Programmed Wrapping and Assembly of Droplets with Mesoscale Polymers

Dylan M. Barber, Zhefei Yang, Lucas Prévost, Olivia du Roure, Anke Lindner, Todd Emrick,* and Alfred J. Crosby*

Nature is remarkably adept at using interfaces to build structures, encapsulate reagents, and regulate biological processes. Inspired by nature, flexible polymer-based ribbons, termed “mesoscale polymers” (MSPs), are described to modulate interfacial interactions with liquid droplets. This produces unprecedented hybrid assemblies in the forms of flagellum-like structures and MSP-wrapped droplets. Successful preparation of these hybrid structures hinges on interfacial interactions and tailored MSP compositions, such as MSPs with domains possessing distinctly different affinity for fluid-fluid interfaces as well as mechanical properties. In situ measurements of MSP–droplet interactions confirm that MSPs possess a negligible bending stiffness, allowing interfacial energy to drive mesoscale assembly. By exploiting these interfacial driving forces, mesoscale polymers are demonstrated as a powerful platform that underpins the preparation of sophisticated hybrid structures in fluids.

1. Introduction

Nature provides striking examples of mesoscale assemblies featuring properties and architectures that inspire synthetic replication. Some naturally occurring structures take the form of long, fibrous building blocks that act in concert with spheroids, such as droplets, colloidal particles, or live cells. For example, fiber-in-droplet packaging is exemplified by spooling observed in spider capture silk,[1–3] in which a fiber is periodically wetted with aqueous droplets and winds into an internally spooled configuration. The balance between interfacial energy and fiber bending energy drives such assembly, as well as the dissipative, damage-preventing mechanisms activated upon impact-driven disassembly and reassembly. Another example is the integration of flagella and fimbriae with the membrane of bacteria. These long, flexible mesostructures couple with the vesicle-like core to modulate interfacial interactions with their surroundings.[4–11] These examples illustrate how assemblies of fibers and spheroids with well-controlled interactions and length scales give rise to advantageous properties and performance. While some synthetic systems demonstrate isolated principles of such natural phenomena,[12,13] a robust platform with material-, interfacial-, and geometry-enabled tuning of fiber-spheroid assemblies has yet to be realized.

Figure 1a describes our use of polymer ribbons, termed mesoscale polymers (MSPs), at the interface of oil-in-water droplets, in which three modes of interaction were identified: nonadhesion, adhesion without wrapping, and spontaneous wrapping. These interactions are dictated by the critical strain energy release rate, $G_c = \gamma_{ow} + \gamma_{pw} - \gamma_p$ (comprising the oil–water, polymer–water, and oil–polymer interfacial tensions), and the critical elastoadhesive length, $R_c = \sqrt{E t/G_c}$, where $G_c$ is the Young’s modulus ($E$), interfacial strength ($G_c$), and geometry (thickness $t$), above which an adhesive MSP spontaneously wraps droplets.[12,13] A pH-responsive trigger embedded in the MSPs controls the observed assembly mode.

Figure 1b describes MSPs with segments of alternating compositions, termed mesoscale block copolymers (MSBCPs), such that $G_c$ and $R_c$ are partitioned along the ribbon length. When brought into contact with a droplet of radius $R$, selective wrapping is designed to afford droplets with one or many pendent arms. In this paper, we realize the vision in Figure 1, starting from monomer and copolymer synthesis, fabrication of MS(BC)Ps (thickness $t = 100–600$ nm, width $w = 10–35$ µm, and length $2–4$ mm), and MS(BC)P contact with emulsion droplets (radius $R = 6–350$ µm). Key structures were derived from different ribbon interactions with droplets, including weak adhesion (Figure 1c, far left), spontaneous wrapping (Figure 1c, center left), and selective wrapping by specific MSBCP segments to afford structures with one (Figure 1c center right) or many (Figure 1c far right) arms extending into the surrounding fluid, or a mesoscale micelle. By embedding responsive chemistry into MSPs, we modulate the resulting...
ribbon/droplet architecture and in turn produce a new materials toolbox of hybrid structures. Moreover, by providing access to a broad array of structures from mesoscale ribbons and droplets, we build a platform of increasingly sophisticated soft materials that begin to emulate the exquisite examples found in Nature.

2. Materials Preparation

The MSPs described in this work were prepared with reactive and functional polymers using flow-coating methods we described previously. The polymers were designed to exhibit pH response (polymer 1) and amenability to photopatterning (polymer 2), as shown in Figure 2a. Polymer 1 ($M_n = 38$ kDa, $\bar{D} = 2.7$) was prepared by free radical copolymerization of dimethylaminoethyl methacrylate (DMAEMA) with 5 mol% of benzophenone methacrylate (BPMA) and 1 mol% of fluorescein-$$\omega$$-methacrylate (FMA). The tertiary amines enable pH response by transitioning from charge neutral to cationic with increasing acidity, while BPMA imparts a crosslinking mechanism and FMA contributes fluorescence to aid visualization. Copolymer 2 ($M_n = 21$ kDa, $\bar{D} = 2.2$) was prepared by free radical polymerization of $t$-butyl methacrylate (TBMA) with 2 mol% of glycidyl methacrylate (GMA), 4 mol% of triphenylsulfonium 4-vinylbenzenesulfonate (TPS4VBS), and 0.2 mol% of rhodamine B methacrylate (RBMA). In polymer 2, the aromatic sulfonium sulfonate comonomer functions as a photoacid generator upon UV exposure to trigger acid-catalyzed deprotection of the $t$-butyl esters and crosslinking via the glycidyl ethers, affording MSPs with segments of alternating composition, termed MSBCPs.

To prepare the MSPs, a clean glass slide ($24 \times 40 \times 170 \mu m$) was coated with an ≈50 nm layer of poly(styrene sulfonate) (PSS, sodium salt) at 2 or 4 mm intervals to afford stripes of bare glass ≈100 µm wide, over which was flow-coated a toluene solution of polymer 1 or 2 (Figure 2b left). The substrate was translated in 1 mm intervals at 3 mm s$^{-1}$, with a 1.1–1.5 s delay between steps to deposit the MSPs. The ribbons were then irradiated i) at $\lambda = 365$ nm (3300 mJ cm$^{-2}$) (copolymer 1) to afford a crosslinked polyDMAEMA network (schematic Figure 2b, purple) or ii) at $\lambda = 254$ nm (200–695 mJ cm$^{-2}$) through a photomask, then heated to 150 °C for 60 s (copolymer 2), to afford MSBCPs with alternating segments of hydrophobic, glassy poly(t-butyl methacrylate) (PTBMA) and hydrophilic, crosslinked poly(methacrylic acid) (PMAA, Figure 2b, red and blue, Figure S1, Supporting Information). The ribbons were then cut into 2–4 mm long segments with a CO$_2$ laser engraver ($\lambda = 10.6$ µm) and subjected to reactive ion etching with O$_2$ plasma for 30 s to remove any residual polymer film between the MSPs. The MSPs were released from the substrate by submerging the sample in an aqueous solution to dissolve the underlying PSS layer, then brought into contact with oil-in-water droplets; the resulting assemblies were studied as a function of their interfacial activity ($G_c$) and critical elastoadhesive length ($R_c$).

Figure 1. System design. MS(BC)P–droplet interactions are dictated by controlling material properties ($G_c, E$) and geometry ($t, R$) via pH and spatial partitioning: a) MSPs adopt nonadhesive (left), adhesive (center), and wrapped (right) interaction modes, stemming from the pH-dependent work of adhesion ($G_a$) and the relative size of the droplet radius $R$ and critical elastoadhesive length $R_c$; b) MSBCPs, with segments of alternating composition, $G_c$, and $R_c$, enable selective wrapping for all droplet radii $R_{2a} < R < R_{2b}$, affording droplets with 1 (left) or many (right) arms; c) micrographs (left to right) of MSPs in adhesive ($R < R_{c1}$) and wrapped ($R > R_{c1}$) modes, and MSBCPs in selectively wrapped ($R_{2a} < R < R_{2b}$) modes with one or many arms.
3. Controlling Ribbon–Droplet Architectures with pH

Experiments with MSPs prepared from copolymer 1 were performed in pH 1–10 buffer solutions using individual perfluorodecalin (PFD) droplets ($R = 6–350 \mu m$) to avoid coalescence. Pendent drop tensiometry revealed the oil–water surface tension $\gamma_{ow}$ to be roughly constant ($\approx 50 \text{ mN m}^{-1}$) across this pH range. Droplet-to-MSP contact was achieved using a glass microcapillary fixed to a hand-controlled micromanipulator (Figure 3a,b). Droplets were introduced by inflation at the microcapillary tip or by emulsification and injection via pipette. The optical micrograph in Figure 3b features an MSP adhered end-on to the surface of a PFD droplet, alongside the microcapillary tip. The schematics in Figure 3c illustrate a typical experimental setup. The microcapillary tube and translating stage are used to probe MSP/droplet interactions by moving droplets through the fluid phase; pH-dependent assembly spans weak adhesion, possibly mediated by nonuniformities on the MSP surface, to spontaneous wrapping. We note that MSPs were observed to spontaneously curve into wavy structures or well-defined helices, especially in aqueous environments from pH 1–6; the observed curvature, a function of MSP mechanical properties and interfacial interactions with the surrounding aqueous phase, was used to estimate a pH-independent copolymer modulus of $\approx 200 \text{ MPa}$ by helix extension in viscous flow (details in the Supporting Information).[15,22,23]

3.1. Weak Adhesion Modes: Ribbon Stretching and Flagellum-Like Assemblies

From pH 1–6, MSPs and droplets were observed to slide past one another upon contact, with adhesion occurring randomly along the MSP. Figure 3d (left) shows sequential frames from Video S1 in the Supporting Information, in which a coiled MSP (helix radius = 38 $\mu m$) is suspended between the substrate and an adhered droplet ($R = 132 \mu m$). By translating the substrate, the helix transitions from unstretched (top) to extended (center), to fully detach from the droplet (bottom), recoiling like a stretched spring. This adhesion is too weak to macroscopically deform the droplet before detachment. Video S2 in the Supporting Information illustrates similar adhesion at pH 4, while Video S3 in the Supporting Information displays an example of interfacial slip along a smooth MSP helix at pH 6. At pH 8, the adhesion occurred at the MSP ends (Figure 3e,d center) to afford flagellum-like structures. Video S4 in the Supporting Information shows a droplet attached to an MSP segment (length $\approx 400 \mu m$) that is pushed through the fluid with the capillary tip to demonstrate i) adhesion between the droplet and MSP end and ii) a lack of adhesion along the MSP face. This flagellum-like assembly was maintained while the MSP was stretched (Figure 3d center; Video S4, Supporting Information), but when the droplet was brought into contact with the MSP face (time $T \approx 0.4–0.8$ s) the two faces slid past one another without adhering. We speculate that these distinct adhesion modes may result from laser cutting (CO2 laser, $\lambda = 10.6 \mu m$) of the MSPs after flow-coating, which heats the material[24] and potentially alters its surface composition (i.e., via oxidation), $G_c$, and roughness.[25,26] We note that MSPs that were stored under ambient conditions for $\approx 3$ weeks before release into pH 8 buffer qualitatively exhibited a decrease in selectivity for adhesion at the end.

3.2. Capillary Wrapping

At pH 10, the MSPs were observed to spontaneously wrap the droplets upon contact between the ribbon face and fluid–fluid interface, suggesting both large $G_c$ and $R > R_c$. This wrapping...
event is in stark contrast to the weak adhesion observed at lower pH and marks a transition from polycation (in acidic solution) to neutral polymer (in basic solution, Figure 3c inset structures), while a pH-independent $E$ and $\gamma_{ow}$ implicate the polymer surface chemistry as the driving force for wrapping. Wrapping continued until terminated by one of several
mechanisms, including: i) onset of tension in the MSP, supplied by MSP adhesion to the substrate or microcapillary tip; ii) wrapping over an existing coil rather than available oil–water interface; or iii) consumption of the entire MSP length, to afford droplets with partial interfacial coverage. The wrapped droplets were subsequently unwrapped by withdrawing the MSP via the microcapillary tube (Video S5, Supporting Information). Figure 3c (right) schematically depicts the experimental design, while Figure 3d (right) displays frames from Video S5 in the Supporting Information that show clean unwinding of millimeters of an MSP while it maintains its structural integrity. The unwound MSPs then wrap the droplets again when tension is released and the wrapping/unwrapping cycles were repeated up to three times, without noticeable change, for a given MSP–droplet pair. Videos S6 and S7 in the Supporting Information demonstrate cases of partial rewrapping to create assemblies in which droplets are decorated with arms that extend into the continuous phase. Because wrapping stops when the MSP wraps upon itself, we infer that it is confined to the oil–water interface, and further, that the wrapping mechanism requires an uninterrupted 3-phase contact line at the wrapping edge.

From a mechanics standpoint, the MSP-wrapped droplets can be described by a thin, wide elastic beam confined to a curved oil–water interface.\(^\text{[12]}\) The components of a wrapped assembly of contact length \(L_c\) include bending \((U_b = E I_y L_c/2R^3)\) and adhesion \((U_g = G_c wL_c)\) energies, where \(E\) is the elastic modulus, \(I_y\) is the second moment of inertia for axial wrapping, and \(G_c\) is critical strain energy release rate. When \(R = R_c\), the wrapped and unwrapped states are energetically equivalent, affording \(R_c = \sqrt{\frac{2E I_y}{2G_c w^3}}\). Thus, for \(R < R_c\) we expect adhesion without wrapping, while for \(R > R_c\) we expect spontaneous wrapping. This relationship was studied as a function of droplet radius \(R\) in the experiments shown in Figure 4. In Figure 4a (and Video S8, Supporting Information), the microcapillary tip was positioned adjacent to an MSP and used to introduce a droplet, which grew until it contacted the MSP. Figure 4a (left) shows the system at \(T = 0.4\) s, immediately before contact and wrapping. To the left, the MSP is fixed to the glass substrate, and to the right, it is unconstrained and free to wrap the droplet. At \(T = 1.1\) s (Figure 4a, center), wrapping had nearly advanced one turn around the droplet, and the two wrapping edges passed by one another at \(T = 1.4\) s. Approaching wrapping at the droplet circumference, each wrapping edge advanced at \(\approx 350\) \(\mu\)m s\(^{-1}\). After \(T = 1.6\) s, the free MSP end was completely wrapped, while the slack between the droplet and the fixed end was pulled tight at \(T = 7.6\) s (Figure 4a (right) and final frames of Video S8, Supporting Information).

To examine the impact of droplet size on wrapping, a ribbon-wrapped droplet with radius \(R = 279\) \(\mu\)m was pierced with the microcapillary tip and oil was continuously withdrawn to reduce the droplet radius (Figure 4b). At \(R = 136\) \(\mu\)m, deflation stopped as applied force from the tip translated the droplet without piercing the surface. Despite the decrease in droplet dimensions, the droplet remained wrapped, with an appearance of more substantial interfacial coverage. Even in the presence of small droplets \((R = 6–30\mu m)\) prepared by emulsification via pipette, wrapping occurred such that MSPs effectively connected multiple droplets in series. For example, Figure 4c shows brightfield (left) and fluorescence (right) micrographs of an MSP \((w = 14\mu m)\) wrapped around 13 droplets as small as \(R = 6\mu m\) (droplet 7). For even smaller droplets, where \(R < w\), we anticipate edgewise wrapping dictated by a lateral moment of inertia \(I_{xx}\), which becomes infinitesimally small as MSP thickness tapers toward the edges (Figure S2, Supporting Information). Accordingly, we expect wrapping even in cases where the thickness \(t\) of the MSP central axis might otherwise prohibit lengthwise wrapping.

3.3. Evaluating MSP–Droplet Interactions

The energy landscape of elastoadhesive MSP wrapping, as described by \(G_c\), in pH 10 buffer was probed by measuring the peel force, \(F_p\), required to separate a wrapped MSP from the fluid–fluid interface. As described in Figure 5, these measurements utilized deflection of a single carbon fiber fixed to the end of a glass capillary tube that was dipped into a cyanoacrylate glue and cured to afford a cantilever with a hydrophobic, adhesive bead near the tip. A sample of MSPs was released into the buffer and PFD droplets were introduced by pipette. The cantilever was brought into contact with a PFD droplet via a micromanipulator, which adhered to the cured poly(cyanoacrylate) bead, then the cantilever-bound droplet was brought into contact with an MSP to initiate spontaneous wrapping (Figure 5a). For ribbons with one end fixed to the substrate, the MSP–droplet assembly was loaded by substrate translation, enabling direct quantification of the applied force by measuring cantilever deflection. The applied force increased linearly as the MSP stretched and the droplet deformed, as shown by the 3-phase contact line meniscus (Figure 5b), until unwrapping began at a critical force, \(F_c\). Figure 5c,d and Video S9 in the Supporting Information follow the progress of an experiment with droplet radius \(R = 88\mu m\) through two
complete loading cycles, with an unloading step in between the cycles. Force (Figure 5c, left) and the applied energy release rate \( G \) (right, describing the energetics of separating the interface) are plotted as a function of ribbon length (\( L_R \)) between its fixed end and the droplet contact point; on the second cycle, the MSP was unwrapped until detachment, when the ribbon contact length was exhausted. The loading curve exhibited two distinct regimes: linear loading, in which the force increased monotonically with the droplet-to-fixed-end MSP length (\( L_R \)), followed by a plateau of sustained peel at constant force (\( F_c \), blue data points) of 2.6 \( \mu \)N. The initial loading slope was consistent from cycle to cycle, as was \( F_c \). During unloading, the linear force–\( L_R \) curve matched the slope of the loading curve, suggesting elastic recovery in the stretched MSP. At \( F = 0 \), \( \approx 50 \) \( \mu \)m of visible slack spontaneously rewrapped the droplet.

The second load cycle followed a similar stretch-plateau shape and loading continued until the MSP detached completely from the fluid–fluid interface and dispersed in water. Figure 5d corresponds to red data points in Figure 5c during the second loading cycle, with wrapped lengths of i) \( \approx 140 \) \( \mu \)m, ii) \( \approx 85 \) \( \mu \)m, and iii) \( \approx 0 \) \( \mu \)m (end-adhered), iv) marking continuous unwrapping before detachment. The critical force for unwrapping is divided by \( w \) (\( \approx 22 \) \( \mu \)m, measured from video frames) to define a critical energy release rate, \( G_c = 116 \) mN m\(^{-1} \) for the copolymer 1-PFD interface in this solution (Figure 5c, reference line). For an MSP of thickness \( t = 300 \) nm and modulus 200 MPa, the critical elastoadhesive dimension for axial wrapping (bending in \( I_{yy} \)) \( R_c \approx 7 \) \( \mu \)m. We note that \( R_c \) is readily decreased by reducing \( t \), which is accomplished easily during fabrication by flow-coating.\(^{[14–16]} \)

### 4. Building Droplets with Arms by Photopatterning Ribbons

Photopatterned ribbons prepared from copolymer 2 were used to study additional MSP–droplet assembly modes. Here, composition, geometry, and interfacial chemistry are partitioned to afford MSBCPs, reflecting spatial control of \( R_c \) such that only predetermined segments wrap the droplets. Remarkably, only the hydrophobic segments (composed of PTBMA) were observed to wrap PFD droplets, while the hydrophilic PMAA segments exhibited no wrapping tendency, suggesting that for droplet radii \( R = 60–150 \) \( \mu \)m, \( R_{PTBMA} < R < R_{PMAA} \).

Droplet–ribbon assemblies with appendages extended into the aqueous phase were realized by photochemically programmed wrapping with specific MSP segments, enabled by controlling domain size via the photomask and the number of segments via laser engraving. Figure 6a describes MSBCP assembly consisting of 1 segment each of deprotected PMAA and protected PTBMA (block length 500 \( \mu \)m) with a PFD droplet (\( R \approx 110 \) \( \mu \)m) in water; false color (frame 1) highlights the
distinct blocks. Upon contact, the hydrophobic PTBMA block wrapped the droplet until reaching the junction point, affording a droplet with a single PMAA arm (Figure 6a frame 2 and Video S10, Supporting Information). We note that this mechanism of pendent arm formation is distinct from the pH-dependent methods used to prepare extended structures from MSPs of copolymer 1. Subsequent contact with additional MSBCPs decorated the droplet with a second arm (Figure 6a frame 3 and Video S11, Supporting Information), and up to ten arms using mixed assembly modes spanning i) selective wrapping, ii) weak adhesion of PMAA domains, and iii) end-on adhesion (Figure 6a, frame 4 and Video S12, Supporting Information).

Related structures were obtained by using PMAA–PTBMA–PMAA triblock MSBCPs, decorating droplets with two pendent arms per wrapping step. Figure 6b and Video S13 in the Supporting Information show the use of a droplet of \( R \approx 150 \mu m \) to pick up the ribbons, which are resting on a substrate in \( 500 \times 10^{-3} \) m NaOH solution. The central PTBMA block was 500 \( \mu m \) in length, with shorter blocks of approximate length \( \approx 250 \mu m \) in PMAA domains. Here, the crosslinked PMAA domains coiled tightly into helices of \( R \approx 3.5 \mu m \) upon release into solution, suggesting swelling-dependent coiling consistent with MSBCP architectures reported previously.[21] In contrast, the hydrophobic PTBMA domains remained straight until contact with a droplet initiated bending. False coloration in frame 1 of Figure 6b highlights the coiled helical end blocks (blue) and rigid core block (red) of an MSBCP immediately before droplet contact and wrapping. Frames 2–4 represent subsequent frames from Video S13 in the Supporting Information as the droplet is used to remove additional ribbons from the substrate surface by selective wrapping. Wrapping of additional MSBCPs advances until overlap with those present already. Notably, this does not stop the wrapping events as observed for longer, substrate-adhered PDMAEMA MSPs at pH 10; rather, wrapping was seen to continue by pushing the previously wrapped segments across the interface (\( T \approx 7.2–14.0 \) s).

![Figure 6. Droplet–MSBCP assemblies. Assembly of droplets with a) “diblock” MSP in reverse osmosis water and b) “triblock” MSP in 500 \times 10^{-3} \text{ m NaOH}: a) The droplet and ribbon (false color, top, red = hydrophobic; blue = hydrophilic) are brought into contact; selective wrapping affords a droplet with an arm (frame 2); subsequent ribbon addition allows installation of 2 (frame 3) or many (frame 4) arms; b) assembly of MSBCPs (false color, top) enables shorter arms driven to coil in basic solution; c) cantilever deflection of an MSBCP with one wrapped segment to quantify peel force; d) plot of measured force \( F \) (left axis) and \( G \) (right axis) as a function of peel length of an adhered MSBCP subjected to three load-peel cycles. Red data points correspond to frames ci–iv); blue data points denote peeling \( (F_c, G_c) \); cycle averages were combined to calculate peel force and \( G_c \) (dashed reference line with 95% confidence in gray). Scale bars a,b) 200 \( \mu m \) and c) 100 \( \mu m \).](#)
4.1. Quantifying MSBCP Segment–Droplet Interactions

The peel force of PTBMA segments at the PFD–water interface was measured by cantilever deflection. MSBCPs of alternating 50 μm blocks were prepared with one end fixed to the substrate surface, released into pH 10 buffer solution, then brought into contact with a cantilever-bound droplet (R = 60 μm). Measurements were made by translating the substrate with the adhered MSBCP end, pulling on the droplet, and measuring the deflection of the attached cantilever. The system was taken through two complete load–unload cycles, then loaded until detaching completely from the droplet surface (Video S14, Supporting Information). Figure 6c represents successive frames from the first cycle in this experiment, including: i) an unstretched MSBCP; ii) loading until slack is removed; iii) hydrogel segment stretching and droplet deformation; and iv) peeling (false coloration highlights the hydrophobic (red) and hydrogel (blue) domains). The measured force is shown in Figure 6d, revealing continued loading, without peeling, until a critical load of ~1460 nN is reached, when the system transitions to a partially peeled state. For each cycle, the average peel force \( F_c \) is taken from blue data points, with a typical value of ~1100 nN. Four data points are highlighted as red triangles, corresponding to Figure 6ci–iv, revealing the load at each stage of the measurement. i) The initially curved PMAA domains (i) straighten under relatively little force (~60 nN, ii), then stretch ~115 microns (low load) to ~160 microns as the load increases to 1470 nN (iii). The load decreases to 990 nN immediately after peel (iv) and the gel domains elastically recover during unloading, consistent with expectations for a crosslinked hydrogel. Notably, this strain concentration within hydrophilic PMAA gel domains enabled direct measurement of gel modulus \( E_{\text{PMAA}} = 2 \) MPa by tracking the segmental junction points between PMAA and PTBMA domains. By contrast, we estimated \( E_{\text{PTBMA}} \) on the order of 1 GPa based on the known \( T_g \) of 116–118 °C,\[27,28\] a 500-fold modulus difference achieved simply by photopattern-mediated swelling.

The measured \( F_c \) represents the energy per unit length required to unwrap ribbons from the curved oil–water interface. Having demonstrated that capillary interactions dominate bending stiffness at the selected length scales in PDMAEMA MSPs of modulus 200 MPa (\( G_c = 116 \) mN m⁻¹, \( R_c = 7 \) μm for \( t = 300 \) nm), we applied the same assumption when measuring MSBCP segments. Dividing \( F_c \) by segment width \( w = 12 \) μm (measured via optical profilometry before release), \( G_c = 93 \) mN m⁻¹ (Figure 6d reference line) was calculated. Thus, for a hydrophobic MSBCP segment with \( t = 300 \) nm, \( R_c = 17 \) μm, while smaller values are readily accessible by printing thinner MSBCPs. Notably, \( G_c \) for MSPs (~116 mN m⁻¹) and hydrophobic MSBCP segments (~93 mN m⁻¹) are comparable to the oil–water interfacial tension \( \gamma_{ow} = 51 \) mN m⁻¹ measured by pendant drop tensiometry; moreover, MSBCP adhesion at the oil–water interface ceased upon the addition of a polymer surfactant, further connecting the high energy oil–water and polymer–water interfaces to adhesion and wrapping phenomena. Together, our measurements of \( G_c \) and \( \gamma_{ow} \) combined with loss of adhesion in the presence of surfactant implicated the oil–water and polymer–water interfaces as a primary driving force for large scale assembly of mesoscale ribbons. Notably, despite a modulus approximately three orders of magnitude smaller than the glassy PTBMA domains, the PMAA gel segments adhered to droplets without wrapping, suggesting an equally dramatic change in \( G_c \) from segment to segment. Thus, MSBCPs possess partitioned domains of alternating physical and mechanical properties, including a 500-fold difference in elastic modulus, and dramatic differences in \( G_c \) and \( R_c \) that enable selective wrapping and assembly upon contact with oil-in-water droplets.

5. Conclusion

In summary, we described the use of compliant, surface-active, mesoscale polymer ribbons to build assemblies with liquid droplets via the fluid–fluid interface of the droplets. We adapted a model of cylindrical filaments at droplet surfaces to describe the uniquely flat geometry of MSPs in contact with an oil-in-water droplet, spanning wrapping and nonwrapping interaction modes as a function of a modulus-, geometry-, and \( G_c \)-dependent elastoadhesive dimension \( R_c \). Using photo-crosslinked MSPs derived from copolymer 1, we mapped pH-dependent interactions, ranging from i) weak adhesion \( (R_c > R) \) from pH 1–8, including flagellum-like architectures formed by selective adhesion at the MSP tip, to ii) spontaneous wrapping at pH 10, producing spoons amenable to unwrapping, rewrapping, and addition of pendant arms. We employed the “built-in” photocid generators in copolymer 2 to effect chemically amplified deprotection and crosslinking, using a photomask to partition distinct properties into segments along the ribbon length. Within the resulting MSBCP structures, hydrophobic PTBMA segments were observed to selectively wrap oil-in-water droplets independent of pH, enabling the construction of droplets with 1, 2, or many arms extended into solution. Moreover, quantification of \( G_c \) and thickness-dependent \( R_c \) confirms that the bending compliance and strong interfacial activity of MSPs and MSBCPs affords elastoadhesive lengths of microns or smaller. Together, these pH-, light-, and spatially programmable structures provide a robust platform to transform simple soft materials building blocks and interaction modes into sophisticated meso-to-macroscale bio-inspired assemblies.

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.
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