Crystallization-Driven Co-Assembly of Micrometric Polymer Hybrid Single Crystals and Nanometric Crystalline Micelles

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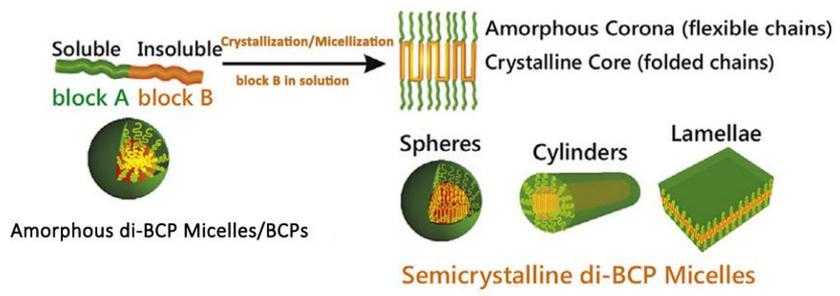
Introduction

Nanoscale two-dimensional (2D) polymer-based platelet structures are of considerable interest for a range of applications from composite reinforcement to liquid crystals. The crystallization-driven self-assembly (CDSA) of block copolymer was utilized by many researchers to construct 1D cylinder, 2D platelet structures and even 3D superstructures. The two-dimensional self-assembly of polyethylene (PE) based diblock copolymer and homopolymer was detailed discussed in this poster.



Scheme 1. Crystallization-driven self-assembly of crystalline BCPs.

Experiment and result

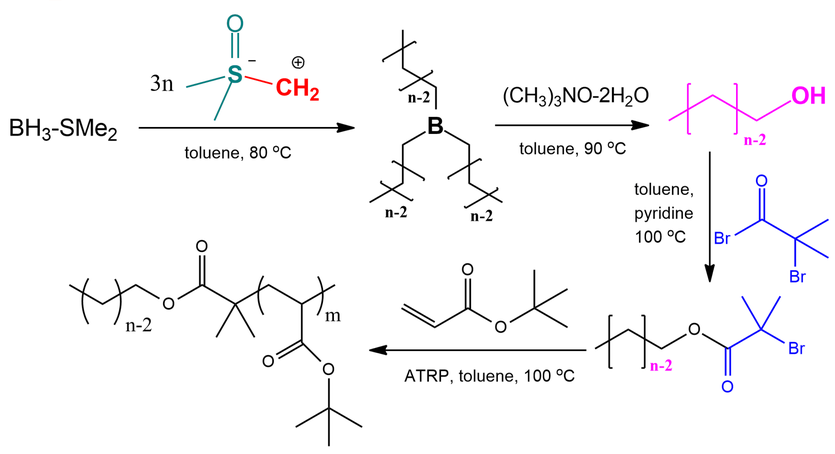


Fig. 1. Synthetic route of polyethylene and polyethylene-*b*-poly(*tert*-butylacrylate) (PE-*b*-P*t*BA).

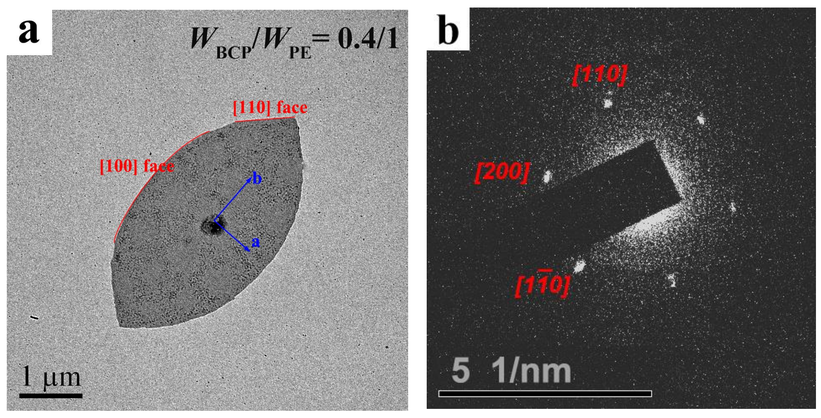
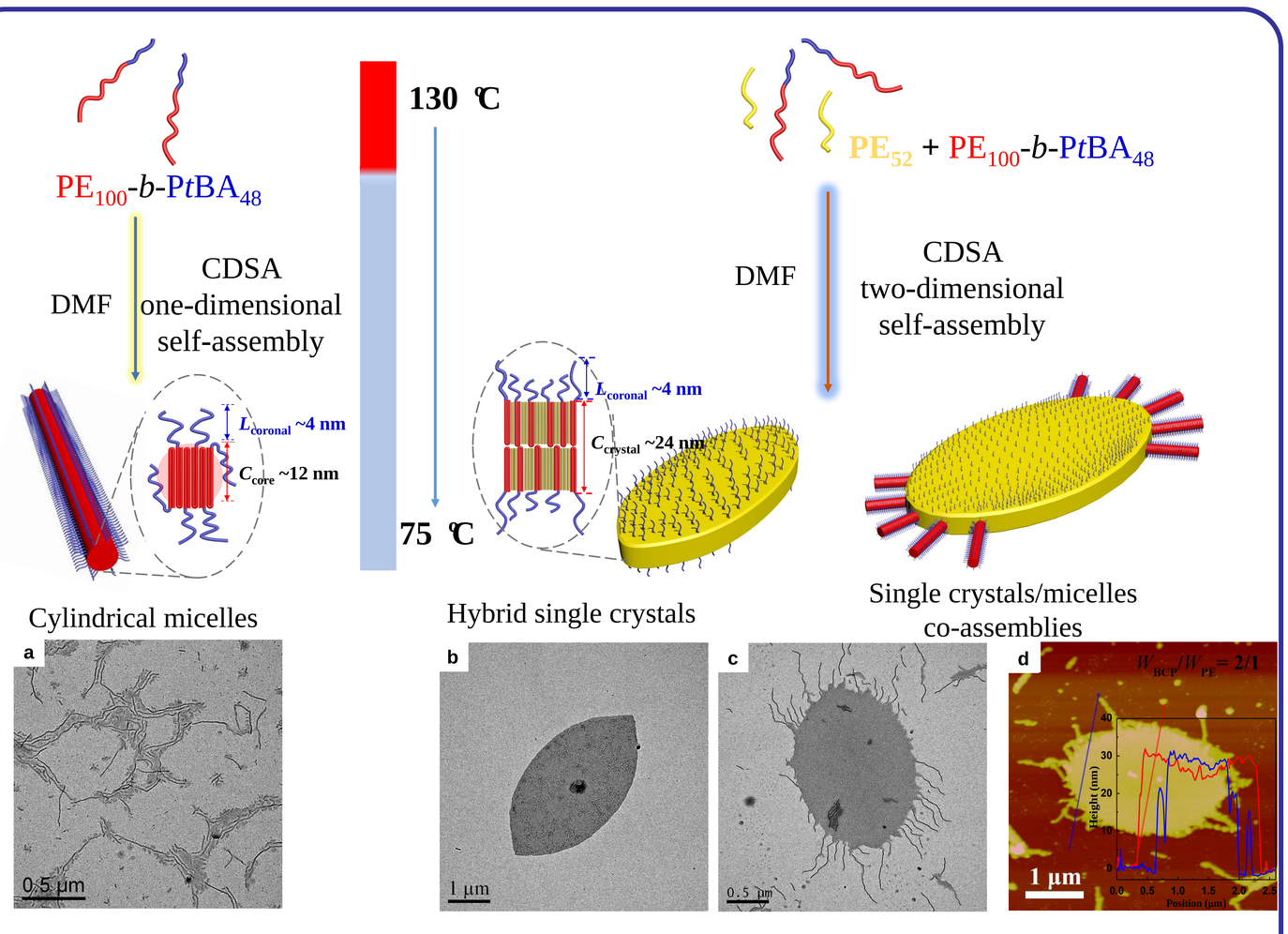


Fig. 2. Representative TEM image (a) and SAED image (b) of the hybrid single crystals formed by 1.0 mg PE_{100}-*b*-P*t*BA_{48} and 2.5 mg PE_{52} (W_{BCP}/W_{PE} = 0.4/1) in 5 mL DMF solution at T_c = 75 ℃.



Scheme 2. Crystallization-driven self-assembly of PE_{100}-*b*-P*t*BA_{48} BCPs and PE_{52} homopolymer in DMF at T_c= 75 ℃ via one-step method. The adding mass ratio of BCPs to PE homopolymer in polymer blend forming Hybrid single crystals: W_{BCP}/W_{PE} = 0.4/1, single crystals/micelles co-assemblies: W_{BCP}/W_{PE} = 2/1. Down below: TEM image of cylindrical micelles(a), hybrid single crystals(b), Single crystals/micelles co-assemblies(c) and AFM height image of Single crystals/micelles co-assemblies(d).

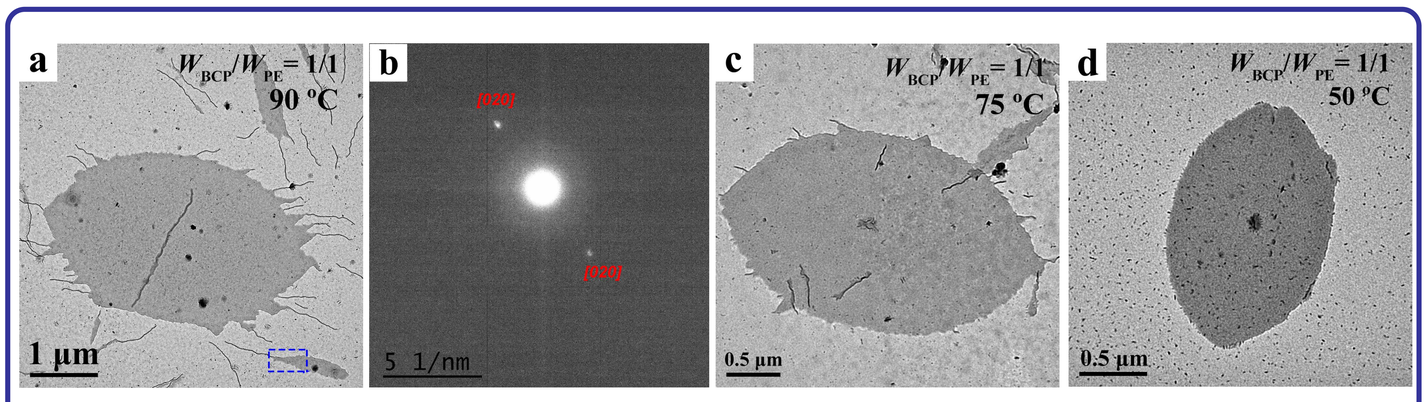
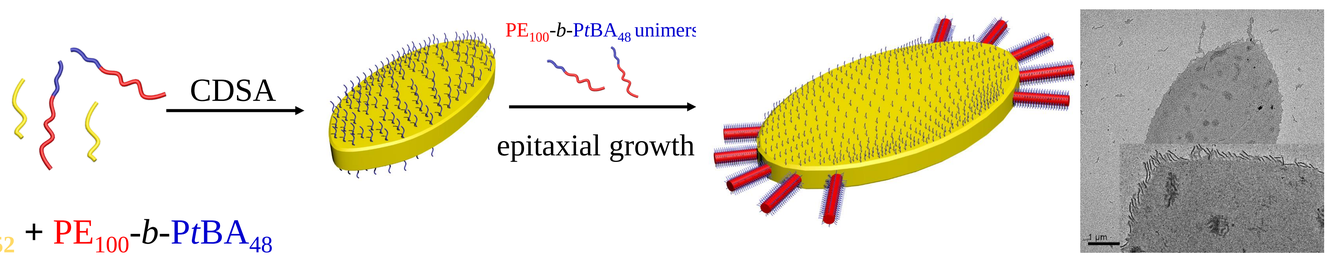


Fig. 3. Representative TEM images (a, c, d), SAED pattern (b) for the blue framed area in figure 3a of crystal/micelles hierarchical co-assemblies formed by 2.5 mg PE_{100}-*b*-P*t*BA_{48} and 2.5 mg PE_{52} (W_{BCP}/W_{PE} = 1/1) in 5 mL DMF at different T_cs.



Scheme 3. Crystal/micelles co-assemblies formed by PE_{100}-*b*-P*t*BA_{48} / PE_{52} in o-xylene / DMF (1/9 v/v) solution at T_c = 75 ℃ via two-step method: [1] the construction of pure hybrid single with polymer blend; [2] the epitaxial growth of BCPs along the lateral faces of hybrid single crystals.

Conclusions

Here we reported the crystallization-driven two dimensional self-assembly of PE-*b*-P*t*BA crystalline-coil diblock copolymer and crystalline PE homopolymer blends. “Ciliate paramecium-like” hierarchical co-assemblies were built through the combination of the one-dimensional self-assembly of diblock copolymer and two-dimensional self-assembly of polymer blends via one-step or two-step method. Because of the difference in crystallization rate, the distribution of PE-*b*-P*t*BA BCP in the hybrid single crystals may be inhomogeneous, leading to a concave gradient surface structure. The hybrid single crystals have a double-layer structure, in which PE homopolymer chains adopt extended conformation and the PE blocks in PE-*b*-P*t*BA are probably once-folded.

Acknowledgement

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References

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