNIPAM _{5.2k}	0.162 ± 0.002	0.0212 ± 0.0004
K ⁺ /PS _{9.5k} -PEO _{9.5k}	0.112 ± 0.003	0.003 ± 0.001
K ⁺ /PS _{9.5k} -PEO _{18k}	0.0089 ± 0.0005	–

[a] Determined by ICP-MS analysis.

block-poly(ethylene oxide) samples (PS_{9.5k}-PEO_{9.5k} and PS_{9.5k}-PEO_{18k}). As received, PS_{16k}-PNIPAM_{5.2k} contained 0.162 Li⁺ species per polymer chain, while PS_{9.5k}-PEO_{9.5k} contained 0.112 K⁺ species per chain; following purification steps described in the Experimental section, these values were reduced to 0.0212 and 0.003, respectively. (We report concentrations on a per-chain basis, as one initiator salt species per chain would be present following synthesis in the absence of any purification.) Interestingly, the as-received sample of PS_{9.5k}-PEO_{18k} contained less than 0.01 K⁺ per chain, and thus no additional purification was conducted.

As the solubilities of lithium and potassium salts in the organic solvents considered here are quite low, their presence in solution must be facilitated by the block copolymer. Indeed, transmission electron microscope (TEM) images of as-received PS-PNIPAM samples cast from chloroform solution revealed domains of 20–80 nm in diameter (Figure 2a). Coupled with dynamic light scattering (DLS) measurements indicating the existence of objects with average hydrodynamic diameters of about 100 nm in solution (Figure 2b), these results suggest that the salts exist in solution as block-copolymer-stabilized aggregates. Following purification to remove lithium salts, PS-PNIPAM solutions showed no signs of such aggregates (Supporting Information, Figure S1), which is consistent with the good solubility of both polymer blocks in chloroform.

We suggest that these salts provide an osmotic driving force that exceeds the Laplace pressure associated with the

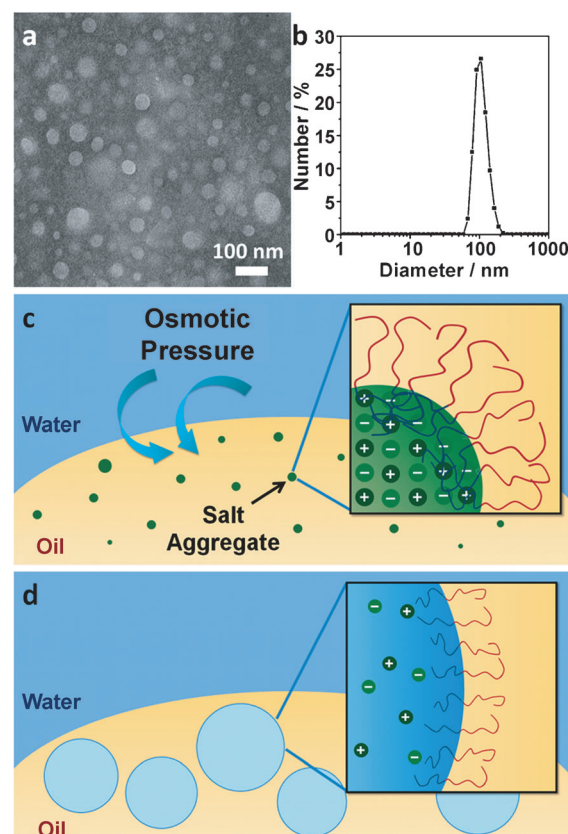


Figure 2. a) TEM image and b) hydrodynamic diameter distribution from DLS of salt aggregates dispersed in the organic solution (chloroform containing 10 mg mL^{−1} of as received PS-PNIPAM). c), d) Illustration of the spontaneous formation of water droplets at an o/w droplet interface: c) water is pulled into the oil phase owing to the presence of salt aggregates, d) leading to osmotically driven formation of a w/o/w double emulsion.

oil/water interface, thereby drawing water out of the surrounding bulk phase and into the spontaneously forming droplets (Figure 2c,d). Specifically, after the organic phase is brought into contact with water, the salt aggregates grow in size owing to the influx of water until they reach a final size R_{eq} , at which the osmotic pressure and Laplace pressure balance. Without the large osmotic driving force provided by the salt species, it might be expected that inverse block copolymer micelles could be swollen by water until a maximum size that is dictated by the characteristics of the copolymer, which is typically about 100 nm or below.^[41,42] Here, the presence of salt causes expansion into macro-emulsion droplets with micrometer-scale sizes dictated by the balance between osmotic stress and interfacial tension.

While the initial formation of droplets near the interface can be seen within about 1 s, as the process relies on diffusion of water through chloroform, the time required for each aggregate to “inflate” into an emulsion droplet of size R_{eq} will depend on the overall dimensions of the organic phase. For example, in Figure 1, the formation of internal droplets within a macroscopic chloroform phase with dimensions of several mm requires about 25 min to reach completion. Notably, as the forming droplets are less dense than the surrounding

organic solvent, they float upwards, which also provides some convective mixing. Owing to the presence of the amphiphilic block copolymer that can continually adsorb to the solvent/water interface during growth, the resulting droplets are highly stable against coalescence. Indeed, we have not observed any coalescence between spontaneously formed droplets or with the external water phase. Based on this stability, we propose that each salt aggregate within the organic phase gives rise to a single emulsion droplet, such that the final details of the osmotically formed emulsions are not sensitive to these kinetics, but instead only to the initial characteristics of the salt aggregates. Here, we neglect the possibility for the salt species to diffuse out of the droplets and into the continuous phase, although for species showing more pronounced solubility in the organic phase, the relative rates of salt and water transport would be an important consideration.

The Laplace pressure difference (ΔP) between the interior of a droplet of radius R and the external phase resulting from the solvent/water interfacial tension (γ) is given by $\Delta P = 2\gamma/R$, where we have ignored the pressure drop across the outer droplet surface owing to the relatively small curvature of this interface.^[26] Approximating the osmotic pressure Π in the fully inflated droplet as that for a dilute ideal solution with a concentration c_s of monovalent salt, $\Pi = 2c_s k_B T$, yields an equilibrium condition of:

$$\Delta P = \frac{2\gamma}{R_{eq}} - \frac{2n_s k_B T}{(4\pi/3)R_{eq}^3} \approx 0 \quad (1)$$

where n_s is the number of salt molecules in the initial aggregate, which we assume remains constant during osmotic inflation of a water droplet. Using pendant drop tensiometry, we measured the interfacial tension of a chloroform solution containing 10 mg mL⁻¹ of purified PS-PNIPAM as $\gamma = 19.4 \pm 0.9$ mN m⁻¹. Thus, for the observed droplet sizes of $R_{eq} = 1.4$ μ m, Equation (1) indicates a value of $n_s = 6.5 \times 10^{-17}$ mol. This value is in reasonably good agreement with the measured aggregate sizes; while the exact nature of the salt is unknown, if we take them to be crystals of LiOH, the value of $D_h \approx 100$ nm from DLS (Figure 2b) yields $n_s = 3.2 \times 10^{-17}$ mol.

Further support for the proposed mechanism is provided by a series of experiments using purified copolymers. In this case, we prepared primary o/w emulsions with droplet sizes of about 100 μ m by agitation of copolymer solutions in chloroform with a water phase containing 5 mg mL⁻¹ of poly(vinyl alcohol). For as-received PS-PNIPAM, secondary primary water droplets with diameters of 2–3 μ m formed near the primary o/w emulsion interface within a few seconds, as seen in Figure 3a. In contrast, purified PS-PNIPAM showed no evidence of secondary emulsion formation (Figure 3b). Finally, the addition of 4.2 mg mL⁻¹ LiCl to the chloroform solution of PS-PNIPAM caused the spontaneous formation of double emulsions to be recovered with similar secondary droplet size ($R_{eq} = 1.4 \pm 0.8$ μ m), as seen in Figure 3c.

Similar behaviors were also found for toluene solutions of the two PS-PEO copolymers described in Table 1. As-received PS_{9.5k}-PEO_{9.5k} showed spontaneous formation of secondary w/o droplets, while the purified polymer did not

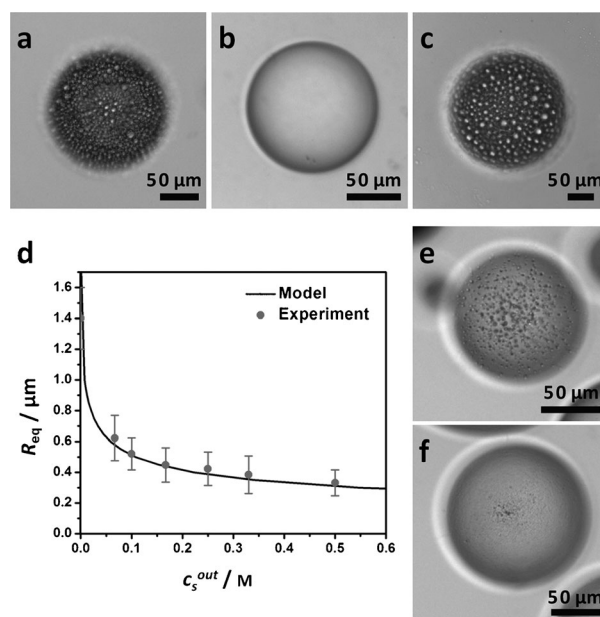


Figure 3. a)–c) Optical micrographs of primary o/w emulsion droplets, where the continuous phase is 5 mg mL⁻¹ PVOH in deionized water and the droplet phase is chloroform containing: a) 10 mg mL⁻¹ of as-received PS-PNIPAM, b) 10 mg mL⁻¹ of purified PS-PNIPAM, and c) 10 mg mL⁻¹ of purified PS-PNIPAM with 4.2 mg mL⁻¹ LiCl. d) Measured equilibrium radius (R_{eq}) of secondary w/o emulsions of chloroform containing 10 mg mL⁻¹ of as-received PS-PNIPAM with different salt concentration of the continuous phase (c_s^{out}) (●), and the calculated values (—). The data point at zero salt concentration ($R_{eq} \approx 1.4$) is partially obscured by the y axis. e), f) Optical micrographs of the deflation of w/o secondary emulsion droplets formed using chloroform containing 10 mg mL⁻¹ of as-received PS-PNIPAM as the oil phase and deionized water containing 5 mg mL⁻¹ PVOH with e) $c_s^{out} = 0.17$ M and f) 0.5 M LiCl.

(Supporting Information Figure S2a,b). Again, the behavior could be recovered by the addition of 7.5 μ g mL⁻¹ KCl to the block copolymer solution (Supporting Information, Figure S2c). In the case of as-received PS_{9.5k}-PEO_{18k}, no spontaneous formation of emulsions was observed, consistent with the much lower salt concentration in the sample. However, the addition of 7.5 μ g mL⁻¹ or 7.5 mg mL⁻¹ KCl to the solvent phase led to self-emulsification (Supporting Information, Figure S2d,f).

For osmotically driven transport of water from the bulk aqueous phase into droplets, the salt concentration of the continuous phase c_s^{out} should provide a means to modulate the formation of spontaneously formed droplets. Treating the external phase as a dilute ideal solution, the pressure balance is modified as $\Delta P = 2\gamma/R_{eq} - [2n_s k_B T / (4\pi R_{eq}^3 / 3)] + 2c_s^{out} k_B T \approx 0$. To test this simple model, as-received PS-PNIPAM in chloroform was first emulsified in a salt-free aqueous phase, then LiCl was added to the outer phase to osmotically “deflate” the spontaneously formed droplets (Supporting Information, Movie S2). As shown in Figure 3c–f, a progressive decrease in final droplet size with c_s^{out} was found, with the measured dependence of R_{eq} matching very closely the prediction of the model (Figure 3d).

We next demonstrate how osmotically driven emulsification can be used to tailor the characteristics of internal compartments within w/o/w double emulsions and polymer capsules. When increasing amounts of LiCl were added to a chloroform solution containing PS-PNIPAM, the resulting secondary water droplets were found to have a larger size. For example, the addition of $4.2 \mu\text{g mL}^{-1}$ of LiCl to purified PS-PNIPAM induced formation of secondary water droplets with $R_{\text{eq}} = 0.8 \pm 0.4 \mu\text{m}$ (Figure 4a), while the addition of

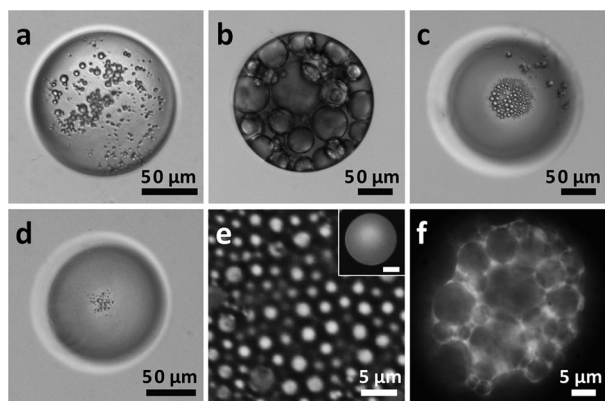


Figure 4. a), b) Optical micrographs of primary o/w emulsion droplets: chloroform containing a) 10 mg mL^{-1} of purified PS-PNIPAM with $4.2 \mu\text{g mL}^{-1}$ LiCl, and b) 10 mg mL^{-1} of as-received PS-PNIPAM with 42 mg mL^{-1} LiCl as the oil phase, and deionized water containing 5 mg mL^{-1} PVOH as the aqueous phase. c), d) Optical micrographs of w/o secondary emulsion droplets formed using chloroform with 10 mg mL^{-1} of as-received PS-PNIPAM and 42 mg mL^{-1} LiCl as the oil phase and water containing 5 mg mL^{-1} PVOH and c) $c_s^{\text{out}} = 1 \text{ M}$ and d) 7.5 M LiCl. e) High-magnification and (inset; scale bar: $50 \mu\text{m}$) low-magnification fluorescence micrographs showing that FITC-dextran (added at 0.1 mg mL^{-1} to a 10 mg mL^{-1} solution of as-received PS-PNIPAM in chloroform) is successfully encapsulated within internal water droplets. f) Fluorescence micrograph of a multi-compartment polymer capsule formed by evaporation of organic solvent from w/o/w double emulsions prepared using 10 mg mL^{-1} of as-received PS-PNIPAM and 0.1 mg mL^{-1} of the hydrophobic fluorophore Nile Red in chloroform as the oil phase.

42 mg mL^{-1} LiCl to as-received PS-PNIPAM yielded $R_{\text{eq}} = 19.6 \pm 7.6 \mu\text{m}$ (Figure 4b). This indicates that higher salt concentrations in the organic phase lead to the formation of larger salt aggregates (that is, with greater values of n_s). However, variations in c_s^{out} provide a further means to control the size of inner water droplets, at essentially constant number density. For the case of 42 mg mL^{-1} LiCl added to as-received PS-PNIPAM, increasing c_s^{out} to 1 and 7.5 M LiCl led to respective reductions in R_{eq} to 1.5 and $0.8 \mu\text{m}$ (Figure 4c,d; Supporting Information, Figure S3 and Movie S3). Together, variations in the amount of salt included in the organic and aqueous phases therefore provide a means to fine-tune the average size of the resulting secondary water droplets. Better control over the size, and size distribution, of the salt aggregates present in the organic phase would allow for even more precise control over double emulsion characteristics.

Notably, this self-emulsification approach allows for the encapsulation of water-soluble ingredients within the inner

aqueous phases of w/o/w double emulsions. To demonstrate this capability, we added 0.1 mg mL^{-1} of dextran labeled with fluorescein isothiocyanate (FITC-dextran) to chloroform solutions of as-received PS-PNIPAM. The resulting double emulsions showed bright fluorescence within the internal water droplets (Figure 4e), and negligible fluorescence of the external aqueous phase (Figure 4e, inset), confirming the highly selective encapsulation of FITC-dextran within the inner emulsion droplets. Furthermore, the excellent stability of the double emulsions formed in this manner against both coalescence and Ostwald ripening allows them to be easily converted into amphiphilic block copolymer capsules by evaporation of the organic solvent, for example the multi-compartment structures shown in Figure 4f (see also the Supporting Information, Figure S4). These findings suggest a straightforward means to prepare polymeric capsules containing hydrophilic and lipophilic species with control over the size and number of internal compartments by osmotically tuning the value of R_{eq} of the secondary w/o emulsions, and controlling the size of the primary o/w emulsions, respectively.

Along with the formation of controlled double emulsions and capsules, osmotically driven uptake of water by block copolymer solutions offers opportunities for fabrication of hierarchically porous polymer films. Specifically, we consider the “breath figure” method, which has been widely used to make porous films of interest for applications in electronics, photonics, biotechnology, catalysis, and separations.^[43–46] We find that chloroform solutions of purified PS-PNIPAM copolymers yield conventional breath figure structures, with a single and fairly uniform pore size ($1.1 \pm 0.1 \mu\text{m}$), as shown in Figure 5a,b. In contrast, solutions of as-received PS-

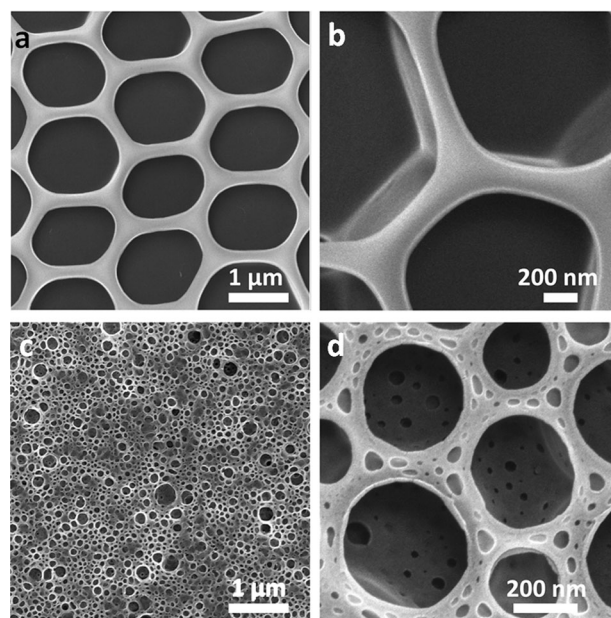


Figure 5. SEM images of a), b) a 2D porous film formed by casting a chloroform solution containing 10 mg mL^{-1} of purified PS-PNIPAM by the breath figure method, and c), d) a hierarchically porous film formed by the combination of breath figures and osmotic emulsification during casting from a chloroform solution containing 10 mg mL^{-1} of as-received PS-PNIPAM.

PNIPAM containing salt yield a hierarchical pore structure with sizes ranging from about 10–400 nm (Figure 5c,d). Presumably, this structure occurs from the combined action of water condensation at the solvent/air interface owing to cooling by solvent evaporation, as is well-known for formation of breath figures, and subsequently osmotically driven emulsification at the solvent/condensed water interface owing to the presence of salt aggregates, as investigated here. This method provides a simple means to greatly increase the surface area of porous block copolymer polymer films.

In conclusion, we have described a simple one-step method for the formation of tailored w/o/w double emulsions with highly stable inner water droplets. The inner water droplets with μm -scale sizes are spontaneously formed the interface of primary o/w droplets owing to an osmotic pressure difference relative to the continuous water phase provided by salt species dispersed in the oil phase. This osmotic driving force, and thus the characteristics of the resulting emulsions, can be easily tuned by varying the amount of salt dispersed in the oil phase, as well as the concentration of salt dissolved in the continuous water phase. These highly stable double emulsions can be converted to multi-compartment polymer capsules with encapsulated species in their cores and shells, and similar effects can also be used to obtain hierarchically structured porous polymer films. We anticipate that the simplicity, versatility, and potential scalability of this route will make it a valuable method in the formulation of multiple emulsions and block copolymer assemblies.

Experimental Section

Large-scale solvent/water interfaces were formed by adding 200 μL of chloroform containing 10 mg mL^{-1} of PS-PNIPAM into 10 mL of deionized water in a 20 mL vial. Formation of primary solvent-in-water emulsions with circa 10–100 μm scale droplets was accomplished by adding the solvent phase (chloroform containing 10 mg mL^{-1} PS-PNIPAM, or toluene containing 10 mg mL^{-1} PS-PEO; with different salt concentrations) to the aqueous phase (deionized water containing 5 mg mL^{-1} poly(vinyl alcohol); $M_w = 13\text{--}23\text{ kg mol}^{-1}$, 87–89% hydrolyzed) in a 1:5 volumetric ratio and gently shaking by hand. After emulsification, a 5 to 10 fold excess of deionized water was added. In the case of adding salts to chloroform solution containing PS-PNIPAM, the solution was stirred continuously for 1–2 d. Experiments were conducted with PS-PNIPAM diblock copolymer ($M_n = 16\text{ kg mol}^{-1}$ –5.2 kg mol^{-1}) and two PS-PEO diblock copolymers ($M_n = 9.5\text{ kg mol}^{-1}$ –9.5 kg mol^{-1} and 9.5 kg mol^{-1} –18 kg mol^{-1}) purchased from Polymer Source Inc. For fluorescent labeling, 0.1 mg mL^{-1} of Nile red or FITC-Dextran ($M_w = 10\text{ kg mol}^{-1}$) were included in the block copolymer solution. All chemicals were obtained from Aldrich and used without purification, except where noted.

Purification of PS_{16k}-PNIPAM_{5.2k} was conducted by dissolving the as-received sample in dichloromethane (DCM) at 100 mg mL^{-1} , and adding the solution (total volume: 2 mL) dropwise over 30 min into 250 mL of methanol with stirring. The re-precipitated polymer was filtered and dried in a vacuum oven. Purification of PS_{9.5k}-PEO_{9.5k} was carried out by forming micelles in aqueous solution using the interfacial instability route described previously.^[47] Micelles were separated by centrifugation at 14 krpm for 15 min, after which the upper circa 80% of solution was discarded and the same volume of deionized water added. This process was repeated 5 times, and the sample subsequently lyophilized to recover dry polymer.

For digestion of polymer samples for ICP-MS analysis, 0.5 mL of nitric acid (70% HNO₃, for trace metal analysis; BDH Chemicals) was added to polymer samples (25–100 mg) in a Teflon tube, which was placed in an oil bath at 50 °C with continuous stirring (250 rpm) for 1–2 days in an acid fume hood. (Caution: Do not leave digestion unattended for the first 20 min. If the sample is overflowing, the digestion temperature may need to be decreased.) Following complete digestion of the polymer, the solution was cooled to room temperature, followed by careful addition of hydrogen peroxide solution (30% H₂O₂, for trace analysis; Fluka Analytical) in about 0.5 mL increments followed by stirring for 3–12 h until no further CO₂ gas bubble formation was observed. This digested solution was next centrifuged at 3800 rpm for 30 min, and the supernatant was collected in a Teflon tube. The absence of carbon in this clean supernatant was confirmed by adding 2 mL of 30% H₂O₂. Next, the solution was filtered using a 0.2 μm pore size Teflon filter and diluted by adding 18 M Ω water to reach an HNO₃ concentration of 2%. Multi-element calibration standard 3 (PerkinElmer, Inc.) containing known concentrations of lithium (Li) and potassium (K) was used for calibration.

Porous PS-PNIPAM films prepared by drop casting of chloroform solution containing 10 mg mL^{-1} of as received and purified PS-PNIPAM, respectively, on pre-cleaned Si substrates under ambient conditions (temperature ca. 20 °C, relative humidity ca. 35%) for 1 day.

Micrographs and movies of osmotically-driven emulsification were taken using a digital camera (PowerShot A640, Canon) on the macro-scale and a Zeiss Axiovert 200 inverted optical microscope with 10 $\times$ and 20 $\times$ objectives and QImaging camera (Retiga-2000R Fast 1394 Mono Cooled) on the microscale. Fluorescence images were obtained using a 100 $\times$ oil-immersion objective. An FEI Magellan 400 FESEM was used at 5 kV accelerating voltage and 30 pA beam current to image porous PS-PNIPAM films which were coated by a thin layer of carbon. Inductively coupled plasma mass spectrometry (ICP-MS) (ELAN-DRC-e, PerkinElmer SCIEX) was used to analyze the concentrations of lithium and potassium elements in diblock copolymer samples. The presence of salt aggregates in chloroform containing 10 mg mL^{-1} of as received and purified PS-PNIPAM, respectively, was observed by drop-casting solutions on TEM grids coated with a carbon film, and performing bright field TEM on unstained samples using a JEOL 2000FX electron microscope operated at an accelerating voltage of 200 kV. The size distribution of salt aggregates were analyzed by DLS (Malvern Zetasizer Zen 3600, Malvern Instruments) using chloroform containing 1 mg mL^{-1} of as received PS-PNIPAM with a 90° scattering angle at 25 °C.

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