Supplementary Information

Accessing the Frank-Kasper Phase of Block Copolymer in the Fuzzy Colloid Regime

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1. Determination of the Kuhn lengths of P2VP and PDMS by SANS.

The SANS profiles of P2VP (M_n = 8,700 g/mol, PDI = 1.05) and PDMS homopolymers (M_n = 10,500 g/mol, PDI = 1.04) in the 1 wt% solution with d-THF were measured to determine their Kuhn lengths. The SANS measurements were performed on the BL-6 EQ-SANS at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). The sample-to-detector distance of 4 m was used covering the q range from 0.015 to 0.5 Å^{-1} with wavelength band 2.11 Å < λ < 5.2 Å and 10.11 Å < λ < 13.2 Å. The samples were held in 2 mm path length Hellma quartz cells and measured at room temperature. The measured intensity was corrected for background, detector sensitivity and the scattering contribution from the empty cell, and placed to an absolute scale using the porous silica as a standard.

Figure S1 displays the measured SANS profiles. The SANS profiles were fitted satisfactorily by the form factor model of flexible cylinder with excluded volume, which yielded the Kuhn lengths of the two polymers as b_{P2VP} = 1.46 nm and b_{PDMS} = 0.99 nm.

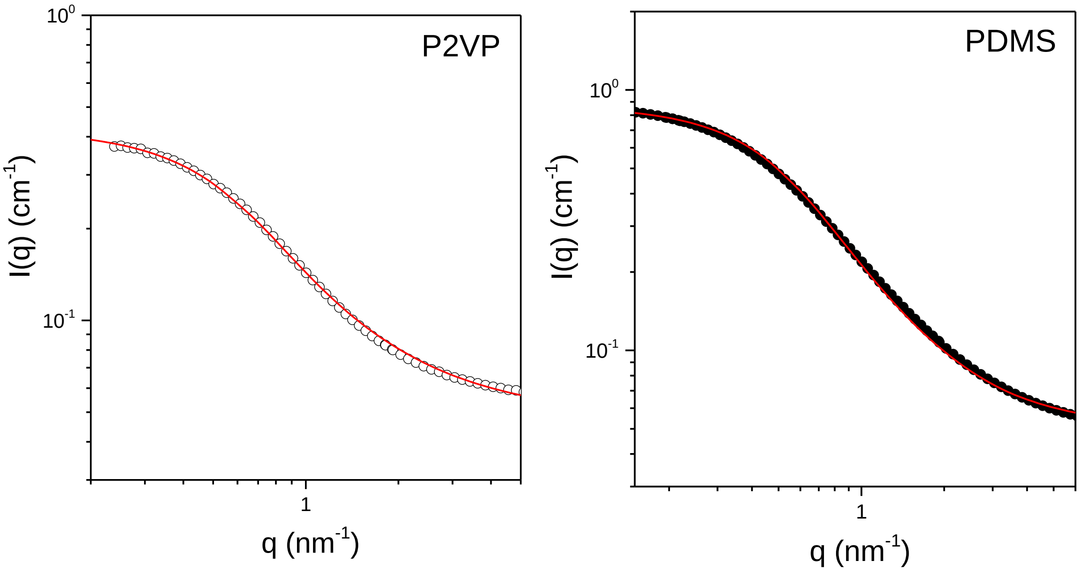

Figure S1. SANS profiles of P2VP and PDMS in 1 wt% solutions with d-THF. The red solid curves represent the fits by the form factor model of flexible cylinder with excluded volume.

2. Fitting of the SAXS profiles of micellar liquid phase by Percus-Yevick model of polydisperse spherical particles

The scattering profiles at 30 °C in Figure 3(a) and 40 °C in Figure 3(b) were fitted by Percus-Yevick hard-sphere model assuming the liquidlike packing of polydisperse spherical particles.[1] The hard-sphere radius, R_{HS}, adopted here covers an impenetrable shell corresponding to the coronal layer surrounding the spherical domain and is related to the actual core radius, R, by a constant C_{HS}, viz. $R_{HS} = C_{HS}R$, according to Kinning et al.[2] The model used here also incorporates the polydispersity effect by assuming

Gaussian size distribution. Figure S2 shows the fitting results and the values of the parameters obtained from the fits are listed in Table S1. It can be seen that the model yielded satisfactory fits to the experimental data, indicating that indicating that the micellar entity of the bcp still retained, but the micelles exhibited only short-range order. That is, the bcp formed the micellar liquid (MLQ) phase.

Table S1 The average radius of P2VP core, polydispersity of size distribution and C_{HS} obtained from the model fit.

SAXS curve	Average radius (nm)	Polydispersity[a]	C_{HS}
30 °C in Figure 1(a)	4.77	0.154	1.68
40 °C in Figure 1(b)	5.84	0.174	1.59

[a] Polydispersity is defined as the ratio of the standard deviation of radius distribution to mean radius.

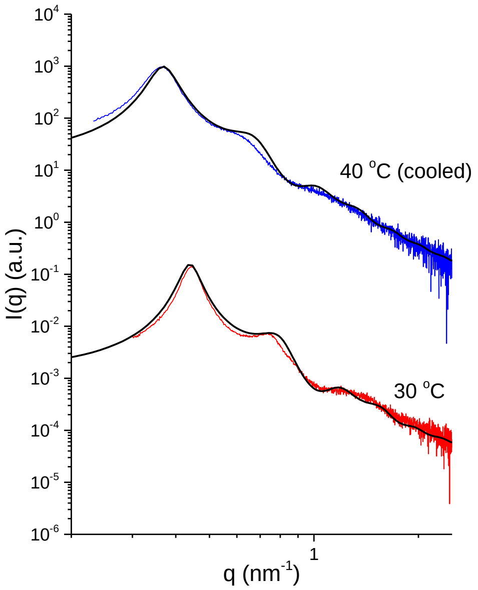

Figure S2 Fitting results of the scattering profiles at 30 °C in Figure 1(a) and 40 °C in Figure 1(b) by Percus-Yevick hard-sphere model assuming the liquidlike packing of polydisperse spherical particles.

References

1. J. K. Percus, and G. J. Yevick, *Phys. Rev.* **110**, 1 (1958).
2. D. J Kinning, and E. L. Thomas, *Macromolecules* **17**, 1712 (1984).

3. **Assignment of the diffraction peaks of the SAXS profile of the sample having been annealed at 30 ºC for 60 days according to the hexagonal unit cell with P63/mmc symmetry of C14 phase.**

Table S2. SAXS peak assignment for C14 phase with hexagonal unit cell dimension of a = 37.6 nm and c = 61.4 nm

Peak no.	h k l	q_{cal} (nm^{-1})	q_{obs} (nm^{-1})	Peak no.	h k l	q_{cal} (nm^{-1})	q_{obs} (nm^{-1})
1	1 0 0	0.193	0.193	17	1 0 5	0.546	0.546
2	0 0 2	0.204	0.204	18	2 1 2	0.549	0.550
3	1 0 1	0.218	0.218	19	2 0 4	0.562	0.563
4	1 0 2	0.280	0.280	20	3 0 0	0.577	0.577
5	1 1 0	0.333	0.333	21	3 0 1	0.587	-
6	1 0 3	0.362	0.362	22	2 1 3	0.594	0.594
7	2 0 0	0.385	0.381	23	3 0 2	0.613	0.613
8	1 1 2	0.391	0.391	24	0 0 6	0.613	0.613
9	2 0 1	0.399	-	25	2 0 5	0.640	0.640
10	0 0 4	0.409	0.409	26	1 0 6	0.642	0.642
11	2 0 2	0.436	0.436	27	2 1 4	0.653	-
12	1 0 4	0.451	0.451	28	3 0 3	0.653	-
13	2 0 3	0.492	0.492	29	2 2 0	0.667	0.667
14	2 1 0	0.510	0.510	30	3 1 0	0.694	0.696
15	2 1 1	0.520	-	31	2 2 2	0.698	0.699
16	1 1 4	0.527	0.527	32	1 1 6	0.698	0.699

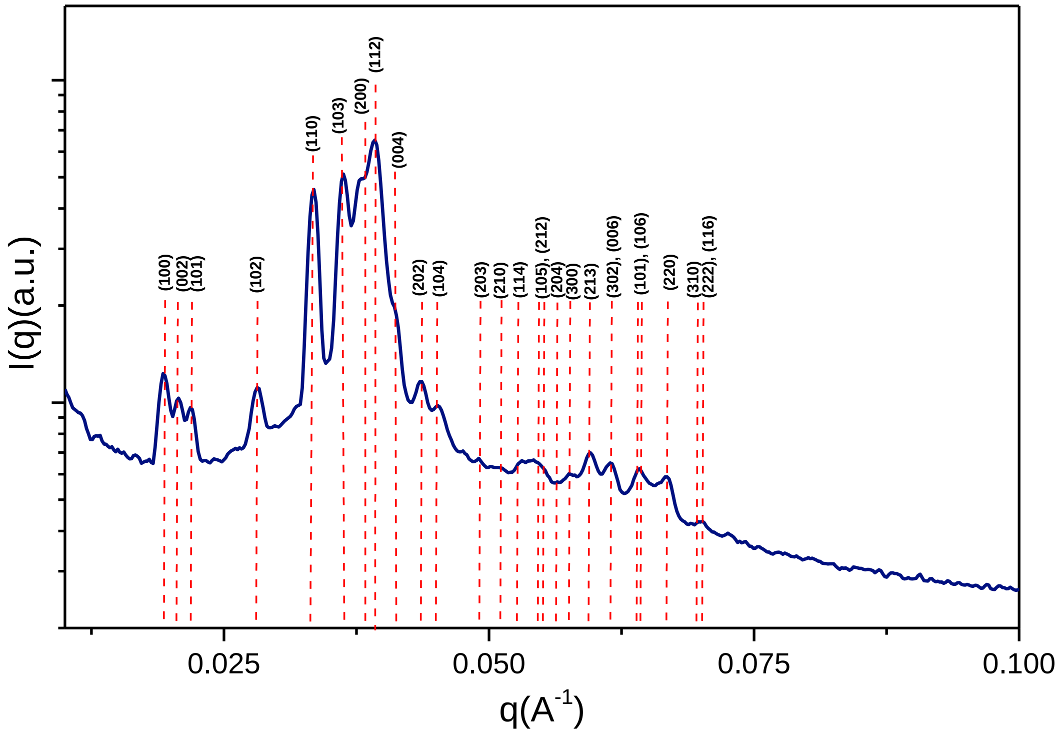

Figure S3 Assignment of the SAXS peaks of the sample having been annealed at 30 ^{o}C for 60 days by C14 phase.