**Electronic Supplementary Information (ESI)** 

## Design of AB Divinyl "Template Monomers" toward Alternating Sequence Control in Metal-Catalyzed Living Radical Polymerization

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**Figure ESI-1.** Tacticity analyses by <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, r.t.) with  $\alpha$ -methyl proton of PMMA at 0.8–1.2 ppm. (A) PMMA via hydrolysis/methylation of poly(BzMA): [BzMA]<sub>0</sub>/[H–(MMA)<sub>2</sub>–Cl]<sub>0</sub>/[Cp\*RuCl(PPh<sub>3</sub>)<sub>2</sub>]<sub>0</sub>/n-Bu<sub>2</sub>NH polymerization of BzMA; = 2000/100/2.0/40 mM in DCE at 80°C [poly(BzMA):  $M_n = 3400$ ;  $M_w/M_n = 1.36$ ]. (B) PMMA hydrolysis/methylation of poly(Naph-MM): polymerization of Naph-MM; via  $[Naph-MM]_0/[H-(MMA)_2-Cl]_0/[Cp*RuCl(PPh_3)_2]_0/n-Bu_2NH = 100/4/0.4/16 \text{ mM in DCE at}$ 60°C [poly(**Naph-MM**):  $M_n = 5900$ ;  $M_w/M_n = 1.19$ ]. See the main text for the condition of hydrolysis/methylation.