Letters

Dewetting Instability during the Formation of Polymersomes from Block-Copolymer-Stabilized Double Emulsions

Ryan C. Hayward,[†] Andrew S. Utada,[†] Nily Dan,[§] and David A. Weitz*,[†,‡]

Division of Engineering and Applied Sciences and Department of Physics, Harvard University, Cambridge, Massachusetts, and Department of Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania

Received January 10, 2006. In Final Form: March 17, 2006

We investigate the formation of polymer vesicles, or polymersomes, of polystyrene-*block*-poly(ethylene oxide) diblock copolymers using double emulsion droplets of controlled architecture as templates. To engineer the structure of the polymersomes, it is important to consider the concentration of diblock copolymer in the middle phase of the double emulsion. We describe how the presence of excess polymer can induce a transition from complete wetting to partial wetting of the middle phase, resulting in polymer shells with inhomogeneous thicknesses.

Introduction

Polymeric vesicles, or polymersomes, are of interest for the encapsulation and delivery of active ingredients. They offer enhanced stability and lower permeability compared to lipid vesicles, and the versatility of synthetic polymer chemistry provides the ability to tune properties such as membrane thickness, surface functionality, and degradation kinetics.[1,2] One approach to form large polymersomes with diameters of $10-100$ μm is to use water-in-oil-in-water double emulsion drops of controlled architecture as templates.[3,4] A volatile organic solvent containing an amphiphilic diblock copolymer is used as the middle phase; evaporation of the solvent leads to polymersome formation, as shown schematically in Figure 1. This technique offers the advantages of high encapsulation efficiencies and controllable vesicle sizes and architectures.
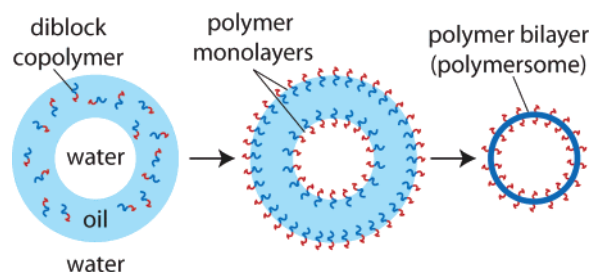

Figure 1. Schematic for the formation of polymersomes from water-in-oil-in-water drops. Initially, a double emulsion consisting of single aqueous drops within drops of a volatile organic solvent ("oil") is prepared using a microcapillary device. Amphiphilic diblock copolymers dissolved in the middle phase assemble into monolayers at the oil−water interfaces. Evaporation of the solvent then leads to the formation of polymer bilayers (polymersomes).

In this approach, the concentration of polymer in the organic phase is a key variable: if it is lower than the amount required to fully coat the oil−water interfaces, then the polymersomes will not be stable. In practice, it is convenient to work with an excess concentration; indeed, this excess may be used to tune the thickness and structure of the polymersome walls through the formation of multilayered copolymer interfaces. Surprisingly, polymersomes formed from double emulsions with poly(butyl acrylate-*block*-acrylic acid) (PBA−PAA) with thick walls (∼1.5

* Corresponding author. E-mail address: weitz@deas.harvard.edu.
† Division of Engineering and Applied Sciences, Harvard University.
‡ Department of Physics, Harvard University.
§ Drexel University.

(1) Discher, D. E.; Eisenberg, A. *Science* **2002**, *297*, 967−973.
(2) Discher, B. M.; Won, Y. Y.; Ege, D. S.; Lee, J. C. M.; Bates, F. S.; Discher, D. E.; Hammer, D. A. *Science* **1999**, *284*, 1143−1146.
(3) Utada, A. S.; Lorenceau, E.; Link, D. R.; Kaplan, P. D.; Stone, H. A.; Weitz, D. A. *Science* **2005**, *308*, 537−541.
(4) Lorenceau, E.; Utada, A. S.; Link, D. R.; Cristobal, G.; Joanicot, M.; Weitz, D. A. *Langmuir* **2005**, *21*, 9183−9186.

μm)[4] still had permeabilities comparable to those of unilamellar polymersomes ($\sim$10−20 nm thick).[2,5] This suggests the presence of "defects" in the copolymer layer, most likely in the form of inhomogeneous thickness.[4] To prepare uniform polymersomes with well-controlled structures, it is important to understand how these thickness inhomogeneities may develop, and how their formation depends on polymer concentration.

In this paper, we investigate the structural evolution during solvent evaporation from double emulsion drops stabilized by a polystyrene-*block*-poly(ethylene oxide) (PS−PEO) diblock copolymer. We find that, during evaporation, the initially homogeneous organic phase undergoes a wetting transition; the result is a state of partial wetting, wherein a lens of the organic phase makes a nonzero contact angle with a thin organic film separating the inner and outer aqueous phases. Ultimately, this leads to a polymersome that is very thin over most of its surface. We refer to the wetting transition simply as "dewetting", due to its similarity to the transition from complete to partial wetting of liquid films at solid−vapor interfaces. The observation of partial wetting implies the existence of an adhesive interaction between the aqueous phases that is comparable to the interfacial tension, as previously observed in both oil-in-water,[6−8] and water-in-oil[9] single emulsion systems. We propose that this arises from a depletion effect due to excess diblock copolymer in the organic phase, and therefore that its strength increases with polymer concentration. Thus, our results suggest that obtaining uniform polymersomes using emulsion techniques requires careful control of the polymer concentration.

Experimental Section

Water-in-oil-in-water double emulsion droplets of controlled architecture (shown schematically in Figure 1) were produced using glass microcapillary devices.[3,4] The inner phase was 5 vol % glycerol in water, and the middle hydrophobic phase consisted of 0.01−1.5 wt % polymer in toluene, chloroform, or a mixture thereof.[10,11] Unless otherwise noted, experiments were conducted with an asymmetric PS−PEO diblock copolymer (M_n = 19/6.4 kg/mol). A symmetric PS−PEO block copolymer (9.5K/9.5K) and a polybutadiene-*block*-PEO polymer (5.5K/5.0K) were also used to test the generality of the observed behavior. The outer phase consisted of 50 vol % glycerol, 50 vol % water, and 5 mg/mL poly(vinyl alcohol) (PVA; M_r $\sim$ 13−23K, 87−89% hydrolyzed). The diblock copolymers stabilized the inner droplets against coalescence with the exterior aqueous phase, while PVA prevented coalescence of the oil droplets. The diblock copolymers were obtained from Polymer Source, while all other chemicals were obtained from Aldrich.

After formation, double emulsion drops were collected into deionized water to yield an exterior phase that was $\sim$5% glycerol. The outer radii, R_o, of the double emulsions varied from 25 to 100 μm, while the internal droplet radii, R_i, varied from 15 to 50 μm. These values could be tuned by the size of the capillaries used. Typically, the volume of the middle phase in each drop was 1 to 2 times the volume of the inner phase. The formation of polymersomes by evaporation of the solvent from double emulsions was observed via optical microscopy for samples placed onto a glass slide. Characteristic oil−water interfacial tensions were measured by forming a pendant drop of water at the tip of a blunt stainless steel needle immersed in a polymer solution and fitting the Laplace equation to the measured drop shape.[12]

Results and Discussion

When the concentration of diblock copolymer in the middle phase of the emulsion is too low ($\sim$0.01 wt %), stable polymersomes cannot be formed; instead, solvent evaporation leads to rupture of the organic layer and coalescence of the inner aqueous phase with the outer. For typical drop sizes (R_i = 50 μm, R_o = 70 μm), at 0.01 wt % polymer, complete adsorption of PS−PEO at the oil−water interfaces would correspond to an area of $\sim$30 nm^2 per polymer chain. While this surface density is sufficient to stabilize the double emulsion initially, we find that it is too sparse to form stable polymersomes.

For the same drop sizes, a polymer concentration of 0.1 wt % corresponds to an area per chain of $\sim$3 nm^2, which is roughly the expected surface density in a bilayer of diblock copolymers of this molecular weight.[13,14] Indeed, we observe that, under these conditions, stable polymersomes are formed. However, a clear nonuniformity in shape is observed during solvent evaporation. The oil shell separates into two regions: one very thin and uniform, the other much thicker, as seen in Figure 2a. We interpret this as a dewetting of the middle organic phase, resulting in a lens of the organic phase that forms a nonzero contact angle with a thin organic film separating the inner and outer aqueous phases. Although the contact angle is low, there is a distinct contact line between the organic droplet and the thin organic film, as demarcated by arrows in Figure 2a. When one of the thin organic films ruptures, it retracts into the organic droplet as a liquid, implying that it remains solvated. After full solvent evaporation, a polymersome with nearly uniform thickness and a small thicker patch of excess polymer is generated, as shown in Figure 2b. Breakage of the polymersome now occurs by fracture, due to the glassy nature of the unsolvated PS block.

For larger polymer concentrations of 1.0−1.5 wt %, corresponding to a large excess of diblock copolymer in the organic phase, solvent evaporation leads to dewetting with larger contact angles (Figure 2c). Ultimately, polymersomes with thicker patches of excess polymer are formed (Figure 2d). The dewetting phenomenon is apparently quite general, as a symmetric PS−PEO polymer (9.5K/9.5K) and a polybutadiene−PEO diblock copolymer (5.5K/5.0K) show nearly identical behavior;[15,16] the same mechanism is also likely responsible for the inhomogeneous thicknesses in the PBA−PAA polymersomes.[4]

Our results clearly show that the oil phase undergoes a wetting transition during solvent evaporation. This gives rise to a coexistence between a thin organic layer, presumably an oil-solvated bilayer of the diblock copolymer that is similar to the "Newton black" film encountered in soap bubbles,[7,17] and a droplet of the organic phase, as shown in Figure 2e. This partial wetting scenario implies an energy of adhesion, W_{adh}, between the inner and outer aqueous phases, or associated polymer layers, such that

$$\gamma_b = \gamma_m^i + \gamma_m^o - W_{adh} \qquad (1)$$

(5) Discher, B. M.; Hammer, D. A.; Bates, F. S.; Discher, D. E. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 125−131.

(6) Aronson, M. P.; Princen, H. M. *Nature* **1980**, *286*, 370−372.

(7) Poulin, P.; Nallet, F.; Cabane, B.; Bibette, J. *Phys. Rev. Lett.* **1996**, *77*, 3248−3251.

(8) Poulin, P.; Bibette, J. *Phys. Rev. Lett.* **1997**, *79*, 3290−3293.

(9) Poulin, P.; Bibette, J. *Langmuir* **1998**, *14*, 6341−6343.

(10) PEO is known to form aggregates in toluene (see ref 11), so solutions were warmed to $\sim$35 °C before using. This was found by dynamic light scattering to break up any aggregates in solution.

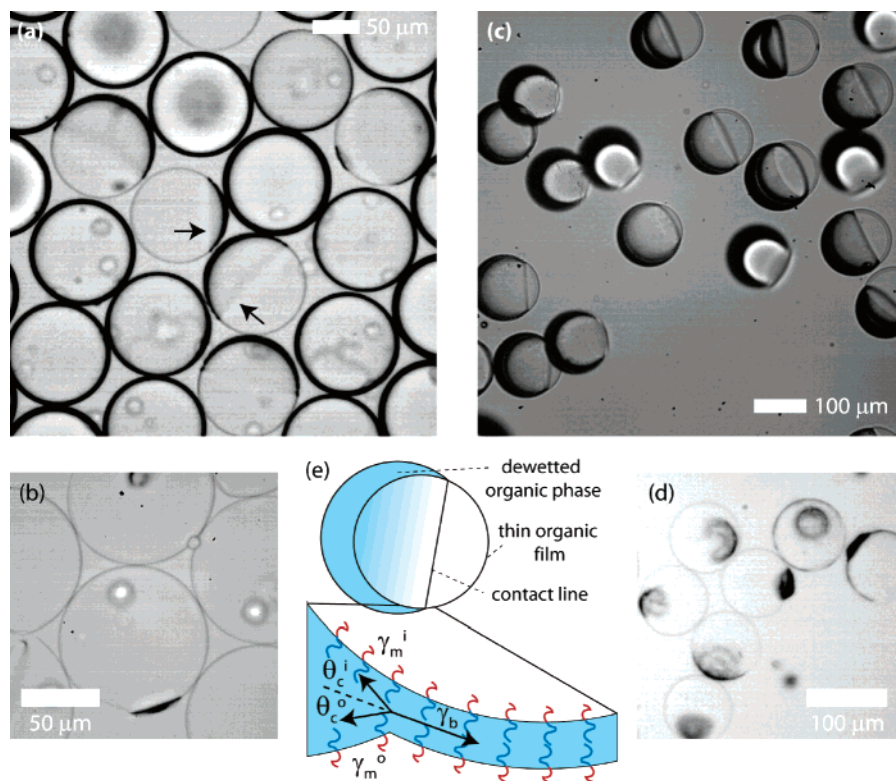(11) Boils, D.; Hair, M. L. *J. Colloid Interface Sci.* **1993**, *157*, 19−23.

(12) del Río, O. I.; Neumann, A. W. *J. Colloid Interface Sci.* **1997**, *196*, 136−147.

(13) Bermudez, H.; Brannan, A. K.; Hammer, D. A.; Bates, F. S.; Discher, D. E. *Macromolecules* **2002**, *35*, 8203−8208.

(14) Battaglia, G.; Ryan, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 8757−8764.

(15) The organic solvent used as the middle phase is also important: dewetting takes place when the organic solvent is purely toluene, whereas, with pure chloroform, rupture and coalescence of the inner and outer aqueous phases is always seen. The PS−PEO diblock copolymer is not as effective as a surfactant at the water−chloroform interface as it is at the water−toluene interface, presumably because of the high solubility of PEO in chloroform (ref 16).

(16) Spitzer, M.; Sabadini, E.; Loh, W. *J. Phys. Chem. B* **2002**, *106*, 12448−12452.

(17) Bergeron, V. *J. Phys.: Condens. Matter* **1999**, *11*, R215−R238.

Figure 2. (a) Optical micrograph revealing dewetting during solvent evaporation from a double emulsion droplet that initially consisted of an aqueous droplet surrounded by a shell of 0.1 wt % PS−PEO diblock copolymer dissolved in a toluene/chloroform mixture (2:1 by volume). Arrows indicate drops in which drainage of the organic phase to the side reveals a clear wetting line. (b) Following complete solvent evaporation, the result is a thin polymersome with a patch of excess polymer. (c) At higher initial polymer concentrations (1.5 wt %), larger contact angles are evident during solvent evaporation. (d) Inhomogeneous polymersome structures formed with 1.0 wt % initial polymer content. (e) Schematic of the proposed structure of a double emulsion droplet with partial wetting of the organic phase on a thin layer of solvated block copolymer brushes.

where γ_b is the interfacial energy of the solvated bilayer film, and γ_m^i and γ_m^o are the interfacial energies of the inner and outer oil−water interfaces with adsorbed polymer monolayers, respectively. Assuming that $\gamma_m^i = \gamma_m^o$,[18] the Young−Dupré equation determining the contact angle, θ_c^o, becomes

$$W_{adh} = 2\gamma_m^o(1 - \cos\theta_c^o) \qquad (2)$$

In Figure 2c, values of θ_c^o are as large as 35°, corresponding to $W_{adh} = 0.36\gamma_m^o$. Thus, the adhesive interaction must be of the same order of magnitude as γ_m^o.

We propose that the driving force for dewetting is a depletion interaction between the inner and outer oil−water interfaces due to the presence of excess block copolymer in the organic phase. The magnitude of the depletion effect increases with the concentration of dissolved polymer; thus it should become more important as solvent evaporation proceeds, and should be more apparent for higher initial polymer concentrations, as we observe. For planar hard walls, the adhesion due to depletion of a polymer solution is

$$W_{adh} = a\xi\pi_{osm} \qquad (3)$$

where π_{osm} is the osmotic pressure, ξ is the size scale of the polymer, and a is a numerical coefficient that depends on the concentration regime. In dilute polymer solutions, ξ is the chain radius of gyration, R_g, $a = 4/\sqrt{\pi}$,[19] and

$$\pi_{osm} = ck_bT \qquad (4)$$

where c is the number density of polymer chains. In the semidilute regime, $a \approx 5$,[20,21] and ξ corresponds to the mesh size, which scales as $c^{-3/4}$, while π_{osm} scales as $c^{9/4}$ in a good solvent.[22] As a result, in the dilute regime, $W_{adh} \sim c$, while, in the semidilute regime, $W_{adh} \sim c^{3/2}$.

To estimate the magnitude of depletion interactions, we treat the excess PS−PEO diblock copolymer as a PS homopolymer of the same molecular weight.[23] At an excess concentration of 1.0 wt %, eq 4 gives $\pi_{osm} = 850$ Pa. Using $R_g \approx 4.9$ nm,[24] $W_{adh} = 0.0094$ mN/m. This is a small interaction energy; however, as solvent evaporates from the double emulsion drops, the concentration of free PS−PEO increases, and the depletion effect becomes stronger. For example, at a concentration of 17 wt % (in the semidilute regime), values of $\xi = 3.2$ nm, and $\pi_{osm} = 65$ kPa can be calculated from the data for PS in toluene,[25,26] yielding $W_{adh} = 1.0$ mN/m.

(19) Tuinier, R.; Vliegenthart, G. A.; Lekkerkerker, H. N. W. *J. Chem. Phys.* **2000**, *113*, 10768−10775.

(20) Evans, E. A. *Macromolecules* **1989**, *22*, 2277−2286.

(21) Evans, E.; Klingenberg, D. J.; Rawicz, W.; Szoka, F. *Langmuir* **1996**, *12*, 3031−3037.

(22) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(23) Toluene and chloroform are good solvents for both the PS and PEO blocks; therefore, we do not expect the PEO block to be collapsed in solution.

(24) Abe, F.; Einaga, Y.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1993**, *26*, 1884−1890.

(25) Noda, I.; Higo, Y.; Ueno, N.; Fujimoto, T. *Macromolecules* **1984**, *17*, 1055−1059.

(26) Watanabe, H.; Tirrell, M. *Macromolecules* **1993**, *26*, 6455−6466.

(18) In reality, the value of γ_m^o is expected to be somewhat lower than that of γ_m^i due to the presence of PVA at the external interface and the compression of the outer interface during solvent evaporation. As a result, the numerical factor in eq 2 should be somewhere between 1 and 2.

This discussion of depletion interactions applies to hard substrates and individually solvated polymer chains. In our system, there are two important differences: (a) the surfaces are not hard, but are covered by an adsorbed "brush"-like polymer layer, and (b) the copolymer chains may aggregate, thereby increasing ξ, but decreasing the number density of aggregates more rapidly, leading to a decrease in W_{adh}.

Polymer solutions spreading on an end-grafted brush of the same polymer may exhibit partial wetting (finite contact angle) or complete wetting, depending on the polymer concentration and brush grafting density.[27-30] The driving force for dewetting in these systems is depletion effects,[31,32] similar to those considered here. Moreover, the depletion interaction may actually be *enhanced* on brushlike polymeric substrates, since the thickness of the exclusion zone is larger, being the sum of the free chain dimension *and* the brush layer.

In contrast, any aggregation of the PS−PEO diblock copolymer would reduce W_{adh}. To check for aggregates, we use dynamic light scattering. We find that a dilute solution of 5 mg/mL of PS−PEO in toluene consists of unimers with hydrodynamic radii $R_h \sim 4$ nm.[33] However, after coming into contact with water, a population of aggregates centered around $R_h \sim 35$ nm (presumably microemulsion droplets) appears, as well as a distribution of larger aggregates with $R_h > 100$ nm. In addition, optical microscopy reveals large aggregates of about $1-5$ μm in the oil phase: these are apparently spontaneously formed water-in-oil emulsion drops.[34-37] This aggregation will lessen the strength of the depletion interaction, although, given the wide distribution of aggregate sizes, it is not clear to what extent.

An essential feature of this behavior is that the adhesive interaction must be comparable to the interfacial tension of the block-copolymer-covered oil−water interface. Therefore, we compare our estimates of the depletion interaction to independent measurements of the interfacial tension, γ, between water and solutions of PS−PEO in toluene. At 0.1 and 1 wt % polymer, the value of γ levels off to $1-2$ mN/m within 30 min. At 0.01 wt %, a similar value is attained within 4 h.[38] Thus, the value of the measured surface tension is indeed of the same magnitude as our estimates of the depletion interaction in the semidilute regime, provided that the excess diblock copolymer chains do not all form large aggregates.

During solvent evaporation from the double emulsion droplets, the shrinking area of the external oil−water interface may lead to nonequilibrium effects that further lower the interfacial tension. To understand how the block copolymer responds as the interfacial area shrinks, polymer was allowed to adsorb to a pendant water drop for 5 min, followed by removal of water at a constant
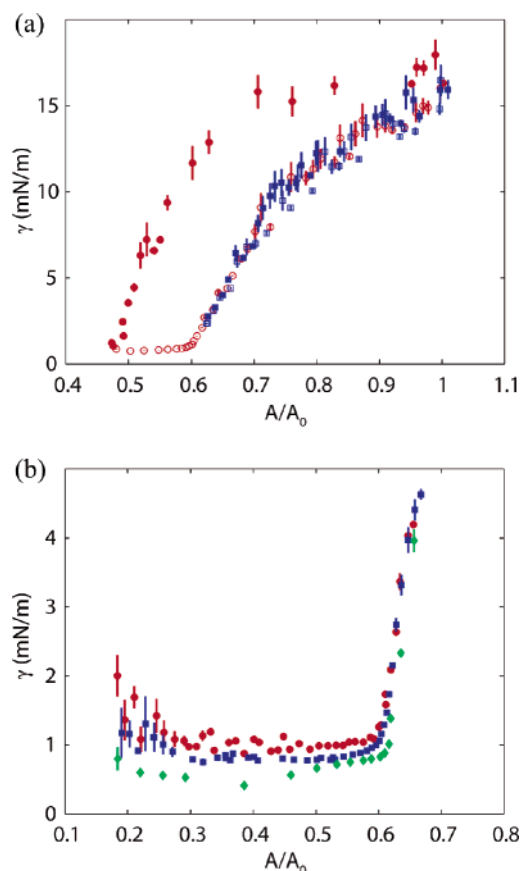

Figure 3. (a) Interfacial tension (γ) between water and toluene containing 0.1 wt % PS−PEO as a function of normalized drop surface area (A/A_0) for two different compression−expansion isotherms. Open symbols correspond to compression, closed symbols to expansion. For the blue squares, compression was stopped prior to reaching the plateau in surface tension, while, for the red circles, compression was continued past the onset of the plateau. (b) Compression isotherms at different rates of water withdrawal from a 5 μL drop: 0.1 μL/min (red circles), 1 μL/min (blue squares), and 10 μL/min (green diamonds). The surface deformation rates, $1/A(dA/dt)$, are roughly 0.002, 0.02, and 0.2 Hz, respectively. Error bars represent the 95% confidence intervals of the values of surface tension fitted by nonlinear least-squares analysis.

volumetric rate. As the surface area of the drop decreases, the interfacial tension decreases as well. If the compression is stopped with γ above 1 mN/m, expansion retraces the path of compression with little hysteresis. However, when the drop surface is compressed further, a plateau in γ is reached at $\sim$1 mN/m, as seen in Figure 3a. The plateau presumably reflects desorption of polymer from the interface when driven below the equilibrium area per chain. Indeed, compression into the plateau region gives rise to hysteresis, as seen in Figure 3a, indicating that polymer is removed from the interface during compression. As may be expected, the rate of compression (or evaporation) is important: faster compression leads to a lower plateau value, as shown in Figure 3b. Solvent evaporation from the double emulsion droplets typically corresponds to characteristic deformation rates of $10^{-4}-10^{-2}$ Hz. Thus, the interfacial tension of the shrinking oil−water interface in the case of our double emulsion system is likely driven somewhat below its equilibrium value, but it is expected to remain in the range of $0.5-1$ mN/m at low concentrations of PS−PEO.[39]

(27) Yerushalmi-Rozen, R.; Klein, J.; Fetters, L. J. *Science* **1994**, *263*, 793−795.

(28) Yerushalmi-Rozen, R.; Klein, J. *Phys. World* **1995**, *8*, 30−35.

(29) Yerushalmi-Rozen, R.; Klein, J. *Langmuir* **1995**, *11*, 2806−2814.

(30) Yerushalmi-Rozen, R.; Klein, J. *J. Phys.: Condens. Matter* **1997**, *9*, 7753−7765.

(31) Carignano, M.; Yerushalmi-Rozen, R.; Dan, N. *Macromolecules* **2000**, *33*, 3453−3460.

(32) Martin, J. I.; Wang, Z. G.; Schick, M. *Langmuir* **1996**, *12*, 4950−4959.

(33) This value compares favorably with the estimate of $R_g = 4.9$ nm used in calculating the magnitude of depletion effects.

(34) López-Montilla, J. C.; Herrera-Morales, P. E.; Pandey, S.; Shah, D. O. *J. Dispersion Sci. Technol.* **2002**, *23*, 219−268.

(35) While the driving force for spontaneous emulsification in this system is not well understood, the phenomenon is observed for all polymers considered here, and other groups have reported the same behavior in similar systems (see refs 36 and 37).

(36) Rother, G.; Findenegg, G. H. *Colloid Polym. Sci.* **1998**, *276*, 496−502.

(37) Wen, L. X.; Cheng, J.; Zou, H. K.; Zhang, L.; Chen, J. F.; Papadopoulos, K. D. *Langmuir* **2004**, *20*, 8391−8397.

(38) The limiting value of γ varies somewhat between measurements ($\pm$ 0.5 mN/m) but does not depend strongly on block copolymer concentration in the range of 0.01−1 wt %.

(39) The presence of PVA at the outer oil−water interface may also be important during solvent evaporation from double emulsion drops. However, compression isotherms with both PVA and PS−PEO present indicate that PS−PEO dominates the surface behavior.
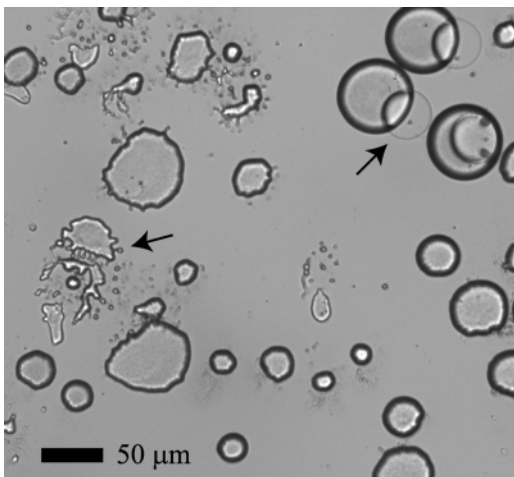
Figure 4. Under some conditions, solvent evaporation leads to dewetting of the organic phase with contact angles approaching 180° (upper right). Further solvent evaporation from organic droplets that have completely detached from the inner aqueous drops leads to an interfacial instability causing breakup into smaller droplets (left side).

Interestingly, we find that, in some cases, the organic phase completely dewets the inner water droplet during solvent evaporation. Continued solvent evaporation from the organic droplets leads to an interfacial instability, as shown in Figure 4, wherein the large droplet spontaneously breaks up into many smaller droplets. This spontaneous increase in the surface area of the system implies that, at sufficiently high polymer concentrations and rates of solvent evaporation, the value of γ can go to zero or even become transiently negative,[40] as has been seen previously for diblock copolymers at interfaces in polymer blends.[41–46] In such cases of vanishing interfacial tension, the presence of even a very small adhesive interaction would be sufficient to drive dewetting.[47,48]

In conclusion, when forming polymersomes from double emulsion templates, it is important to consider wetting of the organic phase on the polymer brushes at the oil−water interfaces. To avoid a dewetting instability in the presence of excess polymer, it will likely be necessary to carefully control the interfacial tension by adjusting the strength of adsorption of the polymer at the oil−water interfaces and the rate of solvent evaporation. In addition, it will be important to independently control the osmotic pressure of the organic phase as solvent evaporation increases the concentration of nonvolatile components, for example, through their size or state of aggregation.

(40) Granek, R.; Ball, R. C.; Cates, M. E. *J. Phys. II* **1993**, *3*, 829−849.

(41) Shull, K. R.; Kellock, A. J.; Deline, V. R.; Macdonald, S. A. *J. Chem. Phys.* **1992**, *97*, 2095−2104.
(42) Xu, Z.; Jandt, K. D.; Kramer, E. J.; Edgecombe, B. D.; Fréchet, J. M. J. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 2351−2357.
(43) Jiao, J. B.; Kramer, E. J.; de Vos, S.; Möller, M.; Koning, C. *Polymer* **1999**, *40*, 3585−3588.
(44) Jiao, J. B.; Kramer, E. J.; de Vos, S.; Möller, M.; Koning, C. *Macromolecules* **1999**, *32*, 6261−6269.
(45) Girard-Reydet, E.; Pascault, J. P.; Brown, H. R. *Macromolecules* **2001**, *34*, 5349−5353.
(46) Kim, B. J.; Kang, H.; Char, K.; Katsov, K.; Fredrickson, G. H.; Kramer, E. J. *Macromolecules* **2005**, *38*, 6106−6114.
(47) For example, van der Waals interactions give rise to an adhesion energy per unit area of $W_{adh} = A/(12\pi h^2)$, where A is the Hamaker constant, (about 10^{-20} J for water−hydrocarbon−water systems; ref 48), and h is the thickness of the oil film. Using 15 nm as a conservative estimate for h gives $W_{adh} = 0.001$ mN/m. This is much smaller than the characteristic values of γ on the order of 1 mN/m, as well as the estimated magnitude of the depletion interaction. However, the observation of vanishing interfacial tension means that even van der Waals forces may be large enough to drive dewetting under some conditions.
(48) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: San Diego, CA, 1991.