(B)

2016　2018

Development of microstructural technology using architecturally complex block copolymer

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This study is aiming at establishing new molecular design concept of block copolymer (BCP) materials for next generation lithography.
Branched and cyclic amphiphilic BCPs as well as tacticity-controlled amphiphilic BCPs were synthesized by using precision polymerization techniques and click reactions. A systematic investigation into those BCPs revealed that the incorporation of branched and cyclic architectures into the BCPs can be an effective mean to reduce the domain-spacing of the microphase-separated structures. Further, the control over the main chain tacticity can be a novel approach to achieve high-quality morphology.
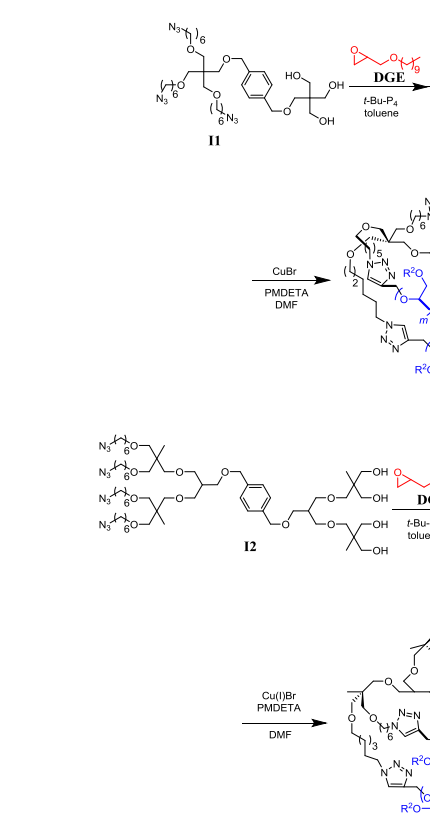
(Flory-Huggins

χ) ... (N) ... $(\chi N) \approx 10.5$ ...

$\chi N > 10.5$ ...

20 × nm (... 10 × nm) ...

>0>, ...

>1>, ...

$d \propto N^{2/3} \chi^{1/6}$ ... N ...

>2>, ...

(1) ...

(Satoh, T. et al. *Macromolecules* **2014**, *47*, 2853-2863 ...)

(Scheme 1)

P1 : X = H
P2 : X = -CH₂C≡CH ← BrCH₂C≡CH, NaH, THF

P3 ... Pd/C, H₂, THF ... P4

P5 : X = H
P6 : X = -CH₂C≡CH ← BrCH₂C≡CH, NaH, THF

P7 ... Pd/C, H₂, THF ... P8

Scheme 1.

3 Xb꒯   3 Xb꒯꒱M•   56ä   **I1**   4 Xb꒯   4 X
b꒱꒯M56ä   **I2 † 0**   **K**   **F8Z**   **X7ö**   *t*-Bu-P$_4$ K
6äb꒱[**DGE** \ **TEGGE**   3 6P>g   4 6P꒱
꒯꒱KS꒯꒱Kq
꒱꒯G[%MK-%gDX-%0vyö꒱�
†   G꒱KS   I꒲   6äg꒱꒯0꒱MG\
[3 6P>g   4 6PP꒱g0vyö꒱꒯bv B꒯KS   7§1e~
   0… X)zS˜   (SAXS) b)꒯   poly(**DGE**) \ poly(**TEGGE**) ꒱꒯e
c꒱MG꒱꒱ZO꒱꒯KS   86P꒱g   ꒱꒯e꒱
(Ė   jB   ꒲M•   6P꒱g ª ꒱꒱꒯꒱6꒱x[꒱MG
꒱G꒱14b꒱꒱8꒱wp≥E꒱꒯S4†
s꒱0… X)zS˜ (GISAXS) ꔚ   0꒱y   ꒯KX•
   ꔚ((6꒱꒲Z   3 Xb꒱꒲
꒱8꒱P꒱gꔚ꒱꒱/KS   7§1ev   GISAXS
b)꒯   g/c꒱P꒱g/꒲QKI꒱x[꒱MG\
꒱꒱SI꒲/[c꒱P꒱g/b   1/2꒱6꒱x   (13 nm) ꒲S

(2) g/0dN꒯꒱꒱KSg0vyö꒱꒯b   ˜꒱3
  t-Bu-P$_4$꒱52ä꒱3b꒱86P꒱g꒱DE[Cg/0dNö
꒱KS   ꒱꒱꒯v꒱6g/0dN꒱0vyö꒱꒯Ñ
꒱꒱꒱8jcG꒲꒱o꒱DI꒱N꒱꒱C   Q
G[꒱c   *t*-Bu-P$_4$ ꒱y꒱S꒱꒱ev꒱
꒱꒱g/0dN꒱꒱KSg0vyö   ꒱꒯e   b꒱†   ꒱꒲ K
S   (Scheme 2)
   ꒱꒱   /*t*-Bu-P$_4$ 6ä꒱꒲   DGE ((R)-**DGE**) \ DEGE ((R)-**DEGE**)
b꒱꒯b꒱6P꒱)b꒱o꒱G[g꒱
꒱   ꒱꒯e   ([*it*-PDGE]-*b*-[*it*-PHDGE]) ꒯KSrS]b2꒱꒯e
꒱꒱   ꒱꒱꒯꒱G[g/0dNbs꒱   3 8b꒱   È
꒱꒯e   ([*at*-PDGE]-*b*-[*at*-PHDGE] [*it*-PDGE]-*b*-[*at*-PHDGE] [*at*-PDGE]-*b*-[*it*-PHDGE])
v꒱KS   7§1ey
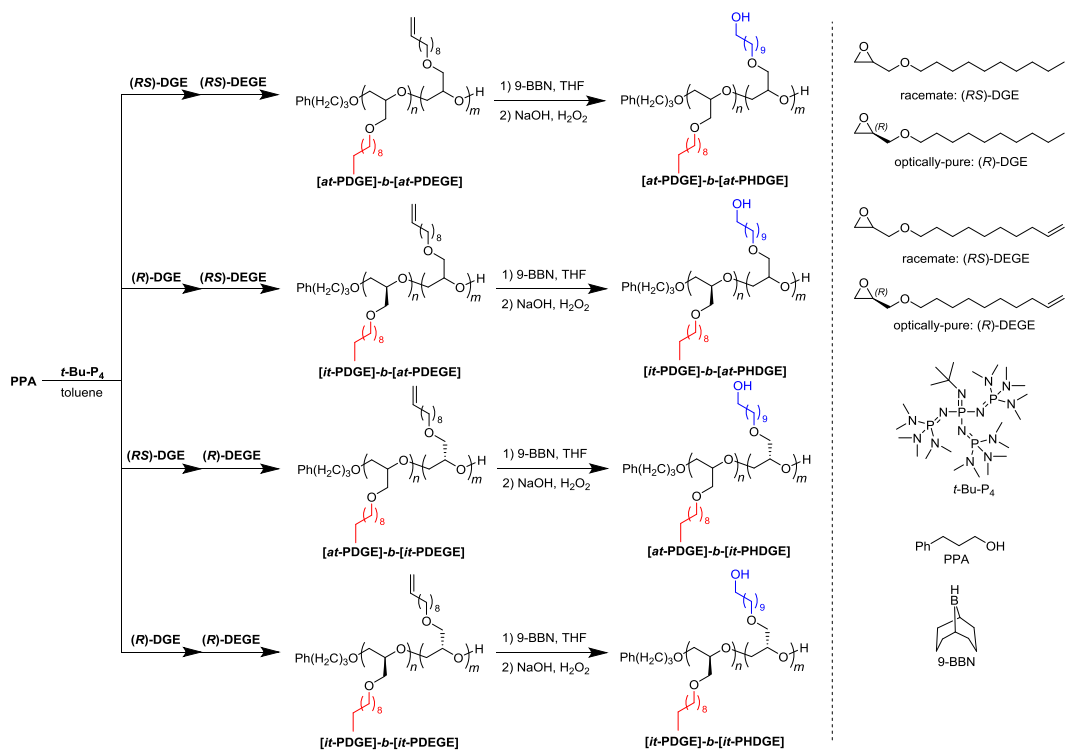
Scheme 2. g/0dNö   Dš g0vyö꒱꒯b

GG[꒱M4b꒱꒱8꒱g2n꒱꒱Ò   (DSC) ꒲S   **PDGE** c
8꒱꒱M@   *it*-**PDGE** c *at*-**PDGE** 3꒱꒱   (T_m) ꒲C꒱Zg
/0dNö@   PDGE b)꒱꒱Cs8jMG꒱bKSM‰   *it*-**PHDGE** \ *at*-**PHDGE**
꒱3꒱M꒲꒒ T_m ꒱꒱ss꒲S)F8꒱/0dN꒱
[PDGE]-*b*-[PHDGE] ꒱8Z   DSC KSG•   BCP c **PDGE** \ **PHDGE** ꒱꒱
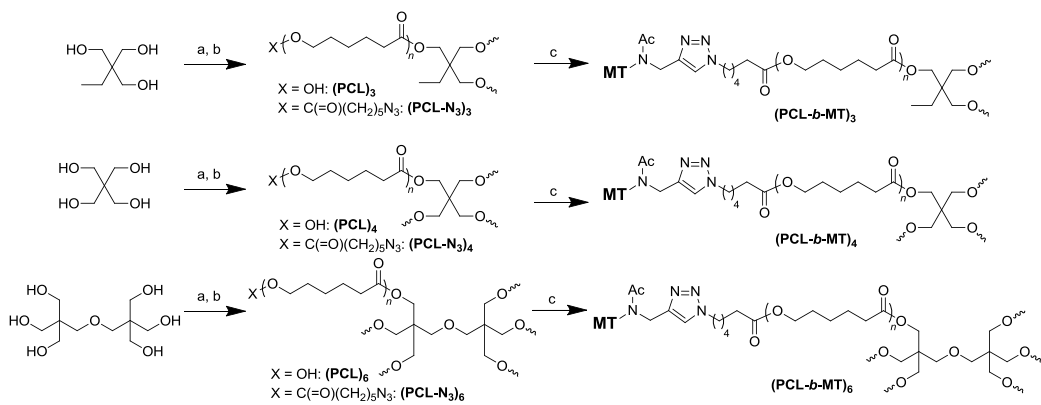
a) ε-Caprolactone, DPP, bulk at 80 °C; b) N₃(CH₂)₅COOH, EDC, DMAP in CH₂Cl₂; c) MT-C≡CH, CuBr, PMDETA in DMF at 60 °C

Scheme 3. ᵢ6Pᵼᵉ   b ᵦ
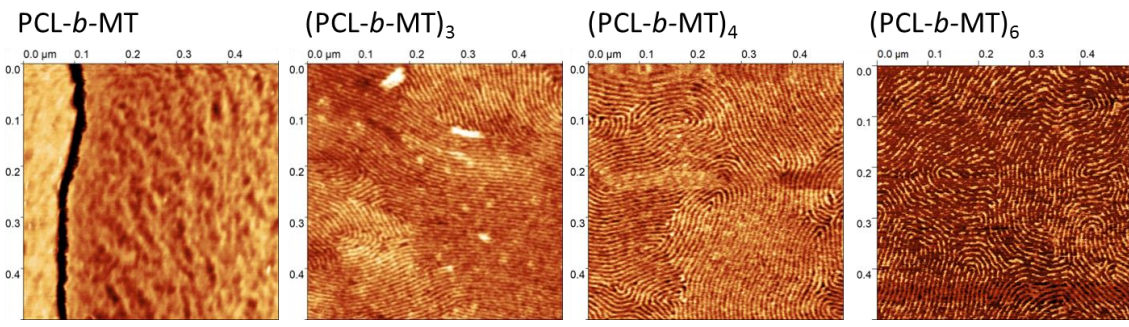
Figure 1. ᵢ6Pᵼᵼ0KS-ᵂb   AFM ᵼ   ()ᵼ   )

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