

Supporting Information for

Photoresponsive Behavior and Self-Organization of Azobenzene-Containing Block Copolymers

*Shu-Chi Tsao and Chieh-Tsung Lo**

Department of Chemical Engineering, National Cheng Kung University

No. 1, University Road, Tainan City 701, Taiwan

Characterization of azobenzene-containing monomer

4-Methoxy-4'-hydroxyazobenzene (M1)

FT-IR (KBr): 3419 cm^{-1} (OH). $^1\text{H-NMR}$ (CDCl_3), δ : 3.9 (s, 3H, ArOCH_3), 5.6 (s, 1H, -OH), 6.9–7.9 (m, 8H, aromatic). Molecular formula: $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$.

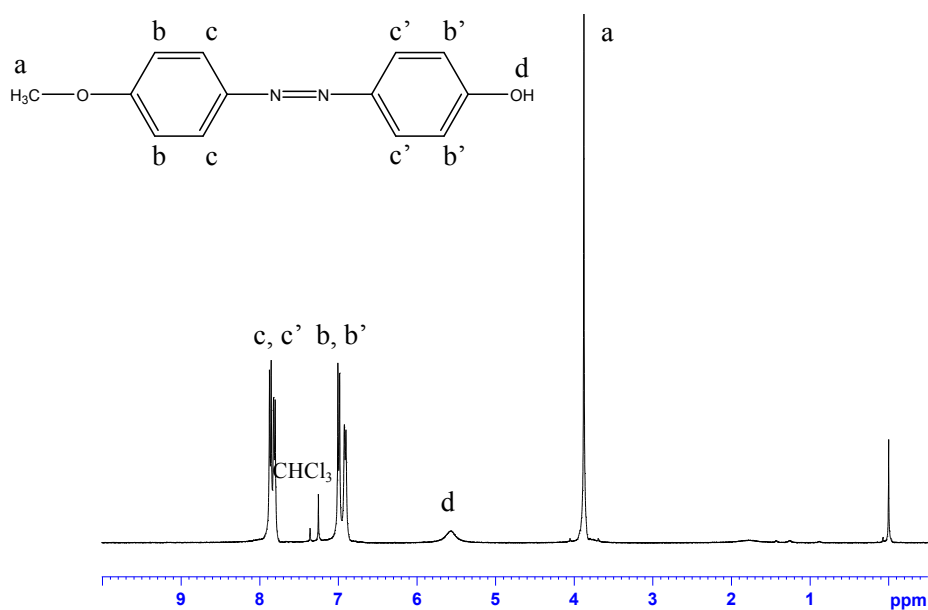
4-Methoxy-4'-(6-hydroxyhexyloxy) azobenzene (M2)

Yield: 64.3%. FT-IR (KBr): 3301 cm^{-1} (OH), 2940, 2862 cm^{-1} (CH_2). $^1\text{H-NMR}$ (CDCl_3), δ : 1.3–1.8 (m, 8H, methylene), 3.66–3.7 (t, 2H, $-\text{OCH}_2$), 3.88 (s, 3H, ArOCH_3), 4.07–4.11 (t, 2H, $-\text{OH}_2$), 6.9–7.9 (m, 8H, aromatic). Molecular formula: $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_3$.

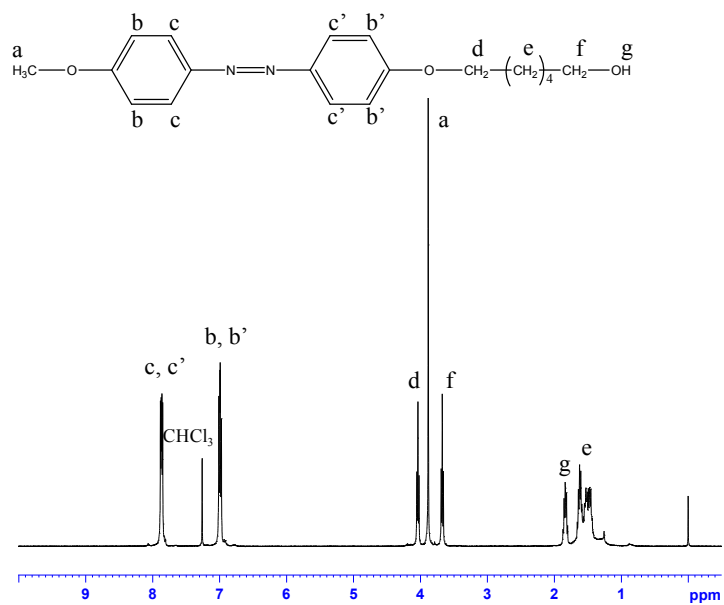
6-[4-(4'-Methoxyphenylazo)phenoxy]hexylmethacrylate (M3)

Yield: 47.2%. FT-IR (KBr): 2945, 2866 cm^{-1} (CH_2), 1710 cm^{-1} (C=O), 1640 cm^{-1} (C=C). $^1\text{H-NMR}$

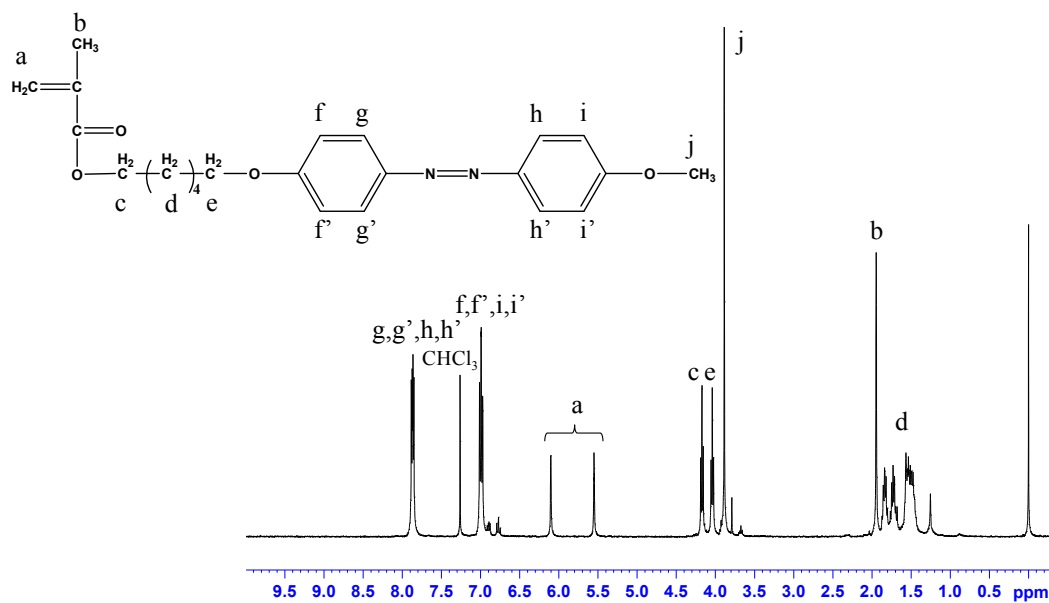
(CDCl₃), δ : 1.4–2.0 (m, 10H, methylene), 3.88 (s, 3H, ArOCH₃), 4.07-4.13 (t, 4H, -OH₂), 5.53-5.67 (dd, 1H, H₂C=C), 6.08-6.17 (dd, 1H, H₂C=C), 6.9–7.9(m, 8H, aromatic). Molecular formula: C₂₃H₂₈N₂O₄.



(a)



(b)



(c)

Figure S1. ^1H -NMR spectra of (a) M1; (b) M2; and (c) M3.

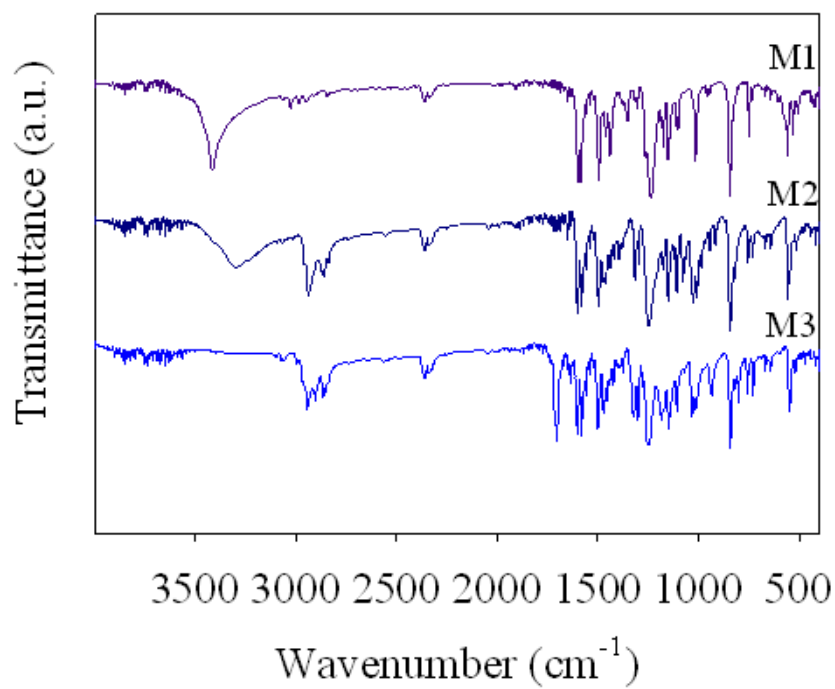
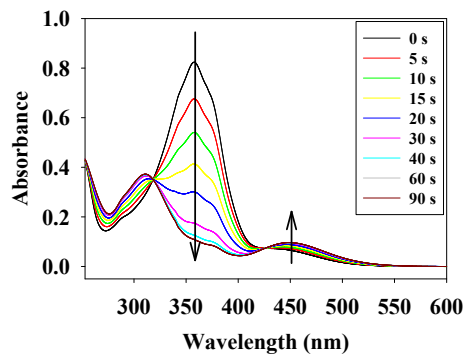
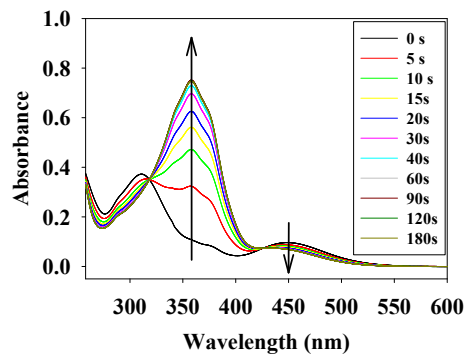


Figure S2. FTIR spectra of M1, M2, and M3.

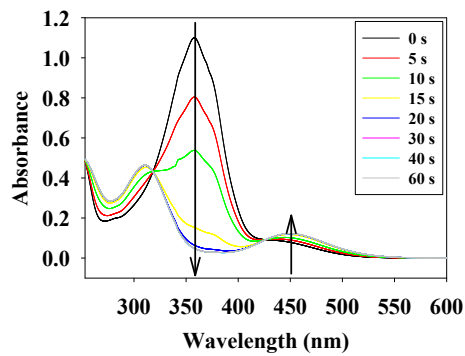
UV-vis spectra of various PtBA-PAzoMA block copolymers in THF



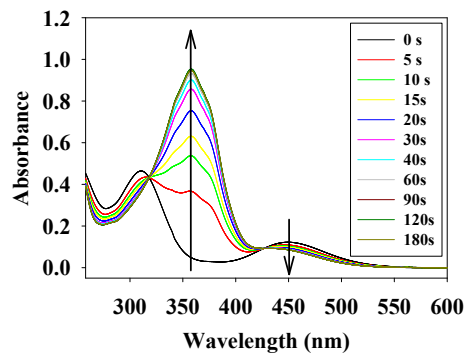
(a)



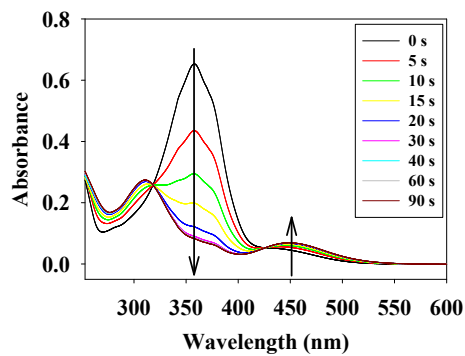
(b)



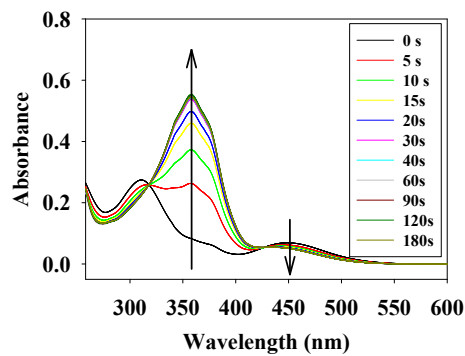
(c)



(d)



(e)



(f)

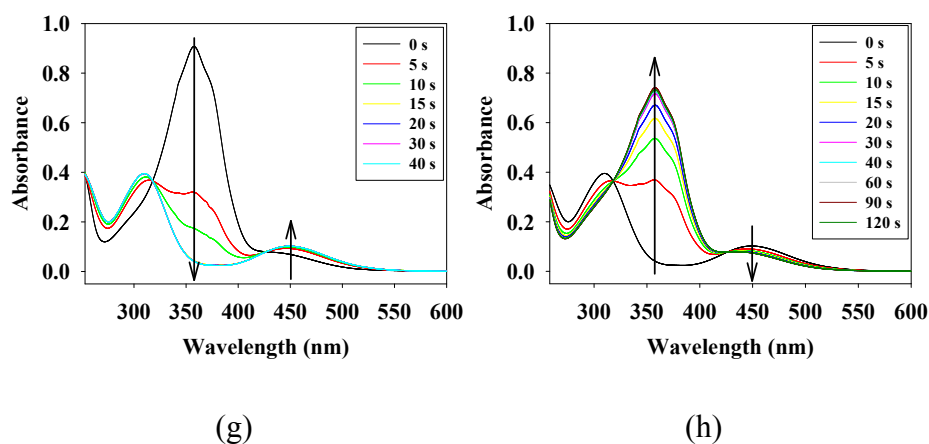


Figure S3. Variation of UV-vis spectra of various PtBA-PAzoMA block copolymers in THF. (a)(b) PtBA₁₁₀-PAzoMA₁₂₈; (c)(d) PtBA₁₇₀-PAzoMA₉₉; (e)(f) PtBA₁₇₀-PAzoMA₄₉; and (g)(h) PtBA₃₀₀-PAzoMA₄₀. (a)(c)(e)(g) Irradiated with UV light; and (b)(d)(f)(h) recovered with visible light for different times. The concentration of polymer solution was 0.05 mg/mL.

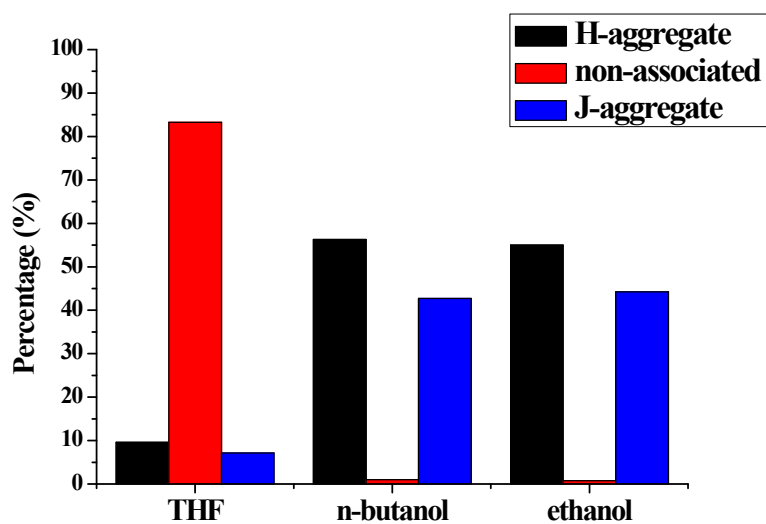


Figure S4. The population of different organizations of azobenzenes in PtBA₃₀₀-PAzoMA₄₀ as a function of the solvency.