

Electronic Supplementary Information

Pathway and Kinetics of Hierarchical Assembly by Ionic Oligomers into Lyotropic Columnar Phase

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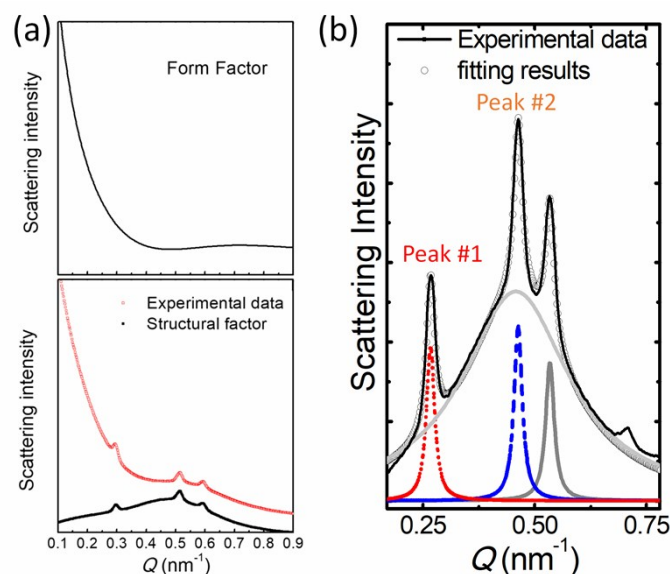


Fig. S1 Process of data analysis. (a) Up: The form factor of a hollow cylinder calculated with SasView software. The core-radius is 4.5 nm and the radius is 7.5 nm. The mean of the length is 1 μm with a polydispersity Gaussian distribution. Bottom: the comparison between SAXS data before and after being divided by the form factor. The structural factor after division gives information on the long-range ordering in the sample and is further analyzed by peak fitting. (b) Multiple-peak fitting of the structural factor. The broad background is fitted with a grey Lorentz curve and the sharp Bragg peaks are fitted with several Lorentz curves respectively. The total sum of all fitting curves is shown as the bold black line in comparison with the experimental data.

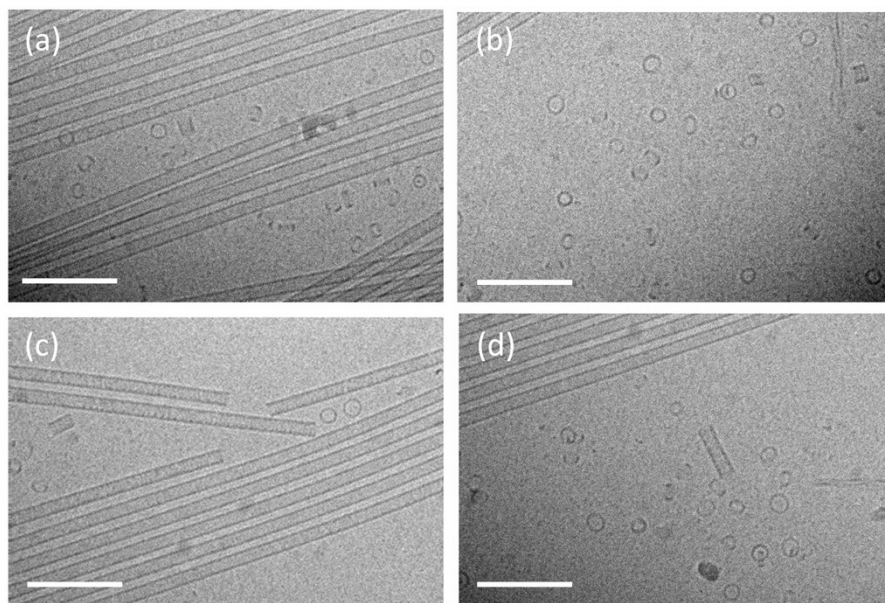


Fig. S2 Ring-like structures are widely observed by Cryo-TEM. The samples are aged for one month. All the scale bars represent 100 nm.

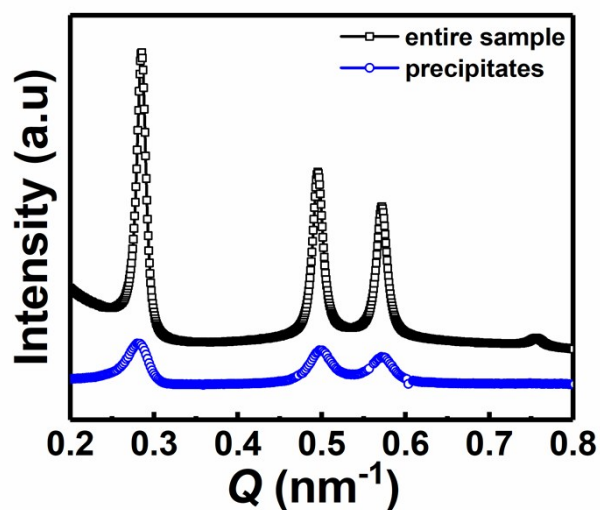


Fig. S3 SAXS of precipitates (blue circle) in comparison with SAXS of the entire solution sample (black squares). The difference in the peak intensity is due to the smaller amount/volume of samples probed by the X-ray beam. Other than that, the two curves share the same peaks positions and relative peak intensity.

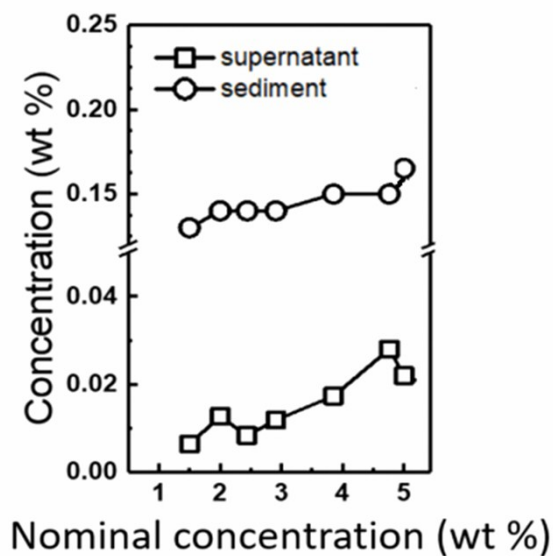
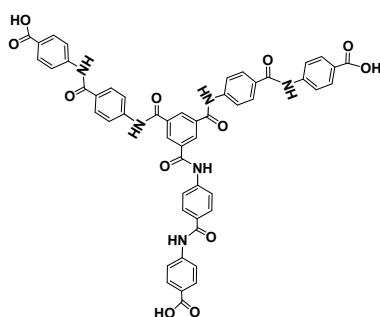


Fig. S4 Molecular concentration of the up clear solution (supernatant) and the precipitates (sediments) measured by UV-Vis absorption vs nominal concentration or total concentration of matured solutions.



Scheme S1 Chemical structure of the molecule $P_7(\text{COOH})_3$. The only difference between $P_7(\text{COOH})_3$ and $P_7(\text{COONa})_3$ is the terminal groups where the sodium atoms are replaced by hydrogen.

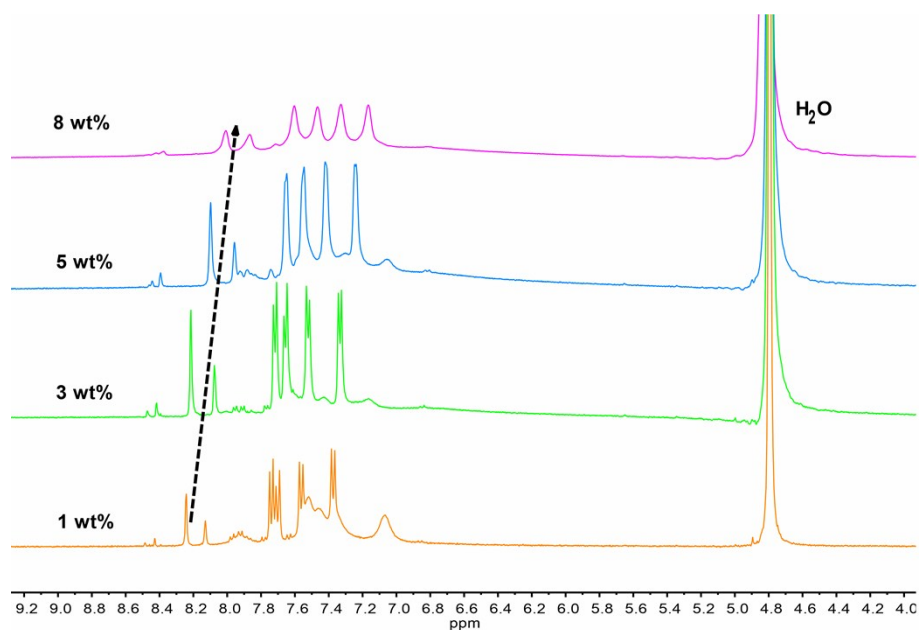


Fig. S5 $^1\text{H-NMR}$ spectra of $\text{P}_7(\text{COONa})_3$ at different concentration performed at Bruker AVANCE III 400. D_2O with 0.05 wt% TSP- d_4 bought from Sigma-Aldrich was used as solvent. The invariable chemical shift of H_2O around 4.79 ppm justifies the use of TSP- d_4 as inner standard.

Table S1 Statistics on structural information in nm unit of fresh sample in Fig. 3c.

Fresh sample										
	Items	Original Data								Average value
Tubes	Inner diameter	10.99	11.23	11.24	11.57	12.75	11.53	10.91	11.24	11.38
		10.99	11.09	10.91	10.58	12.44	12.26	10.90	11.57	
		10.99	11.83	11.24	11.57	13.18	9.19	10.24	11.24	
		13.48	9.19	10.24	11.24	13.18	11.71	10.91	11.57	
		12.87	10.97	9.91	12.56	11.09	11.40	10.91	12.23	
	Outer diameter	17.04	15.21	15.21	15.87	14.78	14.48	14.88	15.20	15.06
		16.73	14.48	15.21	14.53	14.78	12.75	15.54	14.56	
		16.30	14.48	15.21	14.86	14.78	12.32	15.87	14.56	
		17.04	14.94	14.88	15.19	15.08	14.56	15.87	14.56	
		14.78	14.48	15.21	14.86	15.21	14.88	16.20	14.88	
	Length	90.85	137.76	122.51	79.88	164.15	153.98	149.60	209.85	-
		178.45	227.48	160.39	138.99	201.11	53.67	-	-	

Table S2 Statistics on structural information in nm unit of aged sample in Fig. 3d.

Aged sample										
	Items	Original Data								Average value
Tubes	Inner diameter	10.53	11.08	9.89	10.75	10.92	11.15	10.53	10.72	10.73
		10.53	11.08	10.30	10.75	10.92	11.15	10.95	10.53	
		10.53	11.08	10.30	10.72	10.92	10.92	10.53	10.53	
		11.56	11.08	10.52	10.72	11.33	10.52	10.95	10.53	
		11.14	10.51	10.53	10.53	10.92	9.89	10.52	10.53	
	Outer diameter	13.81	14.89	14.84	14.20	14.04	14.04	14.20	14.65	14.38
		14.23	15.32	14.23	14.65	14.46	14.04	13.82	14.23	
		14.84	14.89	14.47	15.26	14.65	14.04	13.93	14.65	
		14.23	14.04	13.82	14.65	14.04	14.23	14.57	14.23	
		13.81	14.04	14.47	14.65	14.89	14.84	14.20	14.23	
	length	1030.62	730.26	775.77	820.12	863.55	1010.37	1064.73	1041.72	-
977.16		867.55	992.04	875.96	1011.30	1009.30	752.31	799.77		

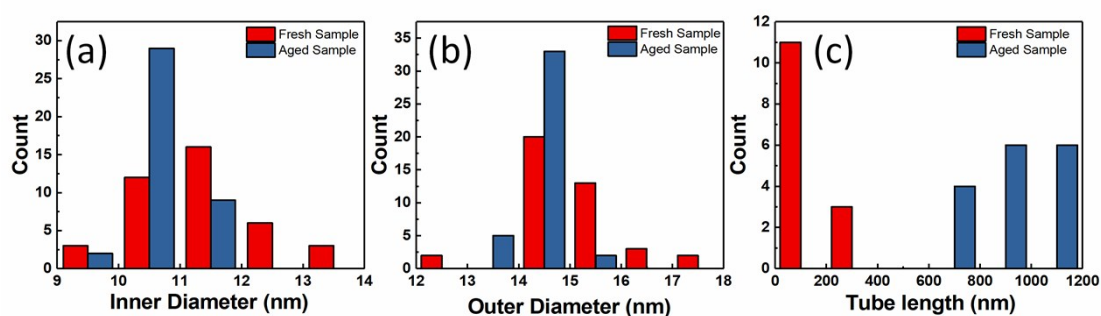


Fig. S6 Comparison of (a) inner diameter, (b) outer diameter and (c) tube length between fresh sample and aged sample in Fig. 3c and Fig. 3d. The numbers can be seen in Table S1 and S2.

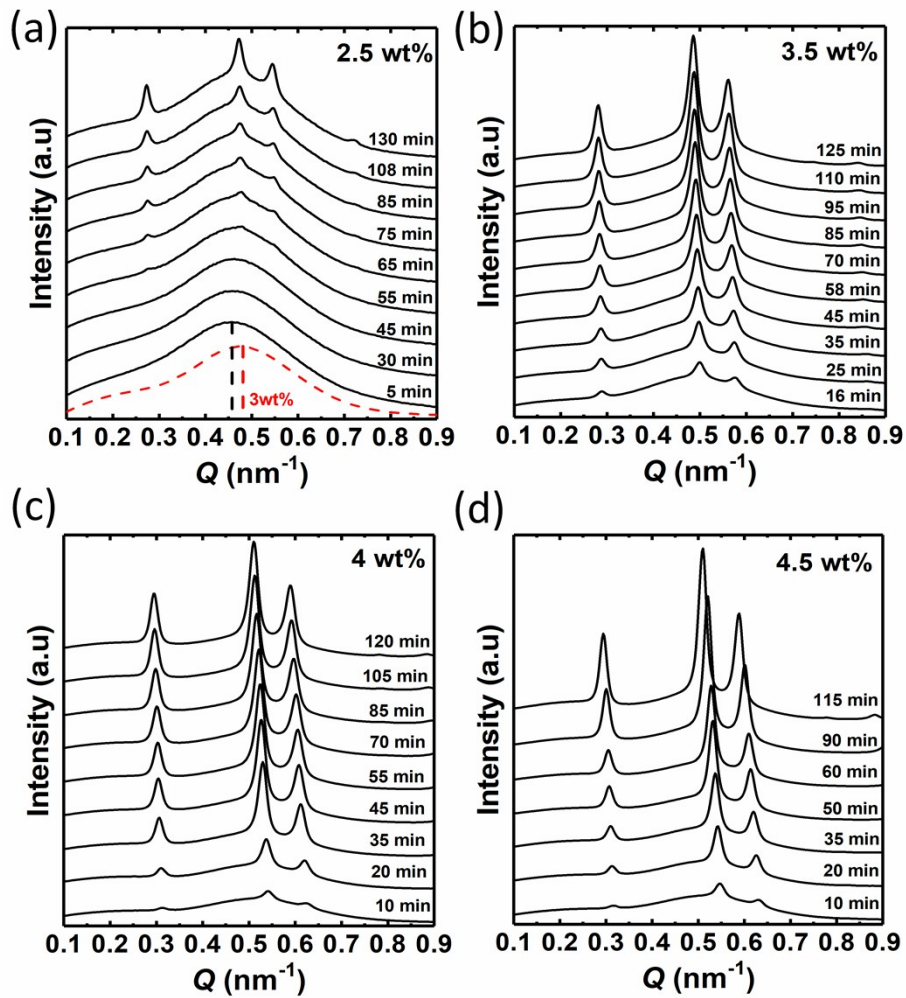


Fig. S7 *In-situ* SAXS at various concentrations. In panel (a) a frame from 3 wt% solution is plotted in red dash, clearly showing the shift of the broad feature toward larger Q in comparison to that at 2.5 wt%.

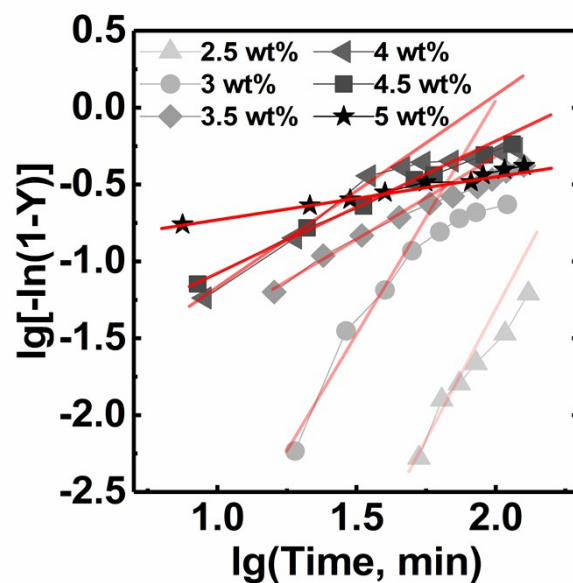


Fig. S8 Lg-lg plot of Avrami equation of the sharp peaks where Y is the relative crystallinity of the sample equal to $\text{Area}_{\text{sharp peaks}}/\text{Area}_{\text{Total}}$ at time t . The two parameters K and n are derived from the intercept and slope respectively from the plot in the figure. Please noted that the Avrami equation is mainly for the initial stage of crystallization, so only a small number of early data points are under considered at fitting process.

The fitting results can be seen as the insert picture in Fig. 4d. The increasing K versus concentration indicates the faster formation of LC phase at high concentration, suggesting the validity of Avrami analysis.