nature portfolio

Peer Review File

Film surface assemblies from chemically distinct block copolymer micelles

Corresponding Author: Professor Ulrich Wiesner

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The paper illustrates an approach to identify difficult to determine micellar contributions to self-assembled mixed micellar structures of block copolymer micellar alloys (BMA's). This is performed using the SNIPS phase inversion technique to highlight and distinguish between different micellar assemblies, followed by analysis by a ML image analyses using segmentation techniques involving Voronoi etc. surface analyses to get at the symmetry of the surface structures. Finally, they use coarse grained Brownian Dynamics (BD) to simulate the structures to compare to determine FFT and structure factor, and correlations etc. The approach invokes concepts of colloidal phenomena such as solution (BMA micellar) composition ratio, size asymmetry and polydispersity ratio. The work is novel and results exciting, and detailed as it considers both binary and ternary BMA mixtures.

However, its very difficult to read the paper in its present form! Thus, I would not recommend the paper in its present form for publication, but the authors may be given the chance to substantially modify the paper, given its overall detailed nature and high degree of novelty, to address the following key issues and comments:

1) While the BMA results and analyses are very interesting, the paper is not by any means an easy read, even for block copolymer (micellar) experts. This is because it applies a number of concepts and techniques (e.g. a 'black box" ML), both for experimental and theoretical analyses, that are not necessarily common or non-specialized knowledge. Further, the cartoons in Figure 1. which outlays the design of experiments is crucial to understand the theme of the paper is not clearly explained in the text of the paper, and even in the captions and schematics is hard to follow. So the initial approach and design and workflow analyses that the paper follows should be laid out in more simplified detail. The Summary does a good job of this, but it comes too late of course. Furthermore, the sentence constructions are often complex and convoluted, which does not make for easy flow in reading. So the main comment is what can the authors do to simplify the flow and readability of the paper. There is quite a bit of acronyms and jargon that hinders the readability of the paper, especially in the ML part that needs a more proper introduction, e.g. say what is segmentation analyses etc.. These are simply put in with no background context. I suggest a friendly feedback read by a BCP expert colleague could help the paper much!

2) There are some other "generalization" of the approach questions/concerns: It is mentioned "Here, we propose an alternative approach to surface structural analysis. We utilize non-equilibrium processing conditions – a combination of solvent evaporation induced self-assembly and phase inversion (SNIPS) – to generate porous BCP micelle surface arrays." While this may be true, aren't the structures being fundamentally modified by SNIPS to become an observable structure, rather than being a general technique for observing the "unperturbed" BCP surface structure? A side comment is that, SNIPS is not properly introduced for those unfamiliar with the method to follow how and why the porous structures are created and what we are measuring that would otherwise not be observable if SNIPS was not used!

3) Details are lacking – like what is the nature of the "surface porosity" in terms of pore depth, is there z-continuity of pores, etc. Can these be quantified by AFM?. ToF SIMS etc in select cases?

4) The authors study multiple micelle systems in single, binary and ternary combinations, and combine different analysis techniques in clever ways, however, the work lacks a detailed hypotheses driven research. What are the key BMA mixing hypotheses and mixing rules for surface morphology that were tested in the paper? Are these unique to SNIPS processing as asked previously?

5) Finally, since the BD analyses assume equilibrium structures, what can the authors do to convince readers that these are near equilibrium structures as opposed to SNIPS specific processed structures? Can they be reasonably perturbed e.g. thermally or by solvents, and regain their structure etc. kind of questions arise in this regard.

Reviewer #2

(Remarks to the Author)
The authors study self-assembly and surface pattern formation in binary and ternary mixtures of multi-block copolymer micelles (PI-b-PS-b-P4VP, PI-b-PS-b-P2VP-b-PEO, PS-b-P4VP-b-PPS) upon drying from a good solvent - THF-dioxane mixture. Due to the poor electron density contrast between the blocks in their native state limiting the use of electron microscopy imaging, non-equilibrium porous morphology is generated by immersion of still-drying films in water (SNIPS process), to help discerning micelles made of distinct BCPs during consecutive SEM examination. SEM images analyzed using the FFT method, Voronoi analysis, and cluster analysis along with the Monte Carlo/Brownian Dynamics simulations all reveal complex yet controllable non-equilibrium surface pattern formation behavior. The authors employed the random forest ML approach for image analysis to discern the pores and create segmentation maps. These maps were then used to analyze the distribution of the pores by employing FFT to analyze the structure of the material as well as modified Voronoi analysis to capture the number of neighboring cells, which allowed them to detect defects in the lattice. The authors used the above-described techniques to analyze the morphology diagrams of binary and ternary films consisting of 3 different BCPs (the latter rarely encountered in previous reports) and determine how the different mixing ratios, as well as different polymer molecular weights, affect the structure defect density. These results were further confirmed by Brownian dynamics simulations.

The analysis provided in the manuscript is very thorough and in my opinion it is of potential interest to the readers of Nature Communications. The authors report the formation of intriguing binary and ternary morphologies formed by square and hexagonal arrays of soft micelles and several interesting findings; some already known in hard colloids e.g. mobility-driven surface enrichment of smaller micelles, well-supported by rich experimental data and simulations. The approach to analyzing structural parameters of BCP materials proposed by the authors can help overcome limitations in currently available structural analysis techniques and allow further progress in the understanding of complex self-assembly scenarios in the field of BCP micelle and colloidal systems alloying.
Although the use of SNIPS aided the visualization of the pores forming in the polar cores of micelles and enabled further analysis, it also seems to be a major factor in increasing the complexity of the approach taken by the authors.
1) Could the authors provide information on the role of evaporation rate on the ordering process and if it has been controlled? What was the rationale for selecting the reported evaporation times before the SNIPS? What was the solvent content at the moment of immersion and how thick were the films? These metrics should be more informative than the reported evaporation times.
2) Under what conditions the equilibrium morphologies are expected to form and how far are they from the conditions reported here?
3) Is the PEO block long enough to prevent the fusion and formation of worm-like micelles after longer evaporation in the ISV-ISOV system?
4) Why the authors did not employ a simpler and well-known P2VP-core staining method i.e., by using platinum complexes? It would be very interesting to cross-compare the results of structural image analysis of surface patterns with the underlying bulk film morphology either by X-ray scattering or by cross-sectional SEM analysis. Have the authors performed such analyses?
Minor comments and remarks:
Information on casting conditions including total typical BCP concentration (main text) and blade velocity (expressed in units other than motor spins-per-second) and the resulting film thicknesses are missing.
In supplementary fig S9d, the inset should be marked in more visible manner (it looks like a part of image)
Supplementary notes, in particular those concerning the choice of material's (#1), cross-micellar chain exchange (#2), and also note #4 are critical for understanding the concept of this work. In particular, the authors should consider extracting the salient points provided in note #2 and moving it to the main text for further support claim from p. 6.

Reviewer #3

(Remarks to the Author)
This work beautifully illustrates new surface analysis methods for the surface of porous films of BCPs via SNIPS methods. BCPs have been synthesized by anionic polymerization, which allowed the resulting BCPs to have well-defined structures and molecular weights. In particular, the MWs of the BCPs used in this study were quite high, presumably, for obtaining mechanically robust structures. SNIPS methods have been widely used for creating isoporous BCP membranes on the top surface, which are supported by microporous structures. The resulting film appeared to have monodisperse-sized surface pores that are arranged in regular order, such as a hexagonal array or a tetragonal array. Considering the thickness of the top layer (~ a few hundred nanometers), the top porous layer could be considered as two-dimensionally ordered pores or three-dimensionally ordered bicontinuous (cubic) structures. In this case, the arrangement of the surface pores reflects the order of the internal structures.

This work is unique because the authors found the co-cosolvent compositions for the micellization of BCPs. Using these conditions, they mixed BCPs to form micellar mixtures rather than simple BCP blends. SNIPS of these micellar mixtures resulted in the formation of porous films having surface pores, of which their arrangements might reflect the mixing or demixing state of the micellar mixture (here, named to a BCP micelle alloy). In general, the detailed structures of the ordered domain of the porous films formed by SNIPS have been studied by SAXS. However, this technique cannot be used for studying the mixing or demixing of the BCP micelles. The authors, in this work, used image analysis techniques to characterize the lattice and lattice constant. Also, the contrast of the SEM image provided information on the pore sizes, which are characteristic of BCP micelles.
If the image-based analysis of the top surface could provide information of the porous structures underneath the top surface, the reported analysis could be unique as X-ray analyses would give the structural details by averaging different micellar domains. However, the manuscript is confusing in some ways:
(1) The self-assembly procedure is similar to conventional SNIPS procedures except for the spinning part. Why did the films spin? Was this to make the film thinner? Or was it related to the evaporation rate of solvents? To avoid confusion, the self-assembly methods should provide more details (for example, concentrations of BCP solutions, and the thickness of the resulting films).
(2) Assuming the thickness of the film is greater than that of the micelle monolayer, solvent evaporation, and non-solvent quenching will introduce phase transition and inversion. How could the final structure after phase separation and inversion be related to the (assumed) micellar aggregation during self-assembly?
(3) Tetragonal arrangements of surface pores suggest that the internal porous structures would be bicontinuous. If the segregated domains of BCP micelles were observed like in this study, could the internal porous structures (or bicontinuous structures) be segregated as well? How can we analyze this?
(4) Some of the analyses of the stoichiometry of the BCP micelles on the surface and the simulations assumed that the micelles behave as small colloidal particles and that the surface structures reflect the results of colloidal assembly. I do not believe this is true for the film created by SNIPS methods. Simulation results are not in line with experimental analyses, which might indicate that SNIPS is different from colloidal assembly.
If the reported analysis and techniques could be related to the characterization of internal structures, this paper merits publication in Nature Communications.

Version 1:

Reviewer comments:

Reviewer #1
(Remarks to the Author)
The authors have done a very nice job of addressing my (and almost all other reviewer comments as I can assess)! For me, not to speak for other reviewers, the only remaining question / possible work they can do is suggested below:

Authors mention to another reviewer's comments: "As this reviewer can imagine, the question about the exact solvent content at the moment of the immersion is non-trivial to answer for such complex multicomponent mixtures (including two solvents and up to three BCPs)."

So one way to do this may/should be to place the sample upon coating immediately on top of a 4 (or 5 decimal place) weighing balance placed inside the film casting glove box, and then compare the initial weight at t=0s, to that after 80 s of evaporation. I think the mass loss in 80s on a 50 micron thickish film should be measurable gravimetrically! Of course they should weigh the dry glass slide / substrate prior to any coating, and then let it fully dry with the film after inversion and maybe even warm it up some for some time to remove residual solvent, and report the dry film weight. Once, all these weights are documented, knowing the (average) density of the dry BCP mix film, and the solvent weight loss in 80 s, the slide area covered by the initial casting mixture, and assume some typical average polymer mix, and solvent mix density, they should be able to calculate the volume at t=0 vs t=80 s. The initial t=0 and final height at t=80 should be calculable knowing the initial area. If the area shrinks in 80s, even then it can be accounted for by measuring it at 80s, to give (corrected) film thickness at 80 s.
Just my suggestion - note this is all done gravimetrically so should be possible. Only thing is that the mass of the glass slide/substrate should be not too high for accuracy and sensitivity for recordable solvent mass loss on a 4 or 5 digit balance.

Reviewer #2

(Remarks to the Author)
I appreciate that the Authors provided detailed explanations and expanded on their choice and critical assessment of experimental methods in response to my comments. They clarified that the film casting and solvent evaporation were tightly controlled in a humidity-regulated environment, with specific experimental parameters now explicitly mentioned. They also provided a previously-reported phase diagram to addressed my concerns about solvent content and morphologies in evaporating films by explaining that, due to the complexity of their multicomponent system, they relied on reproducible metrics rather than attempting to quantify the solvent composition at the moment of immersion in SNIPS. I am now convinced that the Authors have thoroughly explained that SNIPS provides a practical insight into the surface structure of a thin film composed of BCP micelles without substantially modifying its key characteristics. Finally, they justified the choice to avoid staining by citing the high number of samples involved, improved the clarity of supplementary figures, and discussions in the main text.

Overall, I feel that these revisions adequately address my critical comments and, along these made in response to the comments by Referee #1 and Referee #3, improved the overall quality of this manuscript.

Reviewer #4

(Note from the Editor: Reviewer #4 was asked to look also over the response given to Reviewer #3)

(Remarks to the Author)

Dear Editor,

We have carefully reviewed the authors' responses to Reviewer 3 and find that most of the concerns have been thoroughly addressed:
1. Coating parameters and film thickness: The authors have now included the doctor-blade speed (15 mm s-1), block-copolymer concentrations (10–20 wt %) and measured film thickness (40-50 µm) in the Methods section, directly resolving the reviewer's query about "spinning."
2. SNIPS-derived micelle aggregation: They have reinforced their description of evaporative self-assembly in the top ~100 nm, where micellar lattices densify and are preserved upon water-quench, to explicitly connect the SNIPS protocol to the observed surface porosity.
3. Non-equilibrium simulation framework: Their BD simulation now clearly incorporates a time-dependent wall potential to mimic the receding liquid–air interface, and complementary Monte Carlo runs demonstrate that the final structures cannot arise under equilibrium alone.

However, Reviewer 3's principal concern remains: whether the bicontinuous internal pore network truly mirrors the ordered surface layer. At the current stage, the authors have justified their surface-only focus by citing experimental difficulty, but they have not proposed any concrete follow-up. To fully satisfy this point, we recommend that the authors include a brief feasibility discussion of one or more targeted techniques, for example: selective GISAXS on simplified binary blends to isolate individual lattice parameters, cross-sectional SEM images on small sample regions to visualize internal connectivity, or preliminary small-angle neutron scattering experiments using deuterated blocks to enhance internal contrast. We support acceptance of the manuscript after the inclusion of these additional data.

POINT-BY-POINT RESPONSEs TO REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The paper illustrates an approach to identify difficult to determine micellar contributions to self-assembled mixed micellar structures of block copolymer micellar alloys (BMA's). This is performed using the SNIPS phase inversion technique to highlight and distinguish between different micellar assemblies, followed by analysis by a ML image analyses using segmentation techniques involving Voronoi etc. surface analyses to get at the symmetry of the surface structures. Finally, they use coarse grained Brownian Dynamics (BD) to simulate the structures to compare to determine FFT and structure factor, and correlations etc. The approach invokes concepts of colloidal phenomena such as solution (BMA micellar) composition ratio, size asymmetry and polydispersity ratio. The work is novel and results exciting, and detailed as it considers both binary and ternary BMA mixtures.

Response:

We very much thank this reviewer for the very positive overall assessment of our work, and especially for pointing out that these are very *novel, exciting, and detailed* results obtained on binary and ternary BMAs, important qualifiers for publications in *Nature Communications*.

However, its very difficult to read the paper in its present form! Thus, I would not recommend the paper in its present form for publication, but the authors may be given the chance to substantially modify the paper, given its overall detailed nature and high degree of novelty, to address the following key issues and comments:

Comment #1:

1) While the BMA results and analyses are very interesting, the paper is not by any means an easy read, even for block copolymer (micellar) experts. This is because it applies a number of concepts and techniques (e.g. a 'black box" ML), both for experimental and theoretical analyses, that are not necessarily common or non-specialized knowledge. Further, the cartoons in Figure 1. which outlays the design of experiments is crucial to understand the theme of the paper is not clearly explained in the text of the paper, and even in the captions and schematics is hard to follow. So the initial approach and design and workflow analyses that the paper follows should be laid out in more simplified detail. The Summary does a good job of this, but it comes too late of course. Furthermore, the sentence constructions are often complex and convoluted, which does not make for easy flow in reading. So the main comment is what can the authors do to simplify the flow and readability of the paper. There is quite a bit of acronyms and jargon that hinders the readability of the paper, especially in the ML part that needs a more proper introduction, e.g. say what is segmentation analyses etc.. These are simply put in with no background context. I suggest a friendly feedback read by a BCP expert colleague could help the paper much!

Response:

We very much appreciate this reviewer's advice. Based on this feedback, we have substantially reworked introduction and overall text to simplify the flow and readability of our paper. For example, in the revised version of our manuscript, the introduction now (i) explicitly points to the goal of exploring whether control parameters are similar to those of traditional colloidal systems, (ii) provides, in simple language, an explanation of Voronoi and ML based segmentation analyses and what we learn from that, and (iii) better summarizes workflow of the experiments and describes our results similar to the paper summary/conclusion section. Furthermore, for more clarity, we have introduced a revised Figure 1 into our manuscript and have substantially reworked the caption of Figure 1 and associated text.

Comment #2:

There are some other "generalization" of the approach questions/concerns: It is mentioned "Here, we propose an alternative approach to surface structural analysis. We utilize non-equilibrium processing conditions – a combination of solvent evaporation induced self-assembly and phase inversion (SNIPS) – to generate porous BCP micelle surface arrays." While this may be true, aren't the structures being fundamentally modified by SNIPS to become an observable structure, rather than being a general technique for observing the "unperturbed" BCP surface structure? A side comment is that, SNIPS is not properly introduced for those unfamiliar with the method to follow how and why the porous structures are created and what we are measuring that would otherwise not be observable if SNIPS was not used!

Response:

We very much appreciate these very important points raised by this reviewer. A priori, one may indeed assume that the SNIPS approach will substantially alter observed surface structures relative to the "unperturbed" case. Here we need to first distinguish two scenarios for what could be called the "unperturbed" state. The first scenario is an "unperturbed" BCP film surface reflecting equilibrium BCP bulk thermodynamics. We are very far from such bulk equilibrium structures. This has to do with the fact that even before mixing the different BCPs into alloy solutions for SNIPS, we let each BCP form micellar structures in a selective solvent mixture. On the experimental time scale of ~ 1 hour these micelles don't show any appreciable chain exchange (*vide infra*) after mixing in those solvents and are thus kinetically trapped. This trapping does not allow the system to reach BCP bulk thermodynamic equilibrium on the timescale of the experiment.

For the sake of the discussion in the context of colloidal assembly, a second scenario for what constitutes the "unperturbed" state is more useful. Here we assume that the terpolymer chains are trapped in BCP micelles on the timescale of the experiments. After film deposition and doctor blading, in the third step of the SNIPS process (*vide infra*) the binary solvent mixture is evaporated. But rather than evaporation to completion, at a particular time point (80s in our studies), the film is plunged into a water bath (the fourth step in SNIPS). Without going into the details of this so-

called phase inversion process, one way to think about it is that the film densification process is arrested into the glassy state of a high glass-transition temperature matrix (here: polystyrene, PS). The result is therefore a non-equilibrium state. One can now ask the question how far this state is from an "unperturbed" BCP film surface reference structure simply obtained at 80s evaporation in the absence of the quenching step. The following arguments support the notion that close to or at the surface of the films, our observed surface structures track the behavior at the end of the evaporation process (i.e., just before the water plunge) while at the same time being very far from bulk thermodynamic equilibrium as defined in the first scenario:

- *First*, as we (and others) have shown, e.g., in earlier in-situ grazing-incidence small-angle x-ray scattering (GISAXS) experiments *during* solvent evaporation (e.g., see *Macromolecules* **49** (2016), 4195; *Macromolecules* **53** (2020), 4889), the top surface layer of SNIPS derived thin films evolves from disordered micellar assemblies into ordered micellar lattices. These disorder-to-order (as well as subsequent order-order) transitions essentially determine the lattice formation processes we see reflected in the surface structures of our films (e.g., cubic versus hexagonal lattices discussed in the present manuscript). Most importantly, these earlier experiments have demonstrated that these lattices formed during evaporation are essentially maintained after precipitation in the water bath (e.g., see *Macromolecules* **49** (2016), 4195).
- *Second*, our experimental results on films described in the paper suggest that observed surface structures are tailorable via traditional colloidal parameters (i.e., solution stoichiometry, neutral/repulsive colloidal interactions, size asymmetry and size polydispersity).
- *Third*, our results showing surface structures tailorable via traditional colloidal control parameters are consistent with Brownian Dynamics simulations treating the BCP micelles as soft colloids and being "blind" to what additional steps are taken in the experiments after 80s evaporation (i.e. coagulation upon plunging into water).

All these arguments, in turn, suggest that the SNIPS process essentially halts the natural evaporation process on the way to the fully evaporated dense surface layer without substantially altering the micelle assembly (please note that SNIPS does induce other changes, but they are less relevant to the main questions we are trying to answer in this work).

For readers to benefit from this important exchange, in the revised version of our manuscript we have now added the following two sections discussing these points to the introduction as well as the final paragraph of the summary/conclusion section, respectively:

Added to introduction: *"Figure 1b illustrates individual steps in the SNIPS process: (1) film deposition, (2) doctor blading, (3) evaporation, and (4) plunging into water bath...After film deposition and doctor blading, the binary solvent mixture is evaporated. But rather than evaporation to completion, a particular time point (here: 80s) is chosen for plunging the film into a water bath. This arrests the film densification process into the glassy state of a high glass-*

transition temperature matrix (here: polystyrene, PS). The result is therefore a porous, non-equilibrium state."

Added to summary/conclusion section: "*Results show that surface structures are tailorable via traditional colloidal control parameters – consistent with BD simulations treating the BCP micelles as soft colloids – further suggesting that the SNIPS induced top surface porosity may not substantially alter key structural aspects of the micellar (colloidal) surface assembly relative to BCP micelle film surfaces generated without the SNIPS quenching step. The former may therefore be used as a simpler-to-analyze approximation of the latter.*"

In the revised version we have also added the two *Macromolecules* papers cited above as new references (i.e., references 49 and 50).

With respect to the issue of insufficient introduction of the SNIPS process, in the revised version of our manuscript, in addition to the above added section, in both the caption of figure 1 as well as the associated main text at the beginning of the section entitled "*BCP micelles as soft colloidal building blocks*", we now explicitly describe the different steps of the SNIPS process, i.e., "*film deposition, doctor blading, evaporation, and plunging into water bath*." We would like to also point to the Methods section of the original manuscript we submitted which contained a more than a page-long description of details of the SNIPS process.

Finally, to address this reviewer's concern about differentiating this from a regular evaporation process leading to a dense "unperturbed" BCP film in the manuscript, we have included the following additional revision to the Methods section:

"*The subsequent exchange of solvent for non-solvent by inserting the films into a water bath essentially stops the regular evaporation process which would otherwise lead to a dense film. This causes the core chains to retract and collapse against the corona chains, generating pores, which in turn facilitate structure analysis (vide supra). From earlier analysis we know, however, that this solvent exchange essentially maintains the associated lattices (e.g., hexagonal versus cubic) formed during evaporation.*"

Comment #3:

Details are lacking – like what is the nature of the "surface porosity" in terms of pore depth, is there z-continuity of pores, etc. Can these be quantified by AFM?. ToF SIMS etc in select cases?

Response:

We thank this reviewer for this important question. It is well documented for SNIPS derived films that the film/pore morphology underlying the top surface is very heterogeneous and asymmetric. Quantitative analysis of such structures is therefore non-trivial, especially with x-rays, and requires a combination of techniques to fully address. We have done this in the past, indeed using an image-based pore-scale modeling approach, and refer this reviewer to earlier work of our

group on this matter (e.g., see *J. Membr. Sci*. **668** (2023), 121163, now ref. 51 in the revised version). To have this important point also reflected in the main paper, in the *Methods* section under *Scanning electron microscopy (SEM) characterization* we have added the following sentence which now refers the reader to this earlier work:

"*For a detailed description of an SEM imaging-based pore modeling approach characterizing pores in film subsurface domains, the interested reader is referred to an earlier study*[51]*.*"

Comment #4:

The authors study multiple micelle systems in single, binary and ternary combinations, and combine different analysis techniques in clever ways, however, the work lacks a detailed hypotheses driven research. What are the key BMA mixing hypotheses and mixing rules for surface morphology that were tested in the paper? Are these unique to SNIPS processing as asked previously?

Response:

We thank this reviewer for this excellent question. As outlined in our response to comment #1 of this reviewer and now described in more detail in our revised introduction, we want: "*..to probe how neutral/repulsive micelle-micelle interactions, solution stoichiometry, and size asymmetry and polydispersity (i.e., traditional colloidal control parameters) impact film surface structure*." This allows us to establish that BCP micelle alloys (BMAs) studied in our work can be treated as soft colloids with interpenetrating coronas that behave very similar to classical colloidal systems following very similar structure formation trends. Here are some key examples:

- As outlined on page 9 of the revised version, for neutral micelle-micelle interactions: "*Solution stoichiometry therefore presents an experimental dial that can be used to tune the lattice size of two chemically distinct micelle building blocks sitting on a single lattice*."
- On page 13 of the revised version we point out for repulsive micelle-micelle interactions and associated micelle size asymmetry (α): "*With increasing size asymmetry, the smaller entity (SVPS) more readily inserts itself into the interstices of the lattice formed by the larger entity (ISV)*[44]*, leading to a positive correlation between α and SVPS surface composition (Fig. 4e)*."
- Finally, again for repulsive micelle-micelle interactions, we point out on page 15 that: "*In hard sphere colloids, increased size polydispersity can fully suppress ordered lattice formation*" and that our BD simulations conform: "*to the experimental trends – suggesting that the experimental outcomes are likely a convolution of size asymmetry and r-BMA size polydispersity*".

In turn, as outlined in our conclusion section, this provides guidelines to control surface structure of such films promising "*substantial progress academically (e.g., in our fundamental*

understanding of non-equilibrium and equilibrium surface and bulk structure formation) and technologically (e.g., towards emergent properties for applications spanning coatings, microelectronics, and membrane-based separations all the way to self-healing)." We are thankful for this comment as it has allowed us to define our detailed working hypothesis in the revised version of our paper.

Comment #5:

Finally, since the BD analyses assume equilibrium structures, what can the authors do to convince readers that these are near equilibrium structures as opposed to SNIPS specific processed structures? Can they be reasonably perturbed e.g. thermally or by solvents, and regain their structure etc. kind of questions arise in this regard.

Response:

This comment is tightly linked with earlier comment #2 of this reviewer: *"..aren't the structures being fundamentally modified by SNIPS to become an observable structure, rather than being a general technique for observing the "unperturbed" BCP surface structure?"* and our associated response. Here we would like to direct the reviewer to the description of our BD simulations in the *Simulation Methods* section where we describe details of the work:

"*The strength of the second wall changes dynamically throughout the simulation to reflect the changes in the interfacial conditions (vide supra; see main text for a more detailed description). At the start, it is the same for all chemical species (normalized by micelle size), but as the simulation goes on, it is increased for species we expect to be repulsed by the interface (ISV and ISVO) and decreased for others (SVPS). This change drives the surface transition and leads to the observed structures. See Supplementary Fig. 5 for a schematic of the wall potential and its evolution.*"

In other words, the BD simulations take the evolving environment into account, e.g., in the form of changing liquid-air interfacial interactions as solvent evaporation proceeds. It is therefore in and of itself not simply assuming equilibrium structures, but rather assumes, as we have discussed in our response to comment #2 of this reviewer, that the structures we see after the water plunge are essentially reflecting the behavior of the surface structure just before this last step of the SNIPS process. We note that we performed separate Monte Carlo (MC) simulations to probe the expected 2D equilibrium state of the BCP alloys at the same surface compositions as those found in experiments/BD simulations, expectedly showing that the latter are typically inconsistent with equilibrium structures.

Reviewer #2 (Remarks to the Author):

The authors study self-assembly and surface pattern formation in binary and ternary mixtures of multi-block copolymer micelles (PI-b-PS-b-P4VP, PI-b-PS-b-P2VP-b-PEO, PS-b-P4VP-b-PPS) upon drying from a good solvent - THF-dioxane mixture. Due to the poor electron density contrast between the blocks in their native state limiting the use of electron microscopy imaging, non-equilibrium porous morphology is generated by immersion of still-drying films in water (SNIPS process), to help discerning micelles made of distinct BCPs during consecutive SEM examination. SEM images analyzed using the FFT method, Voronoi analysis, and cluster analysis along with the Monte Carlo/Brownian Dynamics simulations all reveal complex yet controllable non-equilibrium surface pattern formation behavior. The authors employed the random forest ML approach for image analysis to discern the pores and create segmentation maps. These maps were then used to analyze the distribution of the pores by employing FFT to analyze the structure of the material as well as modified Voronoi analysis to capture the number of neighboring cells, which allowed them to detect defects in the lattice. The authors used the above-described techniques to analyze the morphology diagrams of binary and ternary films consisting of 3 different BCPs (the latter rarely encountered in previous reports) and determine how the different mixing ratios, as well as different polymer molecular weights, affect the structure defect density. These results were further confirmed by Brownian dynamics simulations.

The analysis provided in the manuscript is very thorough and in my opinion it is of potential interest to the readers of Nature Communications. The authors report the formation of intriguing binary and ternary morphologies formed by square and hexagonal arrays of soft micelles and several interesting findings; some already known in hard colloids e.g. mobility-driven surface enrichment of smaller micelles, well-supported by rich experimental data and simulations. The approach to analyzing structural parameters of BCP materials proposed by the authors can help overcome limitations in currently available structural analysis techniques and allow further progress in the understanding of complex self-assembly scenarios in the field of BCP micelle and colloidal systems alloying.

Response:

We very much thank this reviewer for the very positive overall assessment of our work, and especially for pointing out that our analysis "*is very thorough*" and that our findings are "*interesting*" and "*intriguing*".

Although the use of SNIPS aided the visualization of the pores forming in the polar cores of micelles and enabled further analysis, it also seems to be a major factor in increasing the complexity of the approach taken by the authors.

Comment #1:

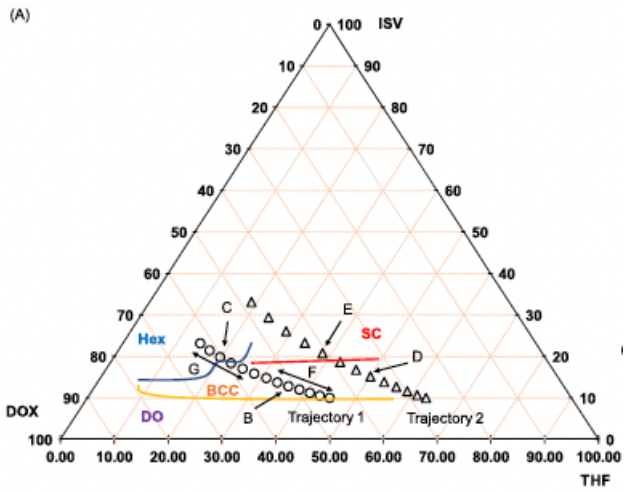
Could the authors provide information on the role of evaporation rate on the ordering process and if it has been controlled? What was the rationale for selecting the reported evaporation

times before the SNIPS? What was the solvent content at the moment of immersion and how thick were the films? These metrics should be more informative than the reported evaporation times.

Response:

We thank the reviewer for this comment and questions. As outlined in the *Methods* section under *Porous film preparation via SNIPS,* film formation and evaporation were controlled to the extent that the whole process was conducted in a humidity-controlled dry box. As stated in this section: "*Before each cast, the gate height was manually adjusted to 0.203 – 0.229 mm, and dry box relative humidity purged to 40 – 45% (ambient temperature 18 – 20 °C) with dry nitrogen gas*." After BCP solutions (60-150 μL depending on viscosity) were pipetted onto glass substrates, casting and water-bath insertion speeds were controlled with a computer-controlled step motor. Furthermore, the evaporation time of 80 seconds was selected so that across all BCP micelle systems studied well-ordered top surface structures were attained. Finally, in the revised version of our manuscript, in the *Porous film preparation* section in *Methods* we now added that the "*resulting film thickness after complete drying was typically of order 40-50 microns*."

As this reviewer can imagine, the question about the exact solvent content *at the moment of the immersion* is non-trivial to answer for such complex multicomponent mixtures (including two solvents and up to three BCPs). Below is an experimental ternary phase diagram of terpolymer ISV (similar to the one used in the current study) in binary DOX and THF solvent mixtures (also used in the current study) that we published earlier (see Fig. 2 in *Macromolecules* 2020, **53**, 4889; now reference 50 in our revised manuscript, see earlier response to comment #2 or reviewer #1). It shows composition changes for a 10 wt.% solution concentration of the ISV terpolymer caused by solvent evaporation in 10 second intervals and predicted assuming ideal solution behavior using Langmuir's considerations of evaporation of pure solvents and Raoult's law for estimations of vapor pressures. BCC, Hex, and SC represent regions where solutions show body centered cubic, hexagonal, and simple cubic structures, respectively. The transition between disordered and BCC structures is indicated by an orange line, that between BCC and Hex with a blue line, and that between BCC and SC with a red line. The left trajectory 1 (circles) starts from 5:5 DOX/THF, while trajectory 2 (triangles) starts from 3:7 DOX/THF:



It is very important to note that even these composition predictions for a ternary system are already gross oversimplifications. This is because the ideal behavior assumes homogeneous solution structure. While true for the model measurements leading to the ternary phase diagram shown above, this is *NOT* the case for the evaporating films described in the current study. In the current study, via evaporation across the film-air interface, the top surface layer densifies much faster than the underlaying sublayer(s), leading to a pronounced concentration gradient along the film normal. It is this concentration gradient which makes the non-solvent induced phase separation process highly valuable for asymmetric membrane formation. But at the same time, it renders estimates of the solvent content and/or component concentrations at the moment of film immersion exceedingly difficult. This is why in our current manuscript we stepped away from an effort to quantify this metric and rather stayed with metrics that are reliable and reproducible for anyone trying to do the same or similar experiments.

It is clear from this discussion that indeed, as this reviewer correctly points out: "*Although the use of SNIPS aided the visualization of the pores forming in the polar cores of micelles and enabled further analysis, it also seems to be a major factor in increasing the complexity of the approach taken by the authors."* In other words, from the SNIPS induced porosity we gain an ease of film surface structure determination and analysis at the expense of complexity of the studied system. Our work is an early effort to shed light on the opportunities as well as complexities associated with such multicomponent BCP micelle alloys. That is why we conclude the paper pointing towards the need of further developments by stating: "*BCP micelle 'alloying' (BMA), i.e., the treatment of chemically distinct BCP micelles as soft colloids, remains largely unexplored. As advocated in the introduction, this is largely due to difficulties in such multicomponent soft nanomaterials characterization. The current experimental surface structure formation study suggests that these limitations can likely be overcome via continuous advances in experimental and computational methods*."

Comment #2:

Under what conditions the equilibrium morphologies are expected to form and how far are they from the conditions reported here?

Response:

For the response to this important question, we would like to point this reviewer to our detailed response to comment #2 of reviewer #1, which covers the exact same topic.

Comment #3:

Is the PEO block long enough to prevent the fusion and formation of worm-like micelles after longer evaporation in the ISV-ISOV system?

Response:

As we discuss in detail in Supplementary Discussion 2, we have very carefully checked that once BCP micelles of individual BCPs are formed, molecular chain exchange does NOT take place on the time scale of our experiments (~1 hour total). We are therefore quite certain that fusion or worm-like micelle formation processes are entirely suppressed in our systems.

Comment #4:

Why the authors did not employ a simpler and well-known P2VP-core staining method i.e., by using platinum complexes?

Response:

We very much appreciate this comment as staining methods were our initial go-to technique in trying to understand details of the structure formation processes in these film surfaces. But as described in the introduction, the very high sample numbers (i.e., hundreds of films) that we have investigated to complete this study have precluded such labor intensive and also more expensive techniques.

It would be very interesting to cross-compare the results of structural image analysis of surface patterns with the underlying bulk film morphology either by X-ray scattering or by cross-sectional SEM analysis. Have the authors performed such analyses?

Response:

We thank this reviewer for this important question and would like to refer to our response to earlier comment #3 of reviewer #1 who asked a very similar question.

Minor comments and remarks:

Information on casting conditions including total typical BCP concentration (main text) and blade velocity (expressed in units other than motor spins-per-second) and the resulting film thicknesses are missing.

The total BCP concentrations are tabulated in Supplementary Table 2 of the SI of our manuscript. As requested by this reviewer, in the main text of the revised manuscript the beginning of the section *BCP micelles as soft colloidal building blocks* now provides the general range of BCP concentrations used which was between 10 and 20 wt%. Finally, in the revised version of our manuscript, in the *Porous film preparation via SNIPS* section in *Methods* we now report that the blade velocity was "*15 mm* s^{-1}" and point out that the "*resulting film thickness after drying was typically of order 40-50 microns*."

In supplementary fig S9d, the inset should be marked in more visible manner (it looks like a part of image)

We thank this reviewer for pointing us to a figure panel in the Supporting Information which was unclear. In response, in the revised version we have replaced Fig. S9d with a revised panel which now should make it easier to understand what we did. We also revised the caption accordingly.

Supplementary notes, in particular those concerning the choice of material's (#1), cross-micellar chain exchange (#2), and also note #4 are critical for understanding the concept of this work. In particular, the authors should consider extracting the salient points provided in note #2 and moving it to the main text for further support claim from p. 6.

We very much appreciate this comment. Following the suggestions (as well as earlier comments), in the section *BCP micelles as soft colloidal building blocks* starting on page 5, the revised version of our manuscript now has been expanded by language not only around the salient points of Supplementary Discussion 2 but also around those of Supplementary Discussion 1. Major revisions include the following revised text passage:

"*Figure 1a schematically depicts the three BCP micelle building blocks (ISV, ISVO, SVPS), where colors reflect distinct core and corona chemistries. Figure 1b illustrates individual steps in the SNIPS process: (1) film deposition, (2) doctor blading, (3) evaporation, and (4) plunging into water bath. All BCPs share the same base (> 80 wt.% PS + PVP), allowing a common solvent mixture (tetrahydrofuran and 1,4-dioxane) to be used. At typical BCP concentrations (10 to 20 wt%), PVP forms the core and PS forms the corona, irrespective of the additional smaller blocks (Supplementary Discussion 1).*"

As well as:

"*Additional experiments confirm negligible cross-population micelle chain exchange on the timescale of film casting due to large micelle core block size, relatively concentrated solutions, and room temperature processing (see Methods, Supplementary Figs. 6,7 and Supplementary Discussion 2), validating this degree of coarse-graining and, fundamentally, the micelle-as-building-block treatment*."

Reviewer #3 (Remarks to the Author):

This work beautifully illustrates new surface analysis methods for the surface of porous films of BCPs via SNIPS methods. BCPs have been synthesized by anionic polymerization, which allowed the resulting BCPs to have well-defined structures and molecular weights. In particular, the MWs of the BCPs used in this study were quite high, presumably, for obtaining mechanically robust structures. SNIPS methods have been widely used for creating isoporous BCP membranes on the top surface, which are supported by microporous structures. The resulting film appeared to have monodisperse-sized surface pores that are arranged in regular order, such as a hexagonal array or a tetragonal array. Considering the thickness of the top layer (~ a few hundred nanometers), the top porous layer could be considered as two-dimensionally ordered pores or three-dimensionally ordered bicontinuous (cubic) structures. In this case, the arrangement of the surface pores reflects the order of the internal structures.

This work is unique because the authors found the co-cosolvent compositions for the micellization of BCPs. Using these conditions, they mixed BCPs to form micellar mixtures rather than simple BCP blends. SNIPS of these micellar mixtures resulted in the formation of porous films having surface pores, of which their arrangements might reflect the mixing or demixing state of the micellar mixture (here, named to a BCP micelle alloy). In general, the detailed structures of the ordered domain of the porous films formed by SNIPS have been studied by SAXS. However, this technique cannot be used for studying the mixing or demixing of the BCP micelles. The authors, in this work, used image analysis techniques to characterize the lattice and lattice constant. Also, the contrast of the SEM image provided information on the pore sizes, which are characteristic of BCP micelles.

Response:

We very much thank this reviewer for the very positive overall assessment of our work, and especially for describing it as both "*beautiful*" and "*unique*", very important qualifier for publications in *Nature Communications*.

If the image-based analysis of the top surface could provide information of the porous structures underneath the top surface, the reported analysis could be unique as X-ray analyses would give the structural details by averaging different micellar domains. However, the manuscript is confusing in some ways:

Comment #1:

The self-assembly procedure is similar to conventional SNIPS procedures except for the spinning part. Why did the films spin? Was this to make the film thinner? Or was it related to the

evaporation rate of solvents? To avoid confusion, the self-assembly methods should provide more details (for example, concentrations of BCP solutions, and the thickness of the resulting films).

Response:

We believe that this reviewer may have been confused by our language in the Method section on the step motor speed for doctor blading originally only provided in spins per second. As pointed out in our response to the *Minor comments and remarks* of Reviewer #2, to prevent this confusion in the revised version we now outline that the spinning of the motor translates to a velocity of the doctor blading process of "*15 mm* s^{-1}". This response also described revisions introduced in the paper that provide BCP solution concentrations (between 10 and 20 wt%; for details please see Supplementary Table 2) as well as total film thickness after complete drying (between 40 and 50 microns).

Comment #2:

Assuming the thickness of the film is greater than that of the micelle monolayer, solvent evaporation, and non-solvent quenching will introduce phase transition and inversion. How could the final structure after phase separation and inversion be related to the (assumed) micellar aggregation during self-assembly?

Response:

We refer this reviewer to our detailed response to earlier comment #2 of reviewer #1 which addresses this important point in detail. To reiterate (in short): Reviewer #3 correctly describes the overall structure of the films after the SNIPS process. Only in the top 100 nm or so is the BCP concentration high enough from evaporation to lead to periodic lattices via micellar aggregation that we describe in our manuscript analyzing the top surface layers. As pointed out in our response to comment #2 of reviewer #1, from earlier work we know that these micellar lattices are generated during the evaporation time and are then phase inverted (via inserting the films into water) into the porous 2D structures we see on the final film surfaces. While details of this inversion/conversion are, to the best of our knowledge, not well understood yet, these lattices formed during evaporation are essentially maintained after precipitation in the water bath.

Comment #3:

Tetragonal arrangements of surface pores suggest that the internal porous structures would be bicontinuous. If the segregated domains of BCP micelles were observed like in this study, could the internal porous structures (or bicontinuous structures) be segregated as well? How can we analyze this?

Response:

We thank this reviewer for this interesting question. We know from in-situ GISAXS experiments referred to earlier that the overall lattices governed by the ISO/DOX/THF model system in the top surface layer are not tetragonal but cubic (either BCC or SC, see Figure in our

response to comment #1 of reviewer #2). The reviewer is correct that this leads to continuous internal pore lattices in the top portion of the films. In-situ experiments on films described in our paper here to analyze such internal structures would be extraordinarily challenging, however. This is because, as suggested by our experimental results described in the current manuscript, rather than one lattice, we often have two lattices that co-exist (cubic and hexagonal lattices, e.g., see Fig. 3 of the current manuscript) and/or have lattices that consist of two chemically distinct building blocks (i.e., micelles) of difference sizes. Furthermore, since we looked at hundreds of film samples to deduce the guiding principles described in our paper reviewed here, performing synchrotron experiments on such a large number of samples needed to understand and control mixed lattice film surface structures would have been impossible. This all led us to the conclusion that, as described in this paper (e.g., see abstract and introduction), novel characterization approaches were needed that at the same time allow large sample numbers to be analyzed *and* provide detailed structural analysis of the complex surface patterns. The results of years of such experimentation are summarized in this paper. As pointed out in our detailed response to comment #1 of reviewer #2 as well as our manuscript's conclusion section, it is well understood, however, that our work can only be the beginning and that *"..continuous advances in experimental and computational methods"* are needed in order to address the question raised by this reviewer about details of the internal structure as well as other important questions that our studies raise.

Comment #4:

Some of the analyses of the stoichiometry of the BCP micelles on the surface and the simulations assumed that the micelles behave as small colloidal particles and that the surface structures reflect the results of colloidal assembly. I do not believe this is true for the film created by SNIPS methods. Simulation results are not in line with experimental analyses, which might indicate that SNIPS is different from colloidal assembly. If the reported analysis and techniques could be related to the characterization of internal structures, this paper merits publication in Nature Communications.

Response:

We thank this reviewer for this comment. First, we would like to refer this reviewer to our detailed response to comment #4 of reviewer #1 which provides examples of how earlier studies in colloidal systems help us to understand the behavior of our soft micellar systems. Second, we feel that the statement that "*Simulation results are not in line with experimental analyses*" is a bit of an over-generalization. Instances of inconsistency and their origin we discuss in the paper are:

(1) for the BD simulations of ISV-ISVO, the simulation shows a stoichiometric dependence, but the segmentation does not. We address this by citing limited mobility of the ISVO (experimentally) and demonstrating presence of ISVO via lattice spacing.
(2) for the monodisperse BD simulations of the size asymmetry series, which we address by considering polydisperse BD simulations

(3) for the MC simulations, which are explicitly meant to contrast calculated equilibrium-based behavior with observed non-equilibrium film surface structure formation.

In the initial response (*vide supra*), reviewer #1 writes that: "*The approach invokes concepts of colloidal phenomena such as solution (BMA micellar) composition ratio, size asymmetry and polydispersity ratio.*" Furthermore, Reviewer #2 points out that: "*The authors report the formation of intriguing binary and ternary morphologies formed by square and hexagonal arrays of soft micelles and several interesting findings; some already known in hard colloids e.g. mobility-driven surface enrichment of smaller micelles, well-supported by rich experimental data and simulations*." This is consistent with our findings, e.g., that our film surface structures are dependent on control parameters, i.e., micelle-micelle interactions (neutral and repulsive), solution stoichiometry, and size asymmetry and polydispersity, in ways known from a wealth of studies in colloidal science. We therefore maintain the assumption that our BCP micelles behave as soft colloidal particles and that the surface structures reflect the results of colloidal assembly mechanisms. It is worth mentioning that this interpretation is also consistent with a wealth of data from earlier investigations (*vide supra*).

We would like to emphasize that the colloidal assembly scenarios we discuss in our manuscript only apply to the surface regions of our SNIPS derived films. Moving away from the surface, beyond the first 100 nm or so, the BCP concentration reached upon the relatively short evaporation time of 80 seconds used remains below the overlap concentration of the micelles and particle-particle interactions do not govern their assembly into well-defined lattices anymore. This description is consistent with the ideas described by this reviewer.

Finally, to address the question of this reviewer whether the: "*reported analysis and techniques could be related to the characterization of internal structures"*, we refer to our response provided to the earlier comment #3 of this reviewer #3.

POINT-BY-POINT RESPONSES TO REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have done a very nice job of addressing my (and almost all other reviewer comments as I can assess)!

Response:

We very much thank this reviewer for this very positive overall assessment of our response to the original reviews and associated revised manuscript.

For me, not to speak for other reviewers, the only remaining question / possible work they can do is suggested below:

Authors mention to another reviewer's comments: "As this reviewer can imagine, the question about the exact solvent content at the moment of the immersion is non-trivial to answer for such complex multicomponent mixtures (including two solvents and up to three BCPs)."

So one way to do this may/should be to place the sample upon coating immediately on top of a 4 (or 5 decimal place) weighing balance placed inside the film casting glove box, and then compare the initial weight at t=0s, to that after 80 s of evaporation. I think the mass loss in 80s on a 50 micron thickish film should be measurable gravimetrically! Of course they should weigh the dry glass slide / substrate prior to any coating, and then let it fully dry with the film after inversion and maybe even warm it up some for some time to remove residual solvent, and report the dry film weight. Once, all these weights are documented, knowing the (average) density of the dry BCP mix film, and the solvent weight loss in 80 s, the slide area covered by the initial casting mixture, and assume some typical average polymer mix, and solvent mix density, they should be able to calculate the volume at t=0 vs t=80 s. The initial t=0 and final height at t=80 should be calculable knowing the initial area. If the area shrinks in 80s, even then it can be accounted for by measuring it at 80s, to give (corrected) film thickness at 80 s.

Just my suggestion - note this is all done gravimetrically so should be possible. Only thing is that the mass of the glass slide/substrate should be not too high for accuracy and sensitivity for recordable solvent mass loss on a 4 or 5 digit balance!

Response:

We very much appreciate this reviewer's suggestion. The proposed work would indeed allow estimation of solvent content at instance of immersion. In response to this comment, we would like to point to our previous response to Comment #1 of Reviewer #2, who raised this question in their initial review (and who was entirely satisfied with our response to their inquiry, see below). In our response we wrote:

"It is very important to note that even these composition predictions for a ternary system are already gross oversimplifications. This is because the ideal behavior assumes homogeneous solution structure. While true for the model measurements leading to the ternary phase diagram shown above, this is NOT the case for the evaporating films described in the current study. In the current study, via evaporation across the film-air interface, the top surface layer densifies much faster than the underlaying sublayer(s), leading to a pronounced concentration gradient along the film normal. It is this concentration gradient which makes the non-solvent induced phase separation process highly valuable for asymmetric membrane formation. But at the same time, it renders estimates of the solvent content and/or component concentrations at the moment of film immersion exceedingly difficult. This is why in our current manuscript we stepped away from an effort to quantify this metric and rather stayed with metrics that are reliable and reproducible for anyone trying to do the same or similar experiments."

In other words, even if we were to follow Reviewer #1's suggested gravimetric approach, the concentration gradient along the film normal would still prevent us from quantifying the desired exact solvent concentration in the film's top surface layer – where the periodic structure formation we discuss in our paper is taking place. This is why we emphasized in our original response above that "*we stepped away from an effort to quantify this metric…*"

Reviewer #2 (Remarks to the Author):

I appreciate that the Authors provided detailed explanations and expanded on their choice and critical assessment of experimental methods in response to my comments. They clarified that the film casting and solvent evaporation were tightly controlled in a humidity-regulated environment, with specific experimental parameters now explicitly mentioned. They also provided a previously-reported phase diagram to addressed my concerns about solvent content and morphologies in evaporating films by explaining that, due to the complexity of their multicomponent system, they relied on reproducible metrics rather than attempting to quantify the solvent composition at the moment of immersion in SNIPS. I am now convinced that the Authors have thoroughly explained that SNIPS provides a practical insight into the surface structure of a thin film composed of BCP micelles without substantially modifying its key characteristics. Finally, they justified the choice to avoid staining by citing the high number of samples involved, improved the clarity of supplementary figures, and discussions in the main text.

Overall, I feel that these revisions adequately address my critical comments and, along these made in response to the comments by Referee #1 and Referee #3, improved the overall quality of this manuscript.

Response:

We very much appreciate this kind assessment of our responses to the original comments of this reviewer and the associated revisions introduced to our manuscript. In the context of Reviewer #1's comment discussed above, we are particularly appreciative of this reviewer's articulation of the following argument: "…*due to the complexity of their multicomponent system, they relied on reproducible metrics rather than attempting to quantify the solvent composition at the moment of immersion in SNIPS*."

Reviewer #4 (Remarks to the Author):

We have carefully reviewed the authors' responses to Reviewer 3 and find that most of the concerns have been thoroughly addressed:

1. Coating parameters and film thickness: The authors have now included the doctor-blade speed (15 mm s-1), block-copolymer concentrations (10–20 wt %) and measured film thickness (40-50 µm) in the Methods section, directly resolving the reviewer's query about "spinning."
2. SNIPS-derived micelle aggregation: They have reinforced their description of evaporative self-assembly in the top ~100 nm, where micellar lattices densify and are preserved upon water-quench, to explicitly connect the SNIPS protocol to the observed surface porosity.
3. Non-equilibrium simulation framework: Their BD simulation now clearly incorporates a time-dependent wall potential to mimic the receding liquid–air interface, and complementary Monte Carlo runs demonstrate that the final structures cannot arise under equilibrium alone.

Response:

We very much appreciate this very positive assessment of our revision work.

However, Reviewer 3's principal concern remains: whether the bicontinuous internal pore network truly mirrors the ordered surface layer. At the current stage, the authors have justified their surface-only focus by citing experimental difficulty, but they have not proposed any concrete follow-up. To fully satisfy this point, we recommend that the authors include a brief feasibility discussion of one or more targeted techniques, for example: selective GISAXS on simplified binary blends to isolate individual lattice parameters, cross-sectional SEM images on small sample regions to visualize internal connectivity, or preliminary small-angle neutron scattering experiments using deuterated blocks to enhance internal contrast. We support acceptance of the manuscript after the inclusion of these additional data.

Response:

To address this suggestion, in the discussion section at the end of the paper we have introduced the following text:

"*For example, it would be desirable to go beyond the top surface discussed here and reveal whether sub-surface layers mirror its structure and order. Continuous advances in X-ray*

ptychography have recently enabled large-volume reconstruction of self-assembled BCP structures[46]. Backfilling the ordered pores of BMAs with inorganic materials exhibiting higher electron density contrast and stability may help such efforts. Alternatively, one could subject BMA film surfaces to controlled reactive ion etching gradients and analyze resulting depth-dependent SEM images via ML assisted image segmentation."