

Self-Assembly of Comb-Coil Block Copolymers with Heteroarm Star Architecture

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Supramolecular comb-coil block copolymers formed by the stoichiometric complexation of an amphiphilic surfactant 3-pentadecylphenol (PDP), with the poly-(4-vinylpyridine) (P4VP) blocks in a linear PS-*b*-P4VP copolymer and a nonlinear A_nB_n-type PS-P4VP heteroarm star copolymer have been investigated. The molecular architecture effect on the ordered hierarchical structure and the relevant order-disorder transitions (ODT) of the systems have been revealed. The molecular characteristics of the materials we used are described in Table 1.

Table 1. Molecular Characteristics of Polystyrene/Poly(4-vinylpyridine)/Surfactant Complexes

samp les	Mn over all	Mn PS- ar m	Mn P4V P- arm	Mw /M n	N	f PS	f _{PS} (PDP complex)
L1	208 83	152 32	5651	1.0 6	- 6	0.7 3	0.41
H1	665 13	157 94	4922	1.1 7	6. 5	0.7 6	0.45

L1(PDP) complex. Figure 1 displays the temperature-dependent SAXS profiles of L1(PDP) complex in the temperature range of 30-290 °C. The profile suggested that between 70 and 120 °C, the P4VP(PDP) blocks were in a disordered state but the copolymer domains attained an ordered structure. The order-disorder transition of the large-scale copolymer domains (T_{ODT}^L) occurred near 120 °C.

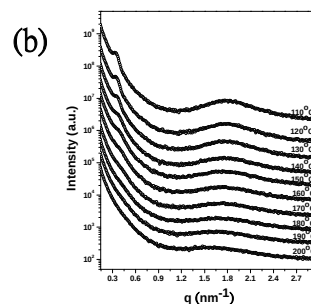
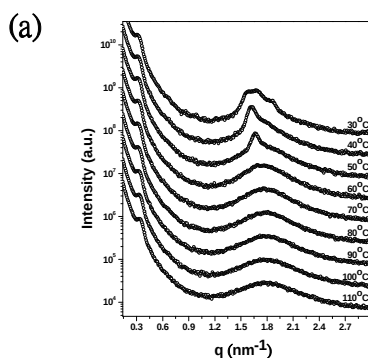


Figure 1. Temperature-dependent SAXS intensity profiles of L1(PDP) comb-coil complex collected in-situ from (a) 30 to 110 °C and (b) 110 to 200 °C in a heating cycle.

H1(PDP) complex. Figure 2 illustrates the temperature-dependent SAXS profile of H1(PDP) complex in the temperature range of 40-200 °C. The profile suggested that H1(PDP) complex self-organized into a lamellae-within-lamellae morphology. Also, an order-disorder transition of the P4VP(PDP) combs (ODT^S) occurred at about 80 °C while ODT^L at 170 °C.

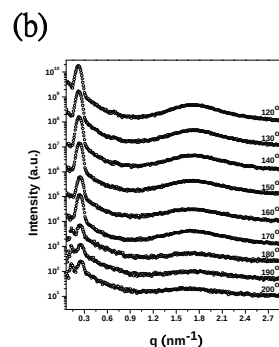
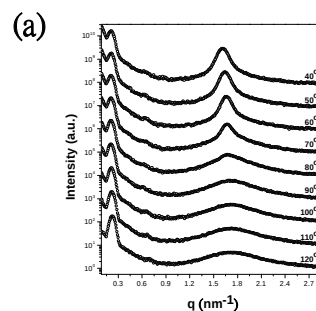


Figure 2. Temperature-dependent SAXS intensity profiles of H1(PDP) comb-coil complex collected in-situ from (a) 40 to 120 °C and (b) 120 to 200 °C in a heating cycle.