Electronic Supplementary Material (ESI) for Polymer Chemistry.
This journal is © The Royal Society of Chemistry 2018

# Electronic Supplementary Information

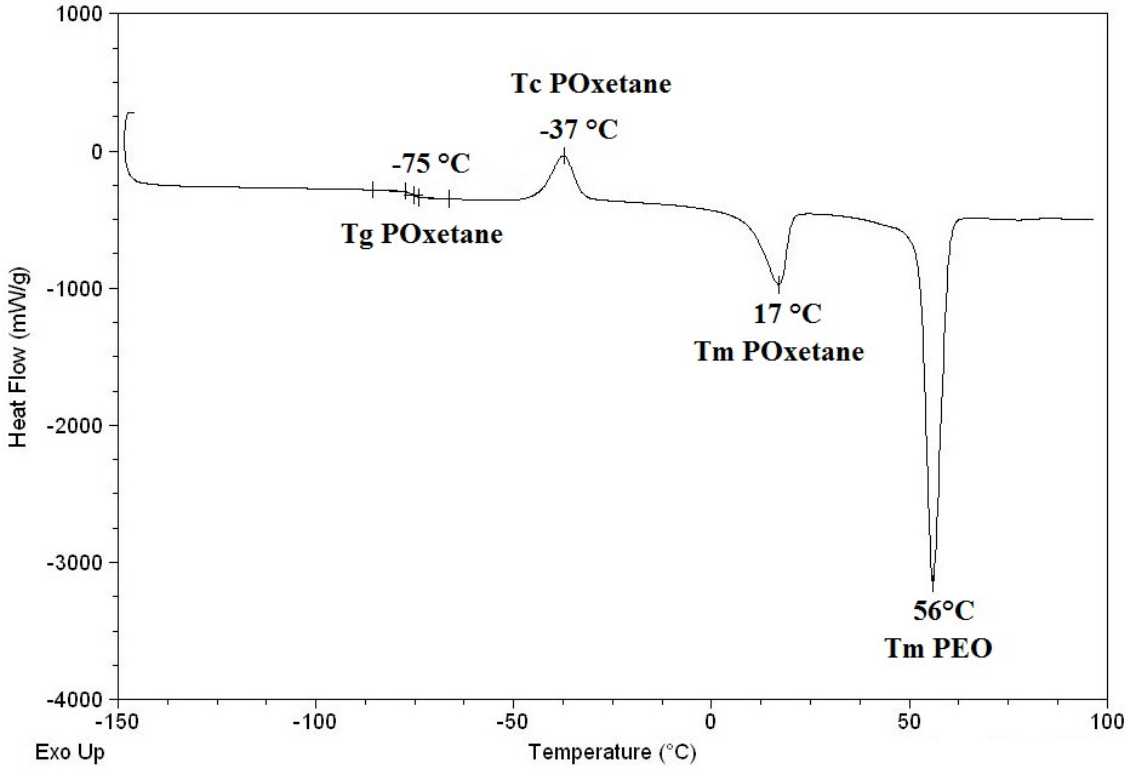


**Figure S1.** DSC analysis of $PEO_{227}$-b-$POxetane_{172}$ ($\overline{Mn}_{SEC}$ = 21000 g/mol, Đ = 1.24, Run 1 Table 2) synthesized by $NOct_4Br$/i-$Bu_3Al$ initiating system and simultaneous addition of both monomers ([i-$Bu_3Al$]/[$NOct_4Br$] = 4, [EO+Oxetane] = 3 M, toluene, 20 °C)

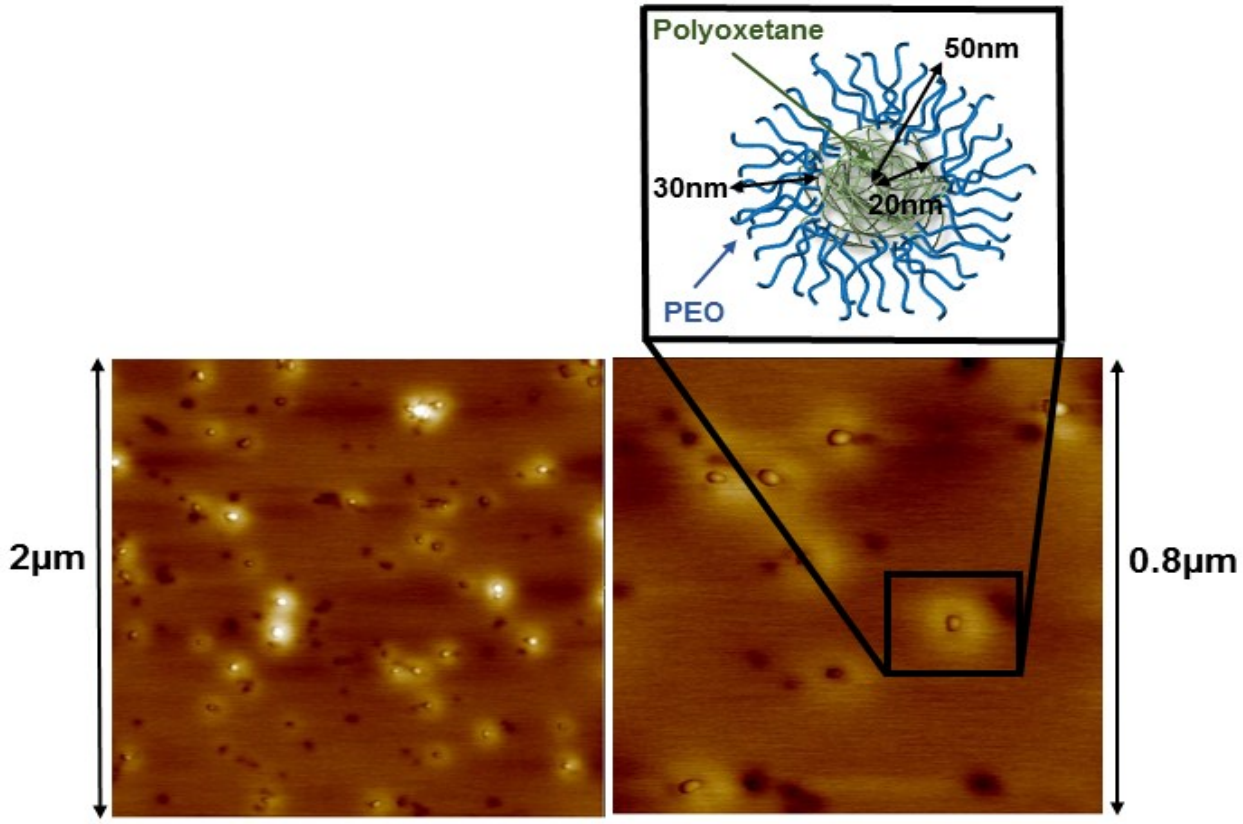


**Figure S2.** AFM pictures of solution of $PEO_{68}$-b-$POxetane_{52}$ (Run 3, Table 2) from water at 50 °C on mica surface

**Table S1.** Evolution of molar masses and composition during copolymerization of oxetane and ethylene oxide with addition of EO after 23 hours of reaction (Run 3 Table 3) ($NOct_4Br$/*i*-$Bu_3Al$ (1/4), toluene, [oxetane] = 3 M) leading to $POx_a$-*b*-PEO-*b*-$POx_b$

| Time (h) | $DP_{PEO}/DP_{POx}$ [a] | $\overline{Mn}$ PEO NMR [b] (g/mol) | $\overline{Mn}$ $POx_b$ [c] (g/mol) | $\overline{Mn}$ NMR [b] (g/mol) | $\overline{Mn}$ SEC [d] (g/mol) | Đ [d] |
|---|---|---|---|---|---|---|
| 23 | / | / | / | / | 4400 | 1.10 |
| 24 | 0.42 | 1400 | / | 5800 | 5900 | 1.08 |
| 46 | 0.29 | 1400 | 1500 | 7800 | 7400 | 1.21 |

a) calculated with ratio [PEO]/[POx] by $^1$H NMR, b) calculated with the molar mass of the first polyoxetane block observed in SEC, c) calculated with SEC results of final polymer with SEC results of diblock copolymer, d) determined by SEC in THF with PEO standards