Phase behaviour of $LiClO_4$-doped poly(ε-caprolactone)-*b*-poly(ethylene oxide) hybrids with competitive interactions in the melt

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Introduction

Composite materials comprising BCP and inorganic salt have received great attention in the past decade because of their potential applications in lithium batteries, fuel cells and high density templates. Previously we studied the phase behavior of a poly(ε-caprolactone)-*b*-poly(ethylene oxide) (PCL-*b*-PEO) BCP doped with different amounts of $LiClO_4$ and observed that $LiClO_4$ could induce microphase separation of the miscible PCL-*b*-PEO in the melt. In this work, a series of PCL-*b*-PEO BCPs with different compositions were doped with $LiClO_4$ at various doping ratios. The phase behavior of the PCL-*b*-PEO/$LiClO_4$ hybrids was studies and the phase diagram (Fig. 1) was constructed.

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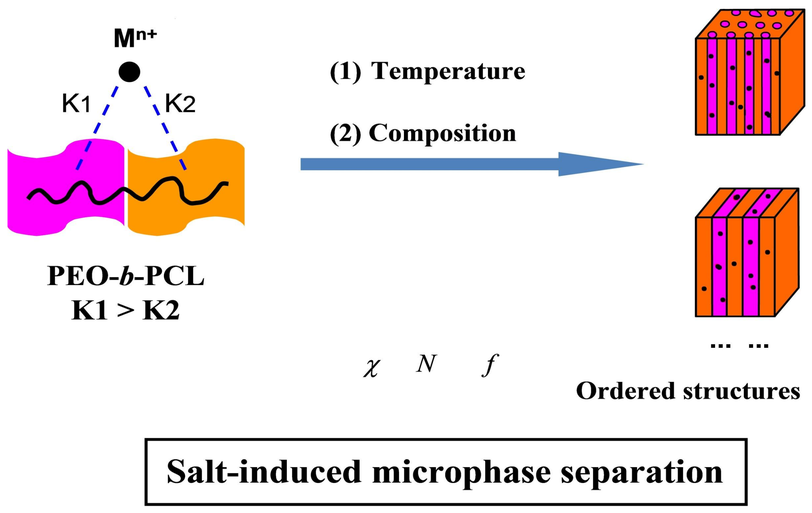


Experiment and result

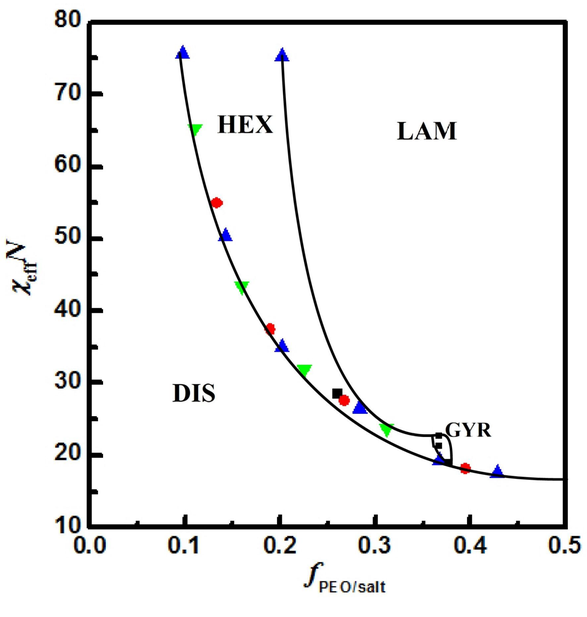
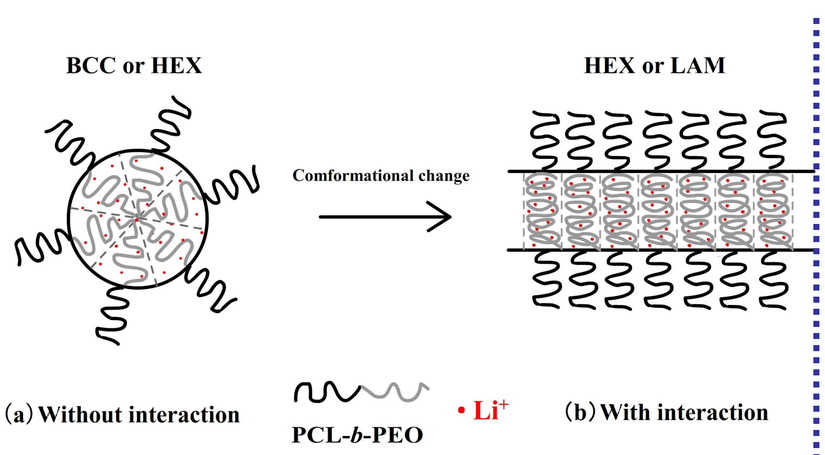


Fig. 1 Phase diagram of PCL-*b*-PEO/$LiClO_4$ hybrids with different composition. ■, ●, ▲, ▼ represent the salt doping ratio *r* =1/24, 1/12, 1/6 and 1/3 respectively.



Scheme 1. Schematic illustration for the morphological transformation due to the conformational change of the PEO block induced by association with Li^+ ions.

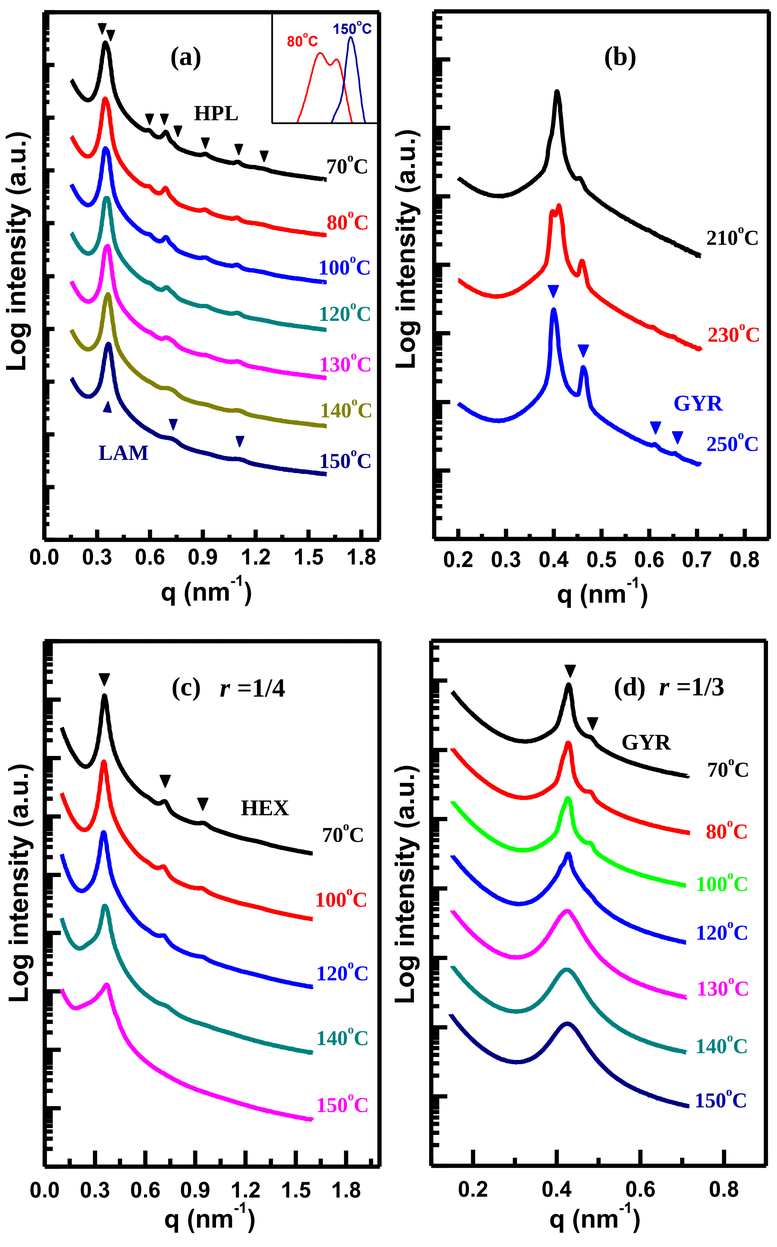
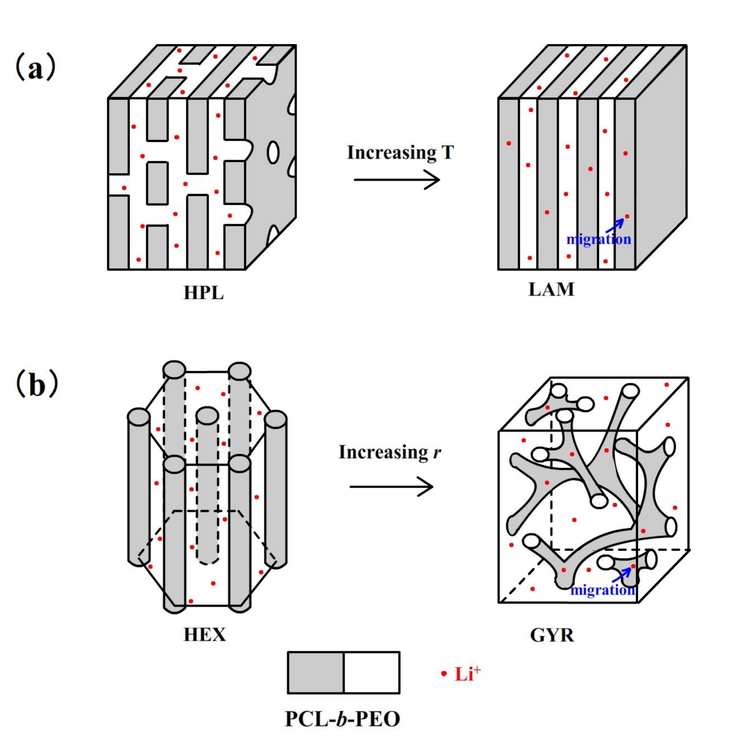


Fig. 2 SAXS profiles of PCL_{46}-*b*-PEO_{113}/$LiClO_4$ hybrids with *r* =1/6 (a, b), *r* =1/4 (c) and *r* =1/3 (d) at various temperatures.



Scheme 2. Schematic illustrations for the abnormal morphological transformations of PCL-*b*-PEO/$LiClO_4$ hybrids induced by increasing temperature (*T*) and doping ratio (*r*).

Conclusion

As compared with the phase diagram of the weakly segregated diblock copolymers, the phase diagram of the hybrids has two features: (a) this boundaries of the LAM and HEX structures shifts to lower $f_{PEO/salt}$ and no BCC structure is observed. (b) Some abnormal phase behaviors were observed for the hybrids with $f_{PEO/salt}$ >0.5, including the HPL to LAM transition upon heating the same hybrid and HEX to GYR transition with the increase of doping ratio at the same temperature. These abnormal phase behaviors are interpreted in terms of the competitive association of the PCL block with Li^+ ions at elevated temperatures and higher doping ratios. .

Acknowledgement

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References

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[2] Huang J., Tong Z. Z., Zhou B., Xu J. T., Fan Z. Q., *Polymer*, 2013, 54:3098.