

Hybrid Liquid Crystal Polymers from the Self-Assembly of Poly(vinylpyridine) and Polyoxometalates via Multiple Non-Covalent Bonds

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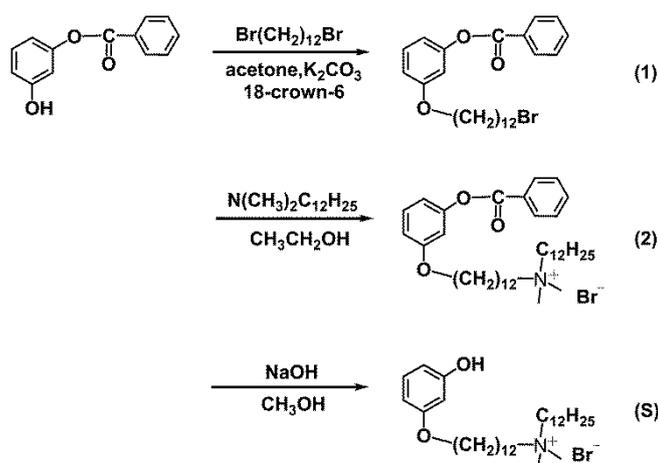
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Supplementary Information

1. Materials:

1,12-Dibromododecane (98%) and 3-hydroxyphenyl Benzoate (99%) were purchased from Aldrich. N,N-Dimethyldodecylamine (97%) was obtained from Aladdin GmbH. All the starting compounds for synthesis were used without further purification. The organic solvents applied in the preparation were analytical grade and obtained from Beijing Chemical Works. Doubly distilled water was used in the experiments. Silica gel (100-200 mesh) was employed for the purification of column chromatography.

2. Synthesis of quaternary ammonium bromide with terminal phenol group.



Scheme S1 Synthetic procedures for quaternary ammonium S.

The detailed synthetic processes are as follows:

3-(12-bromododecyloxy)-1-phenyl benzoate (1). 3-Hydroxyphenyl benzoate (5.00 g, 23.4 mmol), 1,12-dibromododecane (9.20 g, 28.04 mmol), anhydrous K_2CO_3 (2 g, 14.5 mmol) and 18-crown-6 were dissolved in acetone, the resultant mixture was stirred for 24 h under refluxing with a nitrogen atmosphere. After the reaction was completed, the solution was filtered to remove K_2CO_3 , and the filtrate was removed by rotary evaporator, then the residue was treated with water and extracted with chloroform for two times. The organic layer was dried with anhydrous $MgSO_4$, and then concentrated under the reduced pressure. The crude product was purified by column chromatography on silica gel with a mixture of petroleum ether /ethyl acetate (v/v, 50/1) as eluent, giving the product 1 in yield of 31.5 %. 1H NMR ($CDCl_3$, 500MHz): δ = 8.23-8.21 (m, 2 H), 7.66 (t, J = 7.5 Hz, 1 H), 7.54 (t, J = 7.5 Hz, 2 H), 7.33 (t, J = 8 Hz, 1 H), 6.85-6.78 (m, 3 H), 3.98 (t, J = 6.5 Hz, 2 H), 3.43 (t, J = 7 Hz, 2 H), 1.91-1.85 (m, 2 H), 1.83-1.78 (m, 2 H), 1.50-1.42(m, 4 H), 1.38-1.29 (m, 12 H).

N-dodecyl-12-(3-(benzoyloxy)phenoxy)-N-dodecyl-N,N-dimethyl-ammonium bromide (2). Compound 1 (3.40 g, 7.36 mmol), N,N-dimethyldodecylamine (2.04 g, 9.6 mmol) were dissolved in ethanol (120 mL), the resulting mixture was stirred for 4 days under refluxing. After the reaction was complete, the solvent was removed by rotary evaporator, and then the crude product was recrystallized from chloroform/anhydrous ethyl ether (v/v, 1/30), giving the product 2 in yield of 54.92 %. 1H NMR ($CDCl_3$, 500MHz): δ = 8.20-8.19 (m, 2 H), 7.64 (t, J = 6 Hz, 1 H), 7.52 (t, J = 6 Hz, 2 H), 7.31 (t, J = 2 Hz, 1 H), 6.82-6.77 (m, 3 H), 3.96 (t, J = 5 Hz, 2 H), 3.51 (t, J = 6.5 Hz, 4 H), 3.38 (s, 6 H), 1.80-1.76 (m, 2 H), 1.72-1.67(m, 4 H), 1.47-1.43 (m, 2 H), 1.42-1.25 (m, 32 H), 0.88 (t, J=6 Hz, 3 H).

N-dodecyl-12-(3-hydroxyphenoxy)-N-dodecyl-N,N-dimethyl-ammonium bromide (S). Compound 2 (2.73 g, 4.05 mmol), sodium hydroxide (1.62 g, 40.5 mmol) were dissolved in methanol (120 mL), the mixture was stirred for 10 hours under refluxing with a nitrogen atmosphere. The resultant solution was acidified to pH \cong 2 by diluted hydrobromic acid. After remove the solvent by rotary evaporator, the residue was rinsed with water and extracted with chloroform for three times. The organic layer was dried with anhydrous $MgSO_4$, and then concentrated under the reduced pressure. The crude product was recrystallized from chloroform/anhydrous ethyl ether (v/v, 1/30), giving the white powder S in the yield of 90 %. 1H NMR (500 MHz, $CDCl_3$, δ): 8.43 (s, 1 H), 7.03 (t, J = 8 Hz, 1 H), 6.63-6.63 (m, 1 H), 6.58 (t, J = 2

Hz, 1 H), 6.38-6.36 (m, 1 H), 3.91 (t, $J = 6.5$ Hz, 2 H), 3.92-3.89 (m, 4 H), 3.28 (s, 6 H), 1.77-1.71 (m, 2 H), 1.66-1.59 (m, 4 H), 1.47-1.41 (m, 2 H), 1.38-1.19 (m, 34 H), 0.89-0.86 (t, $J = 7.5$ Hz, 3 H).
 Anal. Calcd for the compound S ($C_{32}H_{60}NO_2Br$): C, 67.34 %; H, 10.59 %; N, 2.45 %. Found: C, 67.53 %; H, 10.02 %; N, 2.34 %. MALDI-TOF MS (positive spectrum): m/z : 490.48, corresponding to $[C_{32}H_{60}NO_2]^+$ cation.

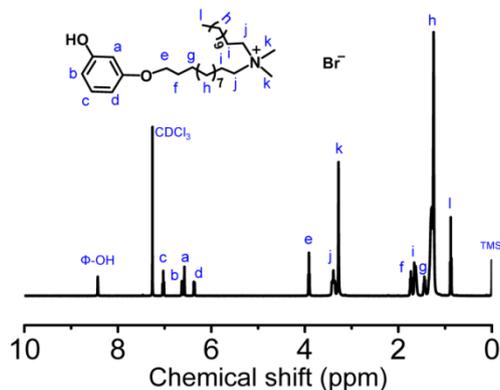


Fig. S1 1H NMR spectra of the synthesized surfactant (S).

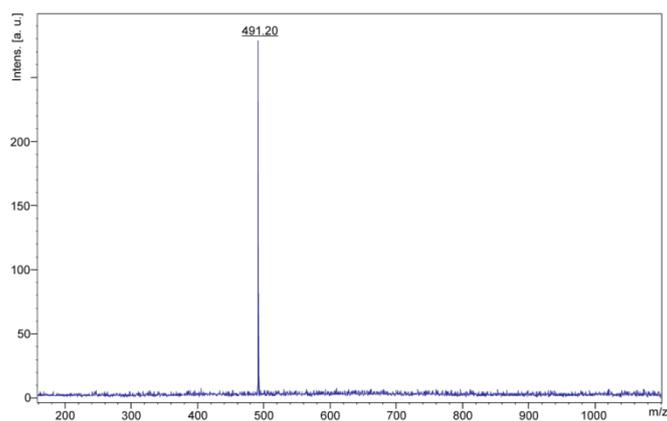
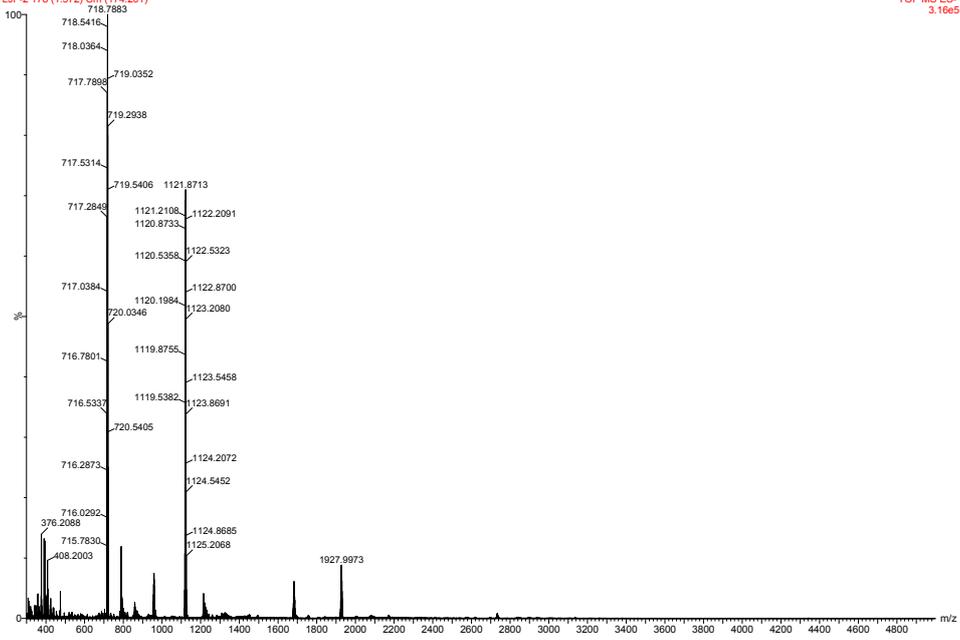


Fig. S2 MALDI-TOF MS spectra of the synthesized surfactant cation ($S^+ = [C_{32}H_{60}NO_2]^+$). (Data was collected in positive mode from a chloroform solution of S)

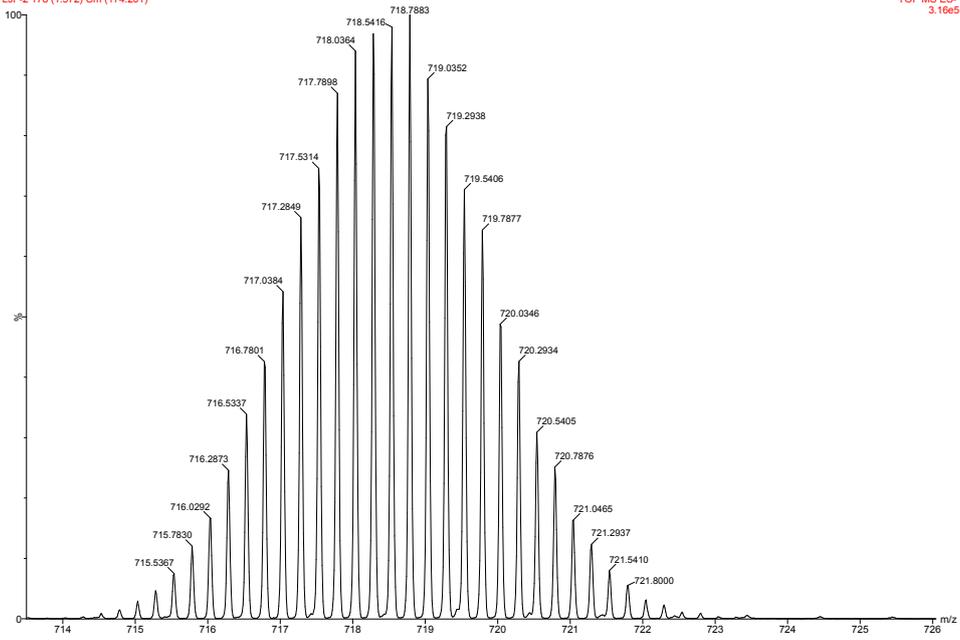
LJF-2 178 (1.572) Cm (174.201)

TOF MS ES-
3.16e5



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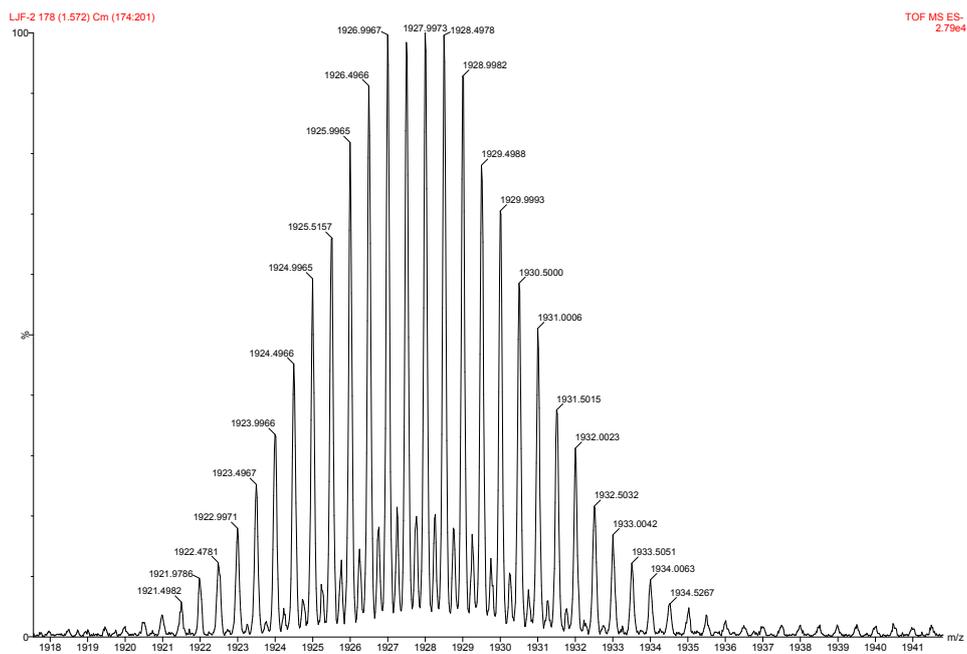
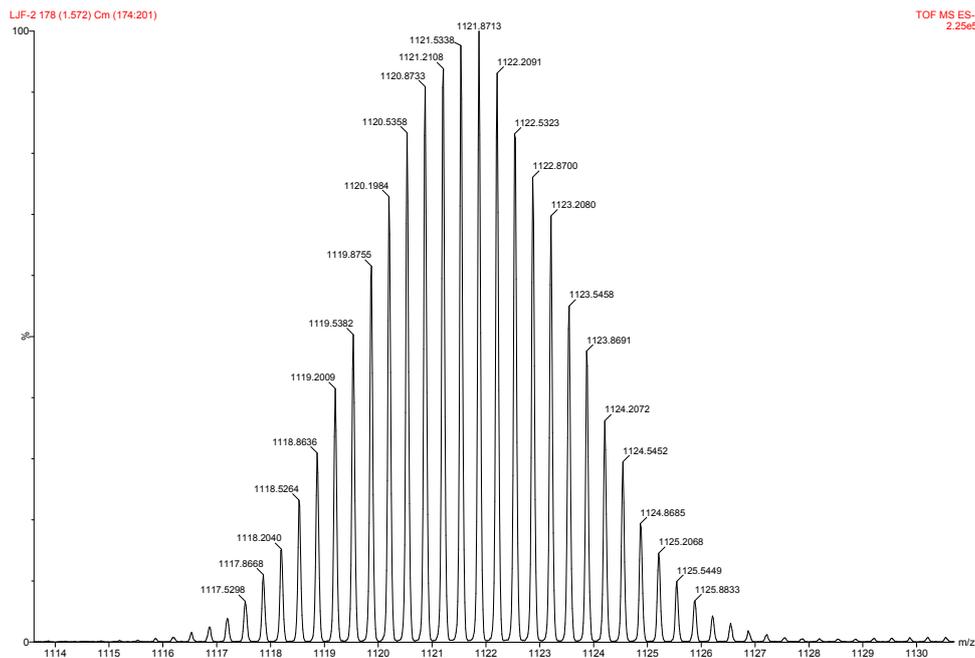


Fig. S3 ESI-MS spectra of SEP-1. (Data was collected in negative mode from a DMF solution of SEP-1).

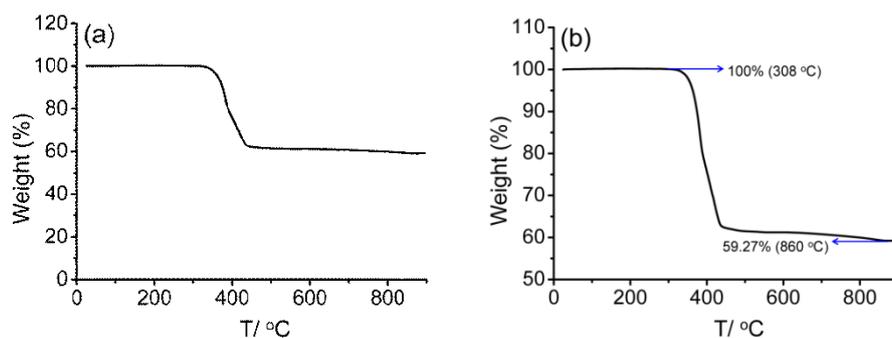


Fig. S4 TGA spectra of SEP-1: (a) weight percent is in the range of 0-100%; (b) weight percent is in the range of 50%-100%.

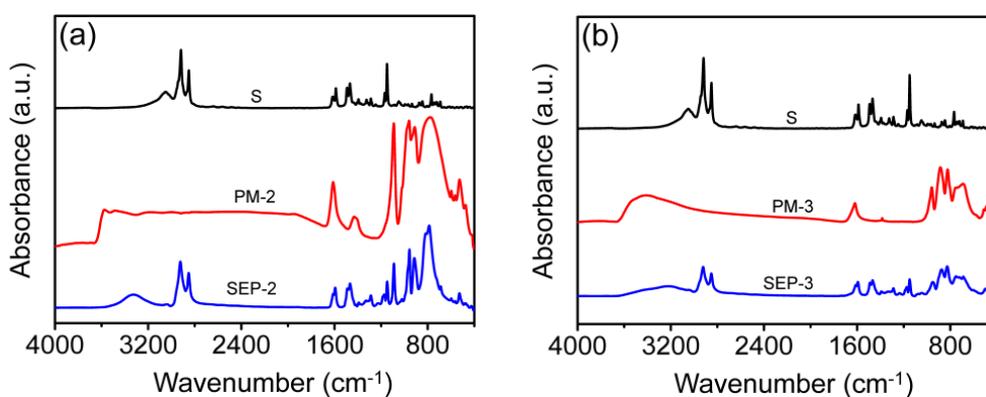


Fig. S5 FT-IR spectra of PMs, surfactant and SEPs: (a) PM-2, S, SEP-2; (b) PM-3, S, SEP-3.

Table S1 FT-IR assignments of surfactant (S) and SEP-n at room temperature.

S	SEP-1	SEP-2	SEP-3	Assignments
—	3376	3327	3223	O-H asym. str.
3049	3037	3037	3039	CH ₃ -N ⁺ asym. str.
2918	2924	2923	2922	CH ₂ asym. str.
2850	2852	2853	2852	CH ₂ sym. str.
1614	1611	1612	1613	C-C framework stretching
1589	1595	1594	1594	C-C framework stretching
1494	1490	1490	1490	C-C framework stretching
1468	1468	1466	1467	CH ₂ scissoring
1394	1394	1393	1392	CH ₃ scissoring
1288	1289	1288	1288	CH ₂ wagging modes
1149	1148	1147	1148	C-N stretching
—	—	1091	—	V _{as} (P-O _a)
—	973	—	—	W-O _d scissoring
—	—	956	—	V _{as} (W-O _d)
—	—	—	952	
—	—	914	—	V _{as} (W-O _b -W)
—	882	—	—	V _{as} (W-O _b -W)

—	—	—	875	
—	—	—	826	
—	794	—	—	$V_{as}(W-O_c-W)$
—	—	786	—	$V_{as}(W-O_c-W)$

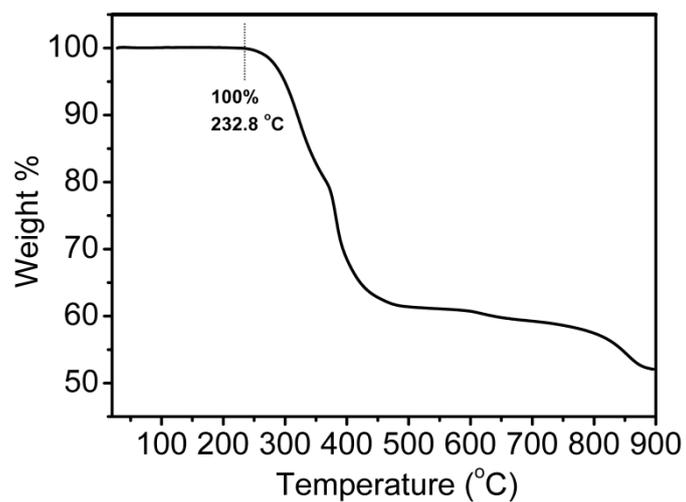


Fig. S6 TGA spectra of P4VP₅₇₁/(SEP-1)_{1.0}.

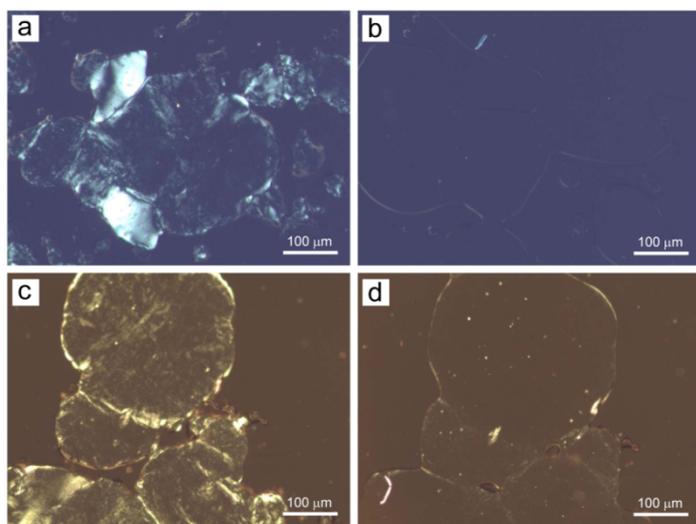


Fig. S7 PLM images of the hybrid polymers at different temperatures: (a) P4VP₅₇₁/(SEP-1)_{1.0} at 128 °C; (b) P4VP₅₇₁/(SEP-1)_{1.0} at 150 °C; (c) P4VP₅₇₁/(SEP-1)_{0.75} at 116 °C; (d) P4VP₅₇₁/(SEP-1)_{0.75} at 130 °C.

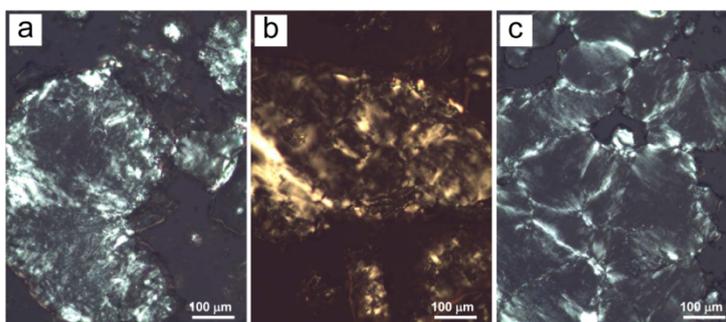


Fig. S8 PLM images of the hybrid polymer: (a) P4VP₃₂₅/(SEP-1)_{1.0} at 125 °C, (b) P4VP₁₄₃/(SEP-1)_{1.0} at 120 °C, (c) P4VP₆₇/(SEP-1)_{1.0} at 115 °C.

Table S2 The phase transition temperature of P4VP₅₇₁/(SEP-1)_{1.0}, P4VP₃₂₅/(SEP-1)_{1.0}, P4VP₁₄₃/(SEP-1)_{1.0}, and P4VP₆₇/(SEP-1)_{1.0}.

LCP samples	Clearing point temperatures (°C)
P4VP ₅₇₁ /(SEP-1) _{1.0}	145
P4VP ₃₂₅ /(SEP-1) _{1.0}	135
P4VP ₁₄₃ /(SEP-1) _{1.0}	133
P4VP ₆₇ /(SEP-1) _{1.0}	129

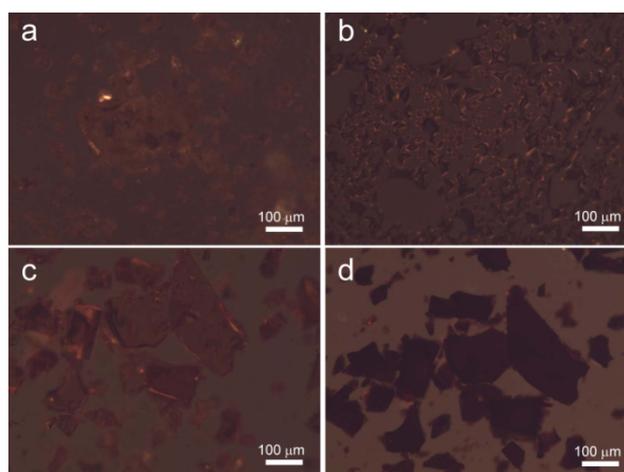


Fig. S9 PLM images of the hybrid polymer: (a) P4VP₅₇₁/(SEP-2)_{1.0} at 25 °C, (b) P4VP₅₇₁/(SEP-2)_{1.0} at 130 °C, (c) P4VP₅₇₁/(SEP-3)_{1.0} at 25 °C, (d) P4VP₅₇₁/(SEP-3)_{1.0} at 240 °C.

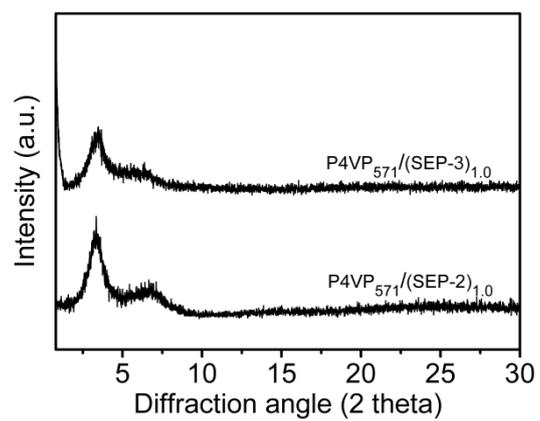


Fig. S10 XRD pattern of hybrid polymer P4VP₅₇₁/(SEP-2)_{1.0} and P4VP₅₇₁/(SEP-3)_{1.0} at room temperature.