Hierarchical self-assembly, photo-responsive phase behavior of azobenzene-containing ABA triblock copolymers

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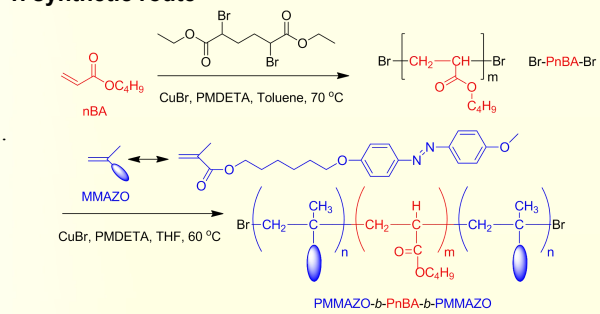
Introduction: Block copolymers (BCPs), in which the different blocks are chemically linked, may produce a variety of ordered nanostructures such as lamellae (LAM), hexagonally perforated lamellae (HPL), gyroid (GYR), hexagonally packed cylindrical (HEX) and body-centered cubic spherical (BCC), through self-assembly or microphase separation.[1] Specifically, BCPs containing azobenzene (azo) moiety are more popular for the development of new functional materials. Azo-containing polymers are of great interest since the azo chromophore can undergo reversible *trans-cis* photoisomerization.[2] The azo chromophore can act both as photo-responsive moiety and LC mesogen.[3] Herein, we prepared a series of ABA-type azo-containing triblock copolymers. Our emphasis was put on the interplay of LC ordering and microphase separation, LC ordering triggered OOT and the effect of UV radiation on the microphase behavior of these BCPs.

1. synthetic route



Scheme 1 The synthetic route of the PMMAZO-*b*-PnBA-*b*-PMMAZO BCPs.

2. Result

Table 1 Characteristics of synthesized polymers

Sample	M_n^{GPC}	PDI	Composition (NMR)	Conv (%)	LC content (wt%)
PnBA-1	26100	1.14	$PnBA_{204}$		
P1	31800	1.12	$PMMAZO_8$-b-$PnBA_{204}$-b-$PMMAZO_8$	21.4	19.5
P2	36600	1.14	$PMMAZO_{18}$-b-$PnBA_{204}$-b-$PMMAZO_{18}$	47.6	35.3
P3	39900	1.13	$PMMAZO_{21}$-b-$PnBA_{204}$-b-$PMMAZO_{21}$	53.6	38.9
P4	43600	1.20	$PMMAZO_{29}$-b-$PnBA_{204}$-b-$PMMAZO_{29}$	75.0	46.8
PnBA-2	56900	1.10	$PnBA_{445}$		
P5	72900	1.17	$PMMAZO_{29}$-b-$PnBA_{445}$-b-$PMMAZO_{29}$	41.6	28.6
P6	81600	1.23	$PMMAZO_{41}$-b-$PnBA_{445}$-b-$PMMAZO_{41}$	50.8	36.5
PnBA-3	72300	1.10	$PnBA_{564}$		

2.1. Self-assembled hierarchical structures at room temperature

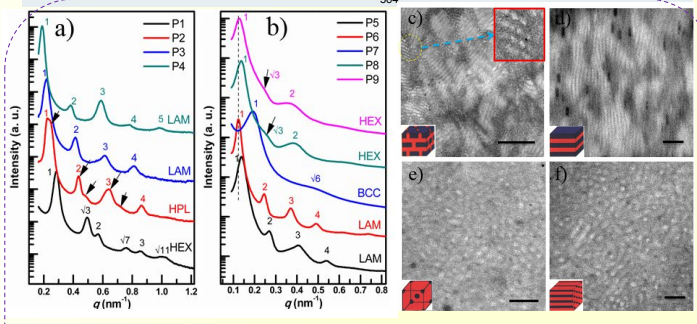


Fig.1 SAXS measurement and TEM observation for triblock copolymers: (a) SAXS profiles of P1-P4 and (b) P5-P9; selected TEM micrographs of (c) P2, inside is the magnification of the dashes circle; (d) P5; (e) P7; (f) P9. The scale bar in the figures is 200 nm.

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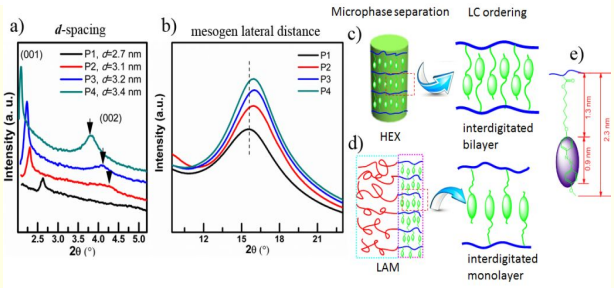


Fig.2 WAXD patterns of P1-P4 samples at room temperature at low angle reflecting the *d*-spacing (a), and at large angle reflecting lateral distance of the LC moieties (b). Illustrations of hierarchical structures from microphase-separated structure to the stacking of the LC moieties for P1 (c) and P4 (d). Side chain structure and length of the PMMAZO block (e).

2.2. effect of LC ordering and UV on phase separation

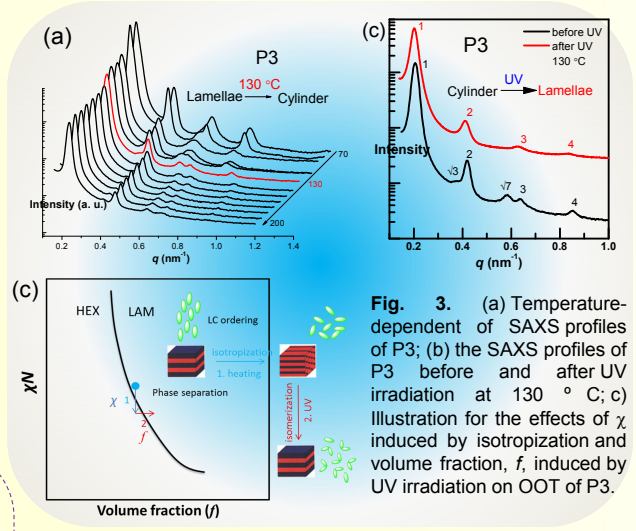
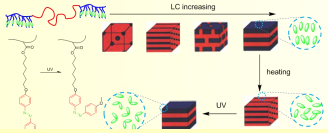


Fig. 3. (a) Temperature-dependent of SAXS profiles of P3; (b) the SAXS profiles of P3 before and after UV irradiation at 130 ° C; c) Illustration for the effects of χ induced by isotropization and volume fraction, *f*, induced by UV irradiation on OOT of P3.

3. Conclusion

Microphase separation can induce the different arrangement of LC ordering at smaller scale. On the other hand, the LC clearing can also induce the LAM to HEX transition; also when upon UV irradiation, HEX morphology can further be back to a LAM structure, as shown in following scheme.



4. References:

[1] I. W. Hamley, *The Physics of Block Copolymers*. Oxford University Press: 1998.

[2] H. F. Yu, J. Li, T. Ikeda and T. Iyoda, *Adv. Mater.*, 2006, **18**, 2213-2215.

[3] H. F. Yu and T. Ikeda, Adv. Mater., 2011, **23**, 2149-2180.