# Phase Diagram and Self-assembly of Rod-coil Block Copolymers

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We describe the synthesis, morphology, and self-assembly behavior of semiconducting poly(diethylhexyloxy-p-phenylenevinylene)-b-poly(2-vinylpyridine) (PPV-P2VP) rod-coil block copolymers. Night different block copolymers with coil volume fraction from 0.14 to 0.93 were synthesized by anionic polymerization. The morphology of the block copolymer was studied by transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and wide-angle X-ray (WAXS). Block copolymers with the lamellar structure are organized in a smectic C monolayer, identified by SAXS experiments through the analysis of the 1D correlation function, and the tilt angle of 29° is identical to all PPV domains. Even though the coil volume fraction increases from 0.74 to 0.88, the hexagonally packed structures consisted of small pucklike or striplike aggregates of rods are observed, and the rod-rod interaction still exists in PPV domains. In low coil fraction copolymers (≦0.3) and the homopolymer PPV, the smectic-C lamellar is destroyed and trandforms to the disorder phase simultaneously as primary peaks of the rod-rod interaction vanish at 180℃. As the coil fraction increases to the symmetric composition, the phase separation could preserve the lamellar phase upon further heating above 190℃, resulting from the primary incompatibility between two blocks.

As shown in Fig. 1, the bulk morphology of all PPV-P2VP samples, as well as the PPV homopolymer, are examined by using small-angle (SAXS) and wide-angle X-ray scattering (WAXS) simultaneously. Differing from the classic coil-coil block copolymer system, the boundary of the phase transformation from the lamellar structure to the hexagonally packed cylinder extends to the coil volume fraction of 0.7. The intensity of the rod-rod interaction decreases as the coil volume fraction increases. Even though the phase transforms from the lamellar phase to the hexagonally packed cylinders, the rod-rod interaction could still observed in PPV domains.

In-situ heating of SAXS and WAXS analyses for homopolymer PPV and a series of block copolymer PPV-P2VP were acquired simultaneously in order to discuss the relation between the rod-rod interaction and morphology. Firstly, we investigate the homopolymer PPV. As shown in Fig. 2a, the characteristic peak of rod-rod interaction of homopolymer PPV still exists below 180℃ and a slight increase in rod-rod spacing of PPV through a range from ambient temperature to 180℃ is attributed to the thermal expansion upon heating. Meanwhile, the SAXS profile shows that a smectic lamellar phase still preserved in the bulk below 180℃ and on distinct shift of the layer spacing be observed. Furthermore, the characteristic peak of the layer spacing and rod-rod spacing showed respectively in SAXS and WAXS profiles disappeared simultaneously around 180℃~190℃. The destruction of smectic lamellar phase is suggested that the rod-rod interaction dominates the formation of PPV layers.

Heating the PPV-P2VP block copolymer is found that as the coil volume fraction is low (≦0.3), the lamellar structure is also destroyed simultaneously as the rod-rod interaction disappears between 180℃ and 190℃. However, as the coil volume fraction is symmetric with respect to that of the PPV, the rod-rod interaction could still preserve in the lamellar structure above 190℃. Thus we speculate that for this symmetric composition, even though the liquid crystalline interaction diminishes between 180℃ and 190℃, the natural incompatibility (Flory-Huggins interaction) between these two blocks could dominate and keep the original lamellar phase, as predicted in the phase diagram of a classical coil-coil block copolymer.

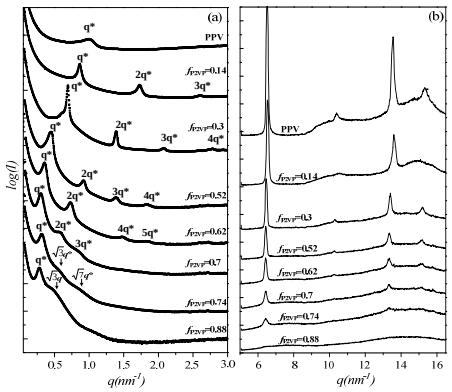


**Fig. 1:** (a) SAXS (b) WAXS spectra of all PPV-P2VP samples.

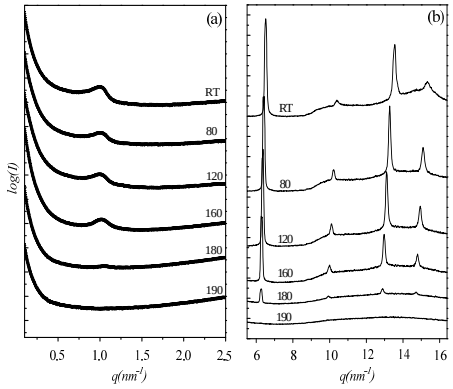


**Fig. 2:** In-situ heating of SAXS and WAXS analyses for homopolymer PPV

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