Quasi-living growth of crystalline micelles of polyethylene-*b*-poly(*tert*-butylacrylate) diblock copolymers in DMF

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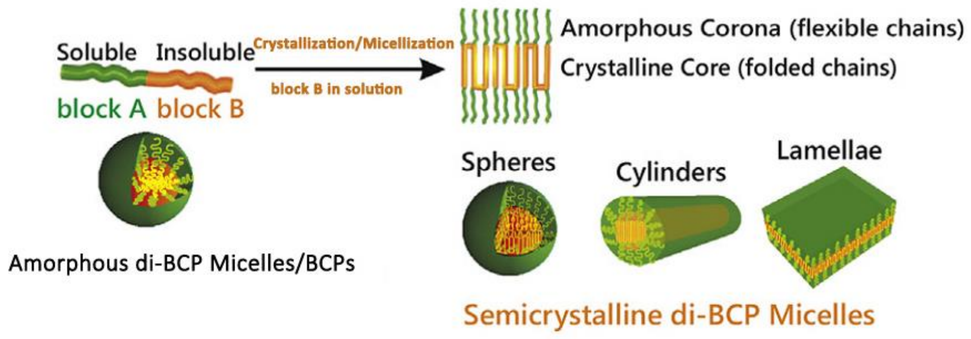
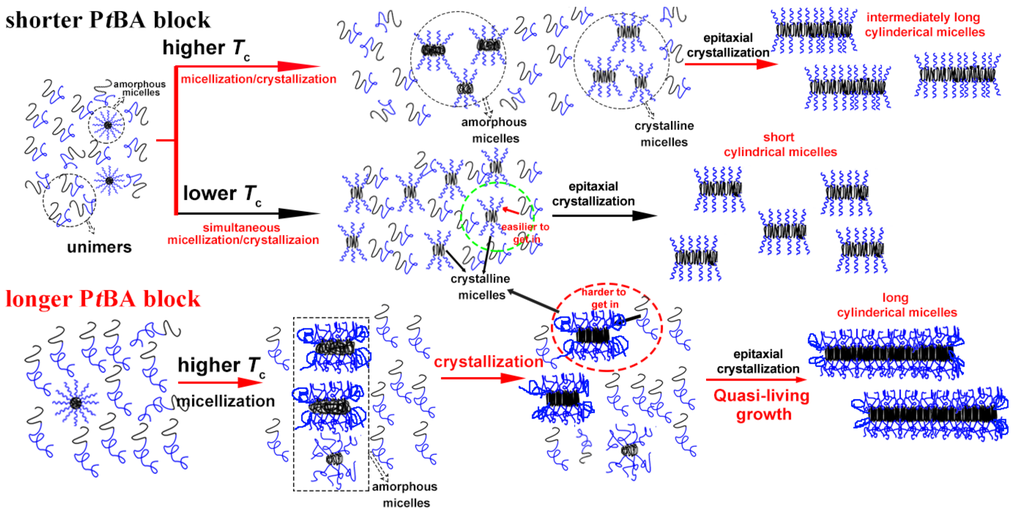
Introduction

The crystallization-driven self-assembly of crystalline-coil block copolymers (BCPs) have attracted significant attention due to their "living-growth" characteristic endowed by crystallization of core-forming block. However, the "living-growth" hasn't been realized for BCPs with highly variable critical micellization concentration or crystallizability at different temperatures. We studied the crystallization-driven one-dimensional self-assembly of polyethylene-*b*-poly(*tert*-butylacrylate) (PE-*b*-P*t*BA) BCPs in *N*,*N*-dimethyl formamide (DMF) and found that the length of the corona-forming block and crystallization temperature (T_c) had significant impacts on the length of micelles. Quasi-living growth was achieved at a high T_c for the PE-*b*-P*t*BA crystalline cylindrical micelles.



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

Experiment and result



Scheme 1. Scheme for the effects of T_c and the length of the corona-forming block on the formation of seed micelles and growth of the cylindrical micelles of PE-*b*-P*t*BA BCPs in DMF.

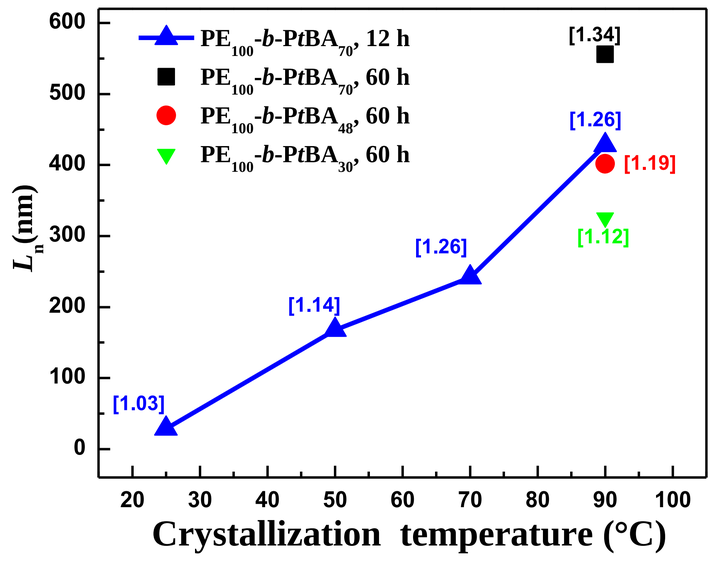


Figure 1. Dependence of the number-average contour length (L_n) on crystallization temperature (T_c) for three different PE-*b*-P*t*BA BCPs. The contour length distributions (L_w/L_n) are indicated in the brackets.

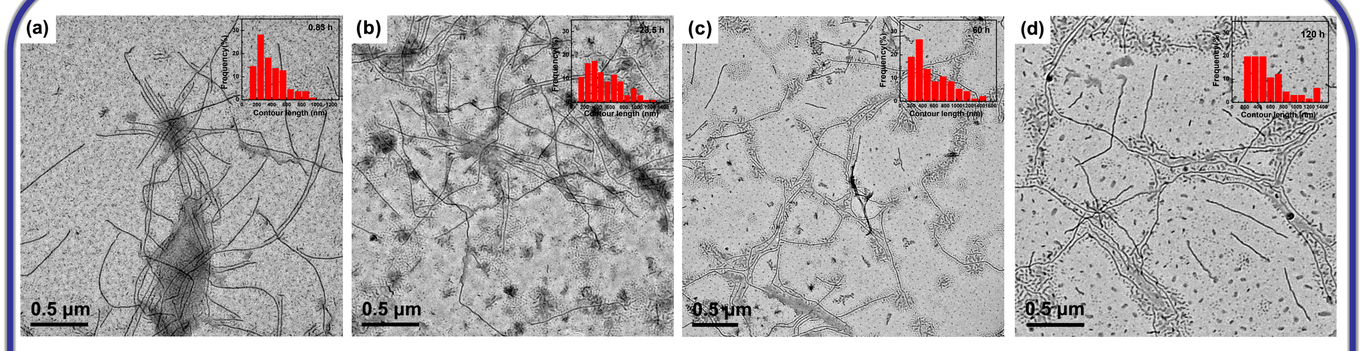
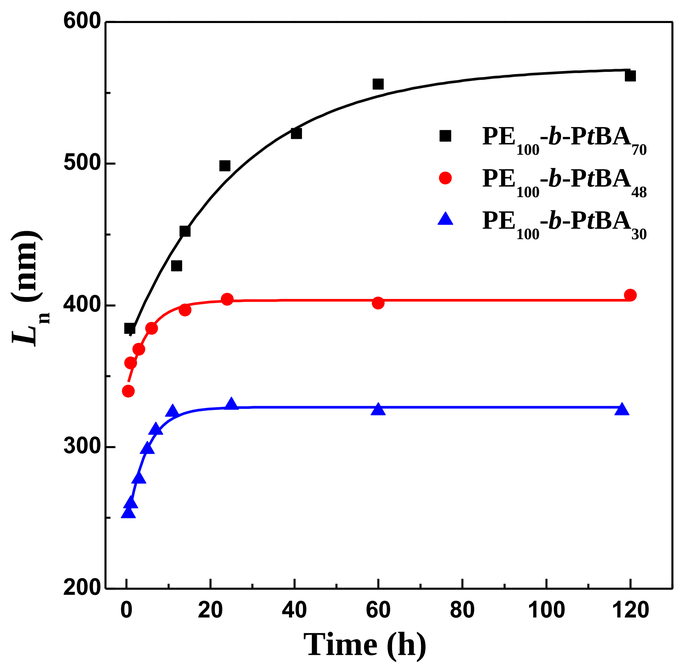


Figure 2. TEM micrographs of the cylindrical micelles for the PE_{100}-*b*-P*t*BA_{70} micelles in DMF solution after annealing at 130 ℃ for an hour and then growth at 90 ℃ for different times. (a) 0.83 h, (b) 23.5 h, (c) 60 h, (d) 120 h.



As for living growth model:

$$d[M]/dt = -k_1[n_s][M] \quad (1)$$

$$L_n = L_0 + Q[M_0](1-\exp(-k[n_s]t))/[n_s] \quad (2)$$

$[n_s]$: the concentration of the crystalline seed micelles
L_0: initial length of the seed micelles
Q: a constant referring to the length of cylindrical micelles with per mole BCP
$[M_0]$ and $[M]$ refer to the concentrations of the unimers at growth time t=0 and t

Figure 3. Variations of the number-average length (L_n) of the cylindrical micelles measured by TEM with growth time for the different PE-*b*-P*t*BA micelles in DMF solution. Fitting with equation(2).

Table 1. Parameters obtained by fitting with equation (2) for different PE-*b*-P*t*BA cylindrical micelles grown in DMF solution at 90 ℃.

Sample	L_0 (nm)	Growth rate(nm/h)	Final length(nm)
PE_{100}-*b*-P*t*BA_{30}	242	18.6	328
PE_{100}-*b*-P*t*BA_{48}	340	12.9	404
PE_{100}-*b*-P*t*BA_{70}	372	7.3	568

Conclusions

Ⅰ. A quasi-living mode can be applied to the growth kinetics of PE-*b*-P*t*BA crystalline cylindrical micelles in DMF at a high T_c. BCPs with longer P*t*BA block results in a smaller growth rate of the cylindrical micelles.

Ⅱ. Longer cylindrical micelles are formed at a higher T_c and for the PE-*b*-P*t*BA with a longer P*t*BA block. As the crystallizability of the PE-*b*-P*t*BA BCPs with a longer P*t*BA block and at a higher T_c is weaker, fewer but longer seed micelles are formed through micellization/crystallization process.

Ⅲ. The crystalline seed micelles are formed via two competitive processes: stepwise micellization/crystallization and simultaneous crystallization/ micellization. As the crystallizability varies with temperature and length of BCPs. The former prevails at a higher T_c or for the BCPs with a longer P*t*BA block, forming fewer but longer seed micelles. Besides, the latter dominates at a lower T_c or for the BCP with a shorter P*t*BA block, leading to more but shorter seed micelles.

Acknowledgement

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References

[1] B. Fan, L. Liu, J. T. Xu,* B.Y. Du, Z.Q. Fan, *Soft Matter*, 2016, **12**, 67-76.
[2] W. N. He, J. T. Xu,* *Prog. Polym. Sci.*, 2012, **37**, 1350-1400.