Reviewer 1

Recommendation: Publish in ACS Nano after minor revisions noted.

Comments:
The paper presents an interesting study of the confinement effects on the structure and stability of the blue phases of chiral liquid crystals. The paper combines experiments with high-level numerical simulations of the structures and properties. An excellent feature is the application of confocal laser scanning microscopy. The paper is richly illustrated and well written.
Minor comments:
1. The references are not in order.
2. It is not clear how Figure 3e could illustrate the reduction in phase transition temperatures (page 5, left column), as it shows a simulated structure. Apparently, the authors meant to refer to Fig.2e
3. The funding source is duplicated and there is a remnant of a template in Funding Sources.

Reviewer 2

Sadati et al. reports the switching between blue phase I (BP-I) and blue phase II (BP-II) as a result of temperature changes to the system, where the chiral liquid crystal is confined within spherical droplets and the blue phase is made more stable through photopolymerization, as established in bulk films in the previous work of Castles. The switch between different blue phases found in their system has not been achieved experimentally before and is a significant finding for the fields of liquid crystals and self-assembly, especially since the disclinations of the blue phases are populated by a polymerized material. The work is fascinating, and the findings should be of interest to the broad ACS Nano readership. However, the following points should be addressed before I can fully support the publication of this work:

1. The authors use super-resolution confocal laser scanning microscopy to capture high-resolution micrographs of the blue phases. Yet, the system conditions necessary to

successfully perform such high-resolution confocal measurements are usually stringent, where index matching of the surrounding solvent is necessary to prevent noise from scattering, and a precise thickness of the coverslip and the type of glass used are all important details. No such details are mentioned in Methods, which makes me wonder exactly how their imaging works... The authors note that their samples are label-free. Does this mean that their confocal images are just a result of scattering of the confocal laser light, since the structures of the material have periodicities that are on the order of the wavelength of visible light...? Discussion of the their imaging technique is necessary, especially if the technique is relatively new and has only been used once before (as the authors reported on pg. 6). Does their captured data change if the index of the surrounding water is altered? Furthermore, many of the experimental images also lack scale-bars. If the authors are obtaining high-resolution images, then scale-bars for the magnified images is needed. Additionally, which laser wavelength is used for which images? Without these details, it would be difficult for others to reproduce their work with the information presented in the manuscript...

2. On pg. 5, the authors also describe the energy contribution from polymerization of the monomers within the disclination lines. They use this to determine that the phase transition temperatures of their system is size-dependent, due to confinement within droplets. Since this is one of the major findings of this work, the assumptions used for the energy contribution from polymerization is necessary within the main text, instead of only placed within supplemental materials. I do not doubt their conclusion from this calculation, but one assumption is that the polymerization is considered only to the extent of polymer cylinders, when indeed polymers must also be populating the junctions. Their energetic contribution from the junctions should have an impact on whether it is possible for BP-I and BP-II to switch between one another (detailed further in the point 3).

3. The most exciting discovery of this work is that, for "larger droplets," the authors find a reversible transformation between BP-I and BP-II, even though the disclination lines are polymerized. This is quite incredible, if true. The polymerization should result in some elasticity in the disclination network. Does the shift from BP-I to BP-II require topological changes to the disclination network? That is, are tears in the network structure necessary to shift from BP-I to BP-II? If so, that would make this shift extremely mysterious, as surely temperature changes alone should not be enough to create tears, if the monomers are truly cross-linked... If tears are not needed, are some of the disclination lines forced to buckle and fold up? If this is the case, then these folded areas would likely introduce imperfections in the crystal structure, that could also show up in their confocal imagining at high enough resolutions... Further discussion of the possible mechanisms behind this shift is needed, and would further highlight the significance of their findings.

4. On page 3, the authors write, "... when low chirality liquid crystals are confined within microdroplets, no droplet size-dependency has been reported on the optical properties of

the polymerized LC droplets and instead the reflected color changes have been achieved by [tuning] the amount of chiral dopant." This statement is too simplified, as it only considers low chirality droplets with planar anchoring, where defects from planar droplet geometries are highly localized and do not span the system. Comparing only this simple planar arrangement to BP's that are filled with defects is too basic of a comparison, especially when past work has indeed demonstrated that low-chirality cholesterics have altered defect structures with changes in their geometrical confinement. This has been seen for cholesteric droplets with homeotropic anchoring (see Sec, Copar, Zumer, Nature Communications, 2014; Posnjak, Copar, Musevic, Scientific Reports, 2016; amongst others) as well as for cholesteric double emulsions with homeotropic anchoring (see Tran, et al., Phys. Rev. X, 2017; Durey, et al., Soft Matter, 2020; Tran, et al., ACS Nano, 2020). The comparison would be more accurate and complete when considering, more broadly, cholesterics with defects that change their structure with system size, especially systems where defects span the system (i.e., when they have homeotropic anchoring). This statement should be modified to reflect this, and studies of cholesterics emulsions with more diverse defects should also be cited.

5. At the end of pg. 3, the authors write "With longer UV exposures, the centers of the distributions of the droplets... were slightly shifted to larger diameters." The data for this should be included, either within Fig. 2 or in supplementary materials.
6. Twice in the manuscript, the authors state that simulation results are in "excellent

agreement" with the experimental data. "Excellent" is too strong of a word, especially since the authors do not state a quantitative comparison from simulations to experimental data. It is more accurate to state that the simulations are in "qualitative agreement" instead.
Despite these points of critique, let me iterate again that I do think that this work is significant and worthy of publication in ACS Nano. Addressing the above points would place the importance of their findings in a more accurate context of the study of chiral liquid crystals under confinement and would allow readers to better interpret their findings and to reproduce their work. The nature of the polymer assembly within the BP disclination lines is an open question, that is newly investigated by their system.