SUPPLEMENTARY INFORMATION

Nematic Colloids at Liquid Crystal-Air Interfaces via Photopolymerization

Xiaoshuang Wei, Nicholas Sbalbi, and Laura C. Bradley*

Department of Polymer Science and Engineering, University of Massachusetts Amherst,
Amherst, Massachusetts 01003, USA
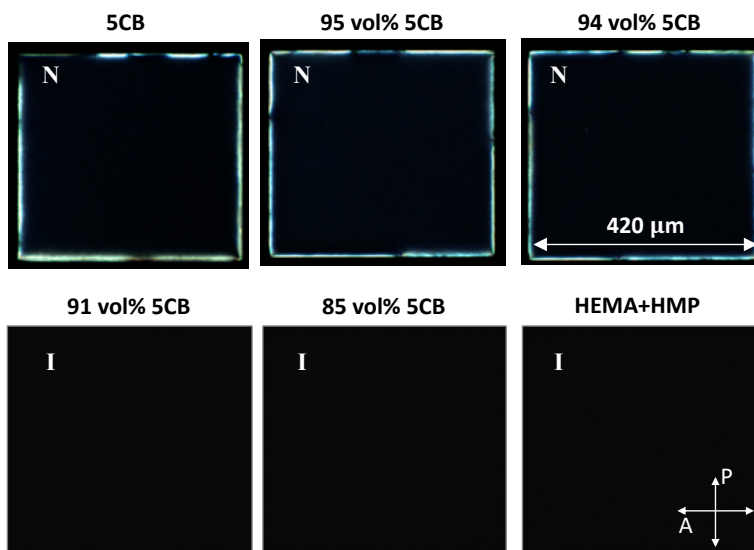*Corresponding Author's Email: laurabradley@umass.edu

Figure S1. Polarized optical microscopy images characterizing the initial phase, nematic (N) or isotropic (I), of reaction solutions at room temperature before UV exposure. Bright boundaries of the square cells in the TEM grid are caused by homeotropic anchoring at the vertical surfaces of the copper TEM grid and represent a nematic phase. The absence of bright boundaries indicates an isotropic phase.

Quantification of Monomer Polymerization and Evaporation in Open-Cell Systems

Monomer polymerization and evaporation in open-cell systems was quantified by measuring the solution composition using ^{1}H NMR spectroscopy. To acquire enough sample volume, multiple 1 μL droplets of the reaction solution were used for this analysis. The droplets were concluded to be an appropriate model system for solutions pinned in TEM grids because of the agreement in the measured droplet composition by NMR and the solution phase in TEM grids determined by polarized optical microscopy. First, the HEMA concentration in reaction solutions as-prepared and after the annealing step was determined. Evaporation was monitored by aging samples at room temperature (no UV exposure). Separate experiments with low power UV exposure (1.2 mW/cm^2) measured the change in the HEMA monomer concentration due to both polymerization and evaporation, as well as the final PHEMA concentration. All concentrations were calculated based on integration of peaks representative of 5CB (7.87 ppm, protons on the benzene ring close to the cyano group) and HEMA (6.11 and 5.63 ppm for the protons on the C=C bond; 4.21 and 3.79 ppm for the -CH$_2$ protons).

Table S1. Comparison of the HEMA concentration measured by ^{1}H NMR spectroscopy for evaporation only and a 3 hour, low power UV exposure for solutions with initial 5CB concentrations of 95 and 85 vol%. The phase (nematic or isotropic) is reported for the solutions as-prepared (initial) and after UV exposure (final).

Sample	$C^o_{5CB} = 95$ vol%		$C^o_{5CB} = 85$ vol%	
	vol% 5CB	vol% HEMA	vol% 5CB	vol% HEMA
Reaction solution, as-prepared	94.9 ± 0.15	5.14 ± 0.15	85.0 ± 0.22	15.0 ± 0.22
Reaction solution, after annealing (10 min. at 40 °C)	95.6 ± 0.22	4.39 ± 0.22	87.0 ± 0.36	13.0 ± 0.36
After 3 hr. evaporation only at 25 °C	99.2 ± 0.13	0.79 ± 0.13	95.4 ± 1.17	4.59 ± 1.17
After 3 hr. UV exposure at 25 °C	99.6 ± 0.31	0.17 ± 0.28	95.6 ± 0.59	2.98 ± 0.55
Final PHEMA concentration	0.27 ± 0.08 wt%		1.56 ± 0.54 wt%	
Initial solution phase	Nematic		Isotropic	
Final solution phase after 3 hr. UV exposure	Nematic		Nematic	

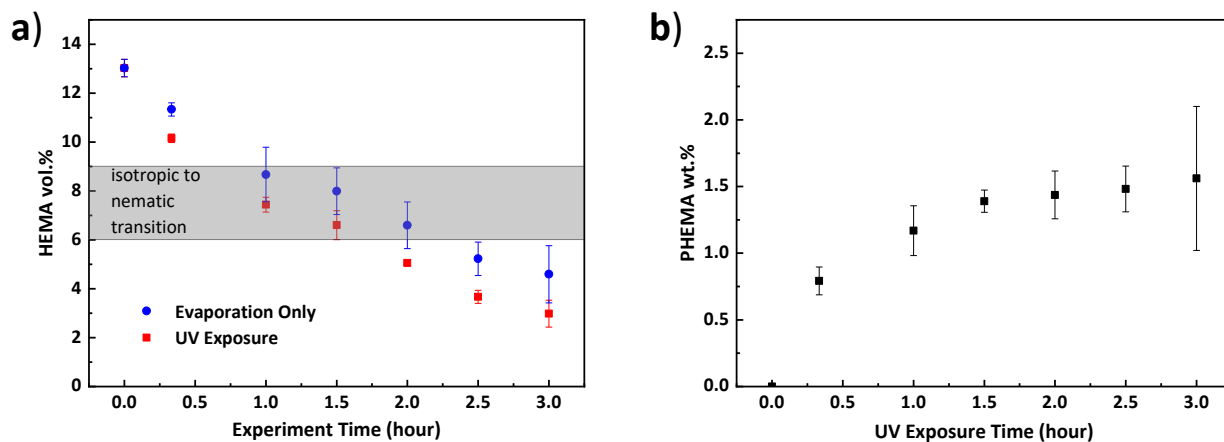**Figure S2.** a) HEMA concentration measured by ^{1}H NMR spectroscopy as a function of experiment time ($C^o_{5CB} = 85$ vol%). b) PHEMA concentration as a function of low power UV exposure time.

Optical Profilometry of Polymer Colloids Adsorbed to the 5CB-Air Interface

Optical profilometry was used to confirm that the PHEMA colloids are pinned at the 5CB-air interface (**Figure S3**). It should be noted that the magnitude of local variations in interface curvature surrounding colloids at the air interface cannot be inferred from Figure S3 due to limited areal resolution associated with the objective aperture and small length scales of the colloid size and spacing. The equilibrium contact angle for 5CB on PHEMA thin films was measured by contact angle goniometry (AttensionTheta) to be $22 \pm 3°$ (average value of 30 individual 5 µL droplets). The low contact angle indicates the majority of a PHEMA colloid would be submerged in the 5CB phase.
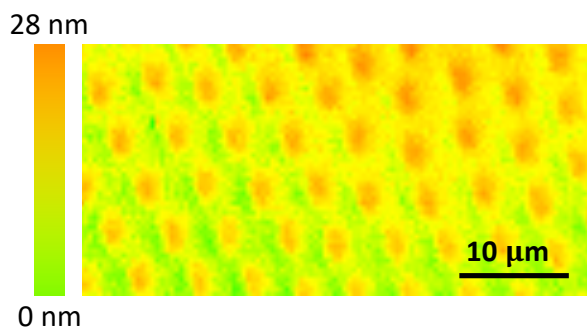

Figure S3. Optical profilometry image of PHEMA colloids at the nematic 5CB-air interface after a 3 hour, low power UV exposure (C_{5CB}^o =85 vol%).

Colloid adsorption was observed while the system was still isotropic (prior to the isotropic-to-nematic transition). Spontaneous adsorption to the air interface is predicted based on attractive van der Waals interactions between PHEMA and air. This attractive interaction is described by a positive Hamaker constant, which can be generally assessed by the refractive indexes of the three phases.[1] PHEMA colloids initially immersed in 5CB are expected to spontaneously adsorb to the 5CB-air interface since the refractive index of the intervening phase ($n_{5CB} \sim 1.53 - 1.71$)[2] is larger than both the interacting phases ($n_{air} = 1.00$; $n_{PHEMA} \sim 1.51$).[3] Additionally, convection due to the presence of monomer evaporation is expected to aid colloid adsorption to the air interface.

Structural Analyses of PHEMA Nematic Colloids at 5CB-Air Interfaces

Structural analyses were performed to assess the local positional and orientational order of 2D PHEMA nematic colloids. Characterization of the assembly organization was performed using MATLAB. All relevant equations are summarized below.[4]

Lindemann Disorder Parameter (α):
Local positional disorder is described by α, defined as the standard deviation of the nearest neighbor distance (NND) Gaussian distribution divided by the mean NND (σ):

$$\alpha = \frac{Std\ Dev}{\sigma} \qquad \text{[Equation 1]}$$

Radial Distribution Function (RDF):
Positional correlations can also be assessed by the RDF which calculates the local colloid density relative to the average density of the sample as a function of distance:

$$g(r) = \left[\frac{1}{N}\left(\sum \frac{dn}{dA}\right)\right] / \left(\frac{N}{A_i}\right) \qquad \text{[Equation 2]}$$

In equation 2, dn is the number of colloids that reside within a shell of inner radius r and thickness dr, dA is the area for the circular ring formed between r and $r + dr$ ($dA = 2\pi r dr$), N is the total number of colloids in the image, and A_i is the image area.

Local Orientational Bond Order (ψ_s):
The ψ_s parameter for an individual colloid assesses the orientational s-fold symmetry of its nearest neighbors. Here, it was calculated relative to perfect 6-fold symmetry ($s = 6$). The values of ψ_6 range from 0 to 1, for which a value of 1 indicates perfect symmetry.

$$\psi_s = \left| \frac{1}{N} \sum_{j=1}^{N} e^{is\theta_j} \right| \qquad \text{[Equation 3]}$$

In equation 3, N is the number of nearest neighbors and θ_j is the angle between an arbitrary reference axis and the line connecting the center colloid and its jth nearest neighbor. Colloids with $\psi_6 \leq 0.7$ were classified as orientationally disordered. The average local orientational order of colloids with $\psi_6 > 0.7$ was also calculated; this fraction of orientationally ordered colloids relative to the entire population is defined as f_6.

Orientational Correlation Function, $g_6(r)$:
Orientational correlations can be expressed by $g_6(r)$ which quantifies the angular correlations between the local orientational bond order ψ_6 for colloids as a function of distance:

$$g_6(r) = \left| \frac{1}{N_B} \sum_{l=1}^{N_B} \frac{1}{n_l} \sum_{k=1}^{n_l} e^{6i(\theta(r_k) - \theta(r_l))} \right| \qquad \text{[Equation 4]}$$

In equation 4, N_B is the total number of colloids in the image, $\theta(r_k)$ and $\theta(r_l)$ are angles between bonds at r_k and r_l and the reference axis, respectively, and n_l is the number of bonds at a distance r from bond l. The first distance at which g_6 decays to zero (< 0.01 in our analysis) represents the characteristic domain size.

Table S2. Summary of the structural analyses for ten representative colloid assemblies at the nematic 5CB-air interface. Photopolymerizations were performed in the open-cell setup using an initial 85 vol% 5CB and 3 hour, low power UV exposures.

	Sample	Analysis Area (μm^2)	# of Colloids	Fraction of Colloids with 6 Nearest Neighbors	Lindemann Disorder Parameter (α)	$\langle\psi_6\rangle$ for All Colloids	$\langle\psi_6\rangle$ for Colloids with $\psi_6 >0.7$	Fraction of Colloids with $\psi_6 >0.7$ (f_6)	Normalized Hexatic Domain Size (Δ_6)	Mean NND (μm)	St. Dev. For NND Gaussian Distribution (μm)
Confined	A	135x135	1116	0.96	0.07	0.85	0.89	0.90	45	4.0	0.3
		340x340	5714	0.92	0.11	0.80	0.88	0.81	32	4.3	0.5
	B	135x135	593	0.92	0.07	0.78	0.87	0.76	17	5.4	0.4
		340x340	3445	0.89	0.12	0.76	0.87	0.72	24	5.5	0.7
	C	135x135	742	0.84	0.08	0.68	0.85	0.57	22	4.7	0.4
		340x340	5750	0.85	0.13	0.69	0.85	0.59	24	4.2	0.5
	D	135x135	1263	0.97	0.06	0.84	0.88	0.89	19	3.7	0.2
		340x340	6537	0.92	0.09	0.81	0.88	0.80	24	3.9	0.4
	E	135x135	1061	0.95	0.06	0.82	0.88	0.85	40	4.1	0.3
		340x340	6007	0.92	0.09	0.79	0.87	0.77	37	4.2	0.4
Unconfined	F	135x135	778	0.63	0.08	0.50	0.81	0.24	3	4.4	0.3
	G	135x135	1025	0.65	0.08	0.52	0.81	0.26	2	3.8	0.3
	H	135x135	1098	0.61	0.09	0.50	0.82	0.22	3	3.7	0.3
	I	135x135	865	0.56	0.09	0.48	0.80	0.19	2	4.2	0.4
	J	135x135	467	0.58	0.08	0.47	0.82	0.18	2	5.7	0.5

Table S3. Summary of the structural analyses for four positions within a large area colloid assembly formed using a TEM grid with an oval slot (~1.8 mm^2) as shown in Figure 3d. Photopolymerization was performed in the open-cell setup using an initial 85 vol% 5CB and a 3 hour, low power UV exposure.

	Sample Position	Analysis Area (μm^2)	# of Colloids	Fraction of Colloids with 6 Nearest Neighbors	Lindemann Disorder Parameter (α)	$\langle\psi_6\rangle$ for All Colloids	$\langle\psi_6\rangle$ for Colloids with $\psi_6 >0.7$	Fraction of Colloids with $\psi_6 >0.7$ (f_6)	Normalized Hexatic Domain Size (Δ_6)	Mean NND (μm)	St. Dev. For NND Gaussian Distribution (μm)
Confined	1	135x135	1153	0.90	0.10	0.73	0.86	0.66	45	5.9	0.4
	2	135x135	983	0.78	0.07	0.68	0.85	0.57	22	5.0	0.4
	3	135x135	499	0.87	0.07	0.75	0.87	0.70	10	3.8	0.4
	4	135x135	670	0.79	0.08	0.67	0.85	0.53	26	4.2	0.3

Observations on the Colloid Size Distribution in Interfacial Assemblies

The local positional and orientational order observed in the nematic colloids are, in part, attributed to neighboring colloids having similar sizes. Previous works demonstrate a relationship between colloid size and spacing.[5,6] Table S2 reports narrow distributions of nearest neighbor distances suggesting colloids have a uniform size locally within small interface areas; this is supported qualitatively by optical microscopy. Across large interface areas, the polycrystalline nature of the assemblies corresponds to variations in colloid size observed by optical microscopy. **Figure S4** compares phase contrast optical microscopy images for two different locations in the same large area assembly. Each area exhibits local positional and orientational order but reports significantly different nearest neighbor distances (**Table S4**). In agreement with prior reports, we observe an increase in colloid spacing corresponds to an increase in the colloid size.[5,6]
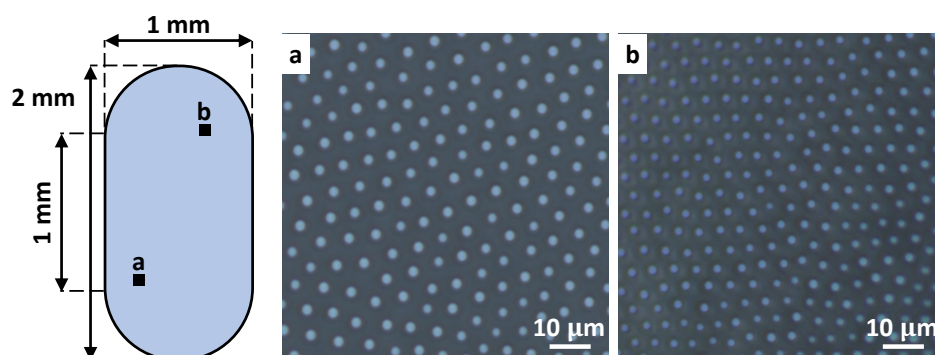

Figure S4. Phase contrast optical microscopy images of two locations (80x80 μm^2) within a confined large area assembly using a TEM grid with an oval slot (~1.8 mm^2); the corresponding structural analyses are reported in Table S4.

Table S4. Summary of the structural analyses for the two positions shown in Figure S4. Photopolymerization was performed in the open-cell setup using an initial 85 vol% 5CB and a 3 hour, low power UV exposure.

Sample Position	# of Colloids	Fraction of Colloids with 6 Nearest Neighbors	Lindemann Disorder Parameter (α)	$\langle \psi_6 \rangle$ for All Colloids	$\langle \psi_6 \rangle$ for Colloids with $\psi_6 > 0.7$	Fraction of Colloids with $\psi_6 > 0.7$ (f_6)	Normalized Hexatic Domain Size (Δ_6)	Mean NND (μm)	St. Dev. For NND Gaussian Distribution (μm)
a	187	0.90	0.06	0.80	0.87	0.84	10	5.8	0.3
b	286	0.97	0.06	0.81	0.87	0.77	S*	4.6	0.3

*S indicates a single crystal in this small analysis area.

Photopolymerization in *Open-Cell* Systems using a *High Power UV* Exposure
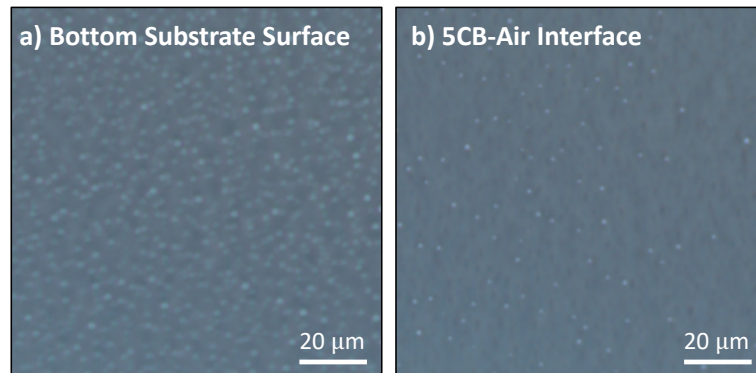

Figure S5. PHEMA colloids formed in an open-cell system (C_{5CB}^o = 85 vol%) by a 15 minute, high power (30 mW/cm^2) UV exposure and subsequent 2 hour and 45 minute aging. Optical microscopy images focus on colloids at a) the surface of the bottom substrate and b) the nematic 5CB-air interface.

Photopolymerization in *Closed-Cell* Systems using *Low Power UV* Exposures
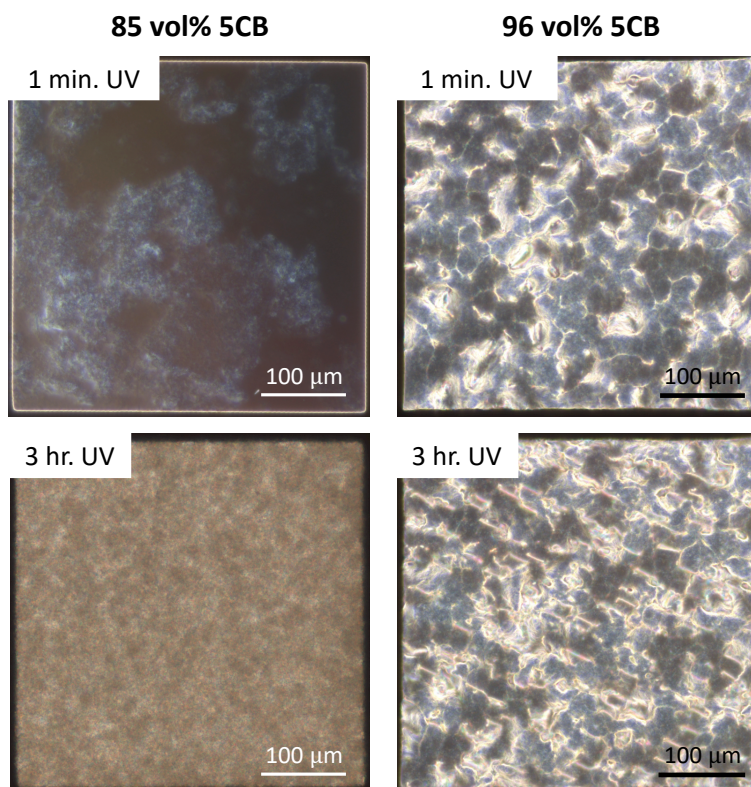

Figure S6. Optical microscopy images of photopolymerization in closed-cell systems in which the reaction solution (85 or 96 vol% 5CB) is sandwiched between two glass slides coated with fluorinated silane. Experiments were performed using low power (1.2 mW/cm^2) UV exposures.

References

(1) V. Garbin, J. C. Crocker and K. J. Stebe, *J. Colloid Interface Sci.,* 2012, **387**, 1.
(2) J. Li, C. H. Wen, S. Gauza, R. Lu and S. T. Wu, *J. Disp. Technol.*, 2005, **1**, 51.
(3) H. Jintoku and H. Ihara, *Chem. Commun.*, 2014, **50**, 10611.
(4) P. Bagheri, A. M. Almudallal, A. Yethiraj and K. M. Poduska, *Langmuir*, 2015, **31**, 8251
(5) I. I. Smalyukh, S. Chernyshuk, B. I. Lev, A. B. Nych, U. Ognysta, V. G. Nazarenko and O. D. Lavrentovich, *Phys. Rev. Lett.*, 2004, **93**, 117801.
(6) T. Yamamoto and M. Yoshida, *Appl. Phys. Express*, 2009, **2**, 101501.