

Photo-responsive block copolymer: Synthesis, Characterization and surface activity control

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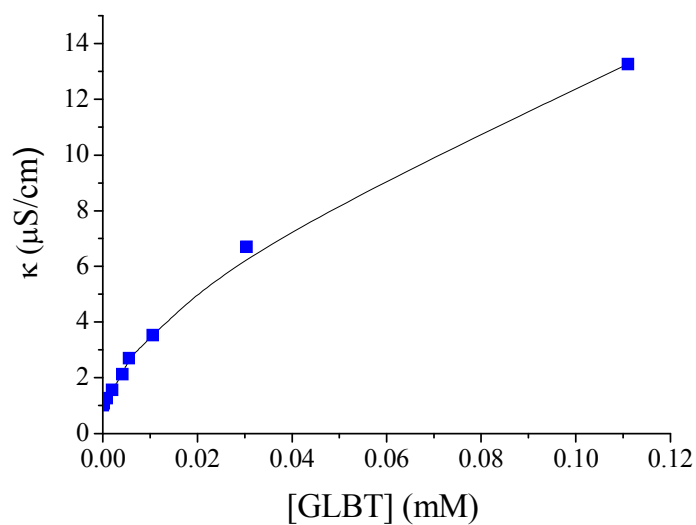


Figure S1 Plot of conductivity versus GLBT concentration at pH 7.

Determination of pKa of GLBT

In order to investigate the dissociation and ionic behavior of betaine, pKa measurement has been performed. 0.3 g of GLBT was dissolved in 0.05 mol/L of 100 ml sodium nitrate solution. 10 ml of 0.1 mol/L nitric acid was added in the solution, pH at 2.488, followed by titration with 0.1 mol/L NaOH solution. Titration plot of pH versus volume of sodium hydroxide is given in Figure S2. At half of the equivalence point concentration of GLBT and its conjugate base are equal hence pH will be equal to pKa of the acid at this point. The pKa of GLBT is determined to 2.81 from Figure S2.

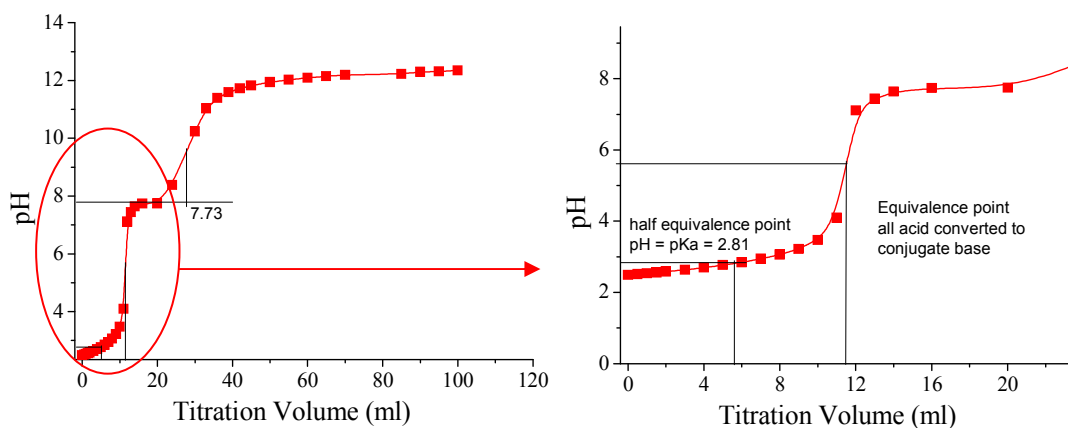


Figure S2 pH titration curve for GLBT against added volume of 0.1 mol/L NaOH.

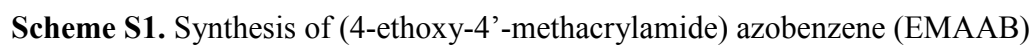
Synthesis of (4-ethoxy-4'-methacrylamide) azobenzene (EMAAB) Synthesis of EMAAB have been done following a method reported elsewhere.¹ (Scheme S1) Characterization of compounds is shown here.

4-hydroxy-4'-nitroazobenzene (NHAB). Yield: 80%. ¹H NMR (400 MHz, CD₃OD, ppm): 8.36 (d, o-ArH to NO₂ 2H), 7.97 (d, m-ArH to NO₂, 2H), 7.86 (d, m-ArH to OH, 2H),

4-Ethoxy-4'-nitroazobenzene (ENAB). Yield: 65 %. ¹H-NMR (400 MHz, δ ppm, CDCl₃): 8.40 (d, 2H, o-ArH to NO₂), 7.97 (q, 4H, o-ArH to -N=N-), 7.01 (d, 2H, o-ArH to OCH₂CH₃), 4.15 (q, 2H, OCH₂CH₃), 1.46 (t, 3H, OCH₂CH₃). UV-Vis: λ_{max}=375 nm (in CH₃OH).

4-Ethoxy-4'-aminoazobenzene (EAAB). Yield: 65 %. ¹H-NMR (400 MHz, δ ppm, CDCl₃): 7.80 (q, 4H, o-ArH to -N=N-), 6.96 (d, 2H, o-ArH to OCH₂CH₃), 6.72 (d, 2H, o-ArH to NH₂), 4.10 (q, 2H, OCH₂CH₃), 3.97 (s, 2H, NH₂), 1.44 (t, 3H, OCH₂CH₃). UV-Vis: λ_{max}=393 nm (in CH₃OH).

4-Ethoxy-4'-methacrylamideazobenzene (EMAAB). Yield 50% ¹H-NMR (400 MHz, δ ppm, CDCl₃): 7.89 (d, 4H, o-ArH to -N=N-), 7.72 (d, 2H, o-ArH to NH), 7.63 (s, 1H, NH), 6.99 (d, 2H, o-ArH to OCH₂CH₃), 5.83 (s, 1H, =CH), 5.51 (s, 1H, =CH), 4.12 (q, 2H, OCH₂CH₃), 2.09 (s, 3H, CH₃ to =CH₂), 1.47 (t, 3H, OCH₂CH₃). UV-Vis: λ_{max}=365 nm (in THF).



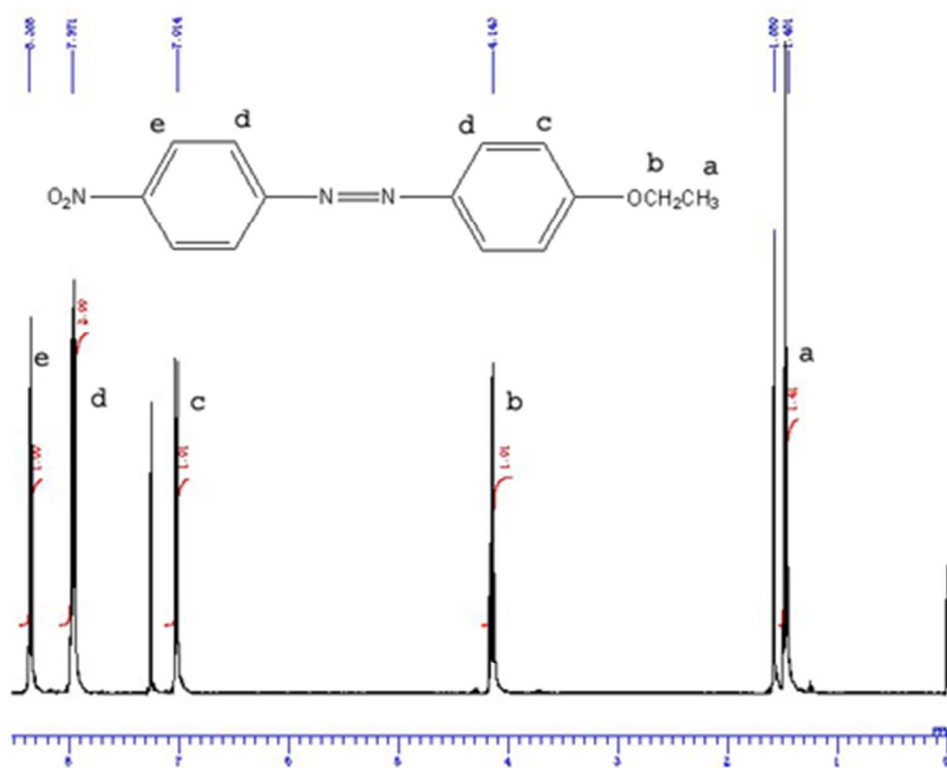


Chart S2. NMR Spectrum of 4-ethoxy-4'-nitroazobenzene in CDCl₃ solvent.

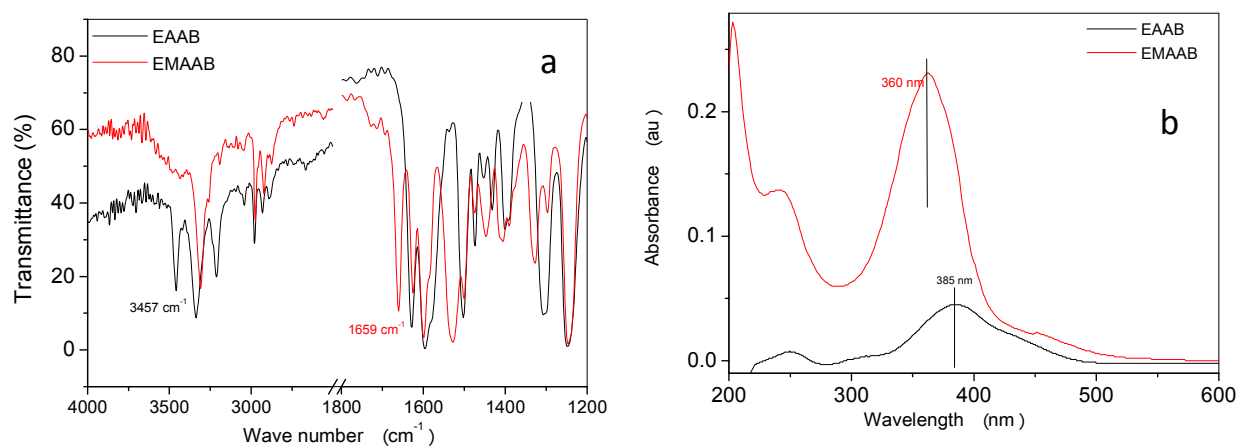


Figure S3. (a) IR and (b) UV (in methanol) spectra of EAAB and EMAAB.

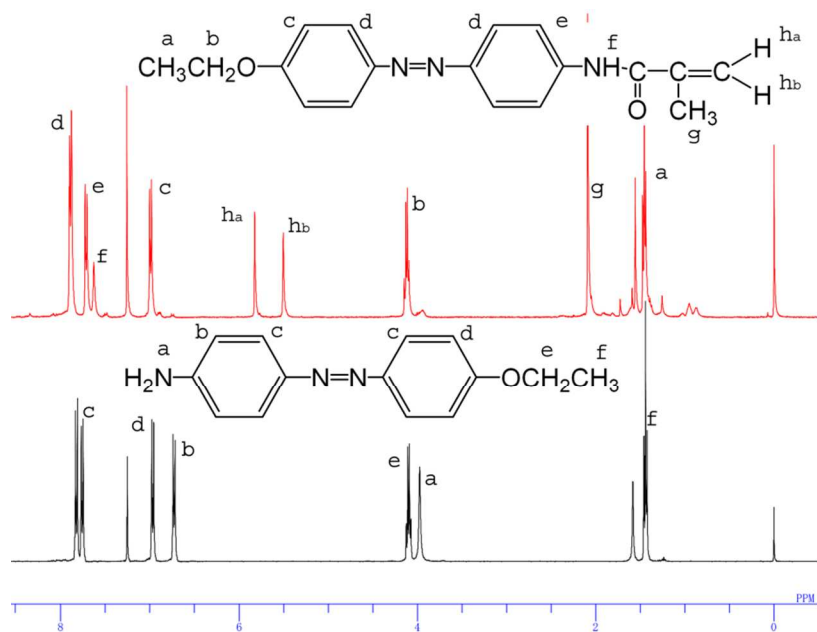


Chart S3. NMR spectra of EAAB and EMAAB.

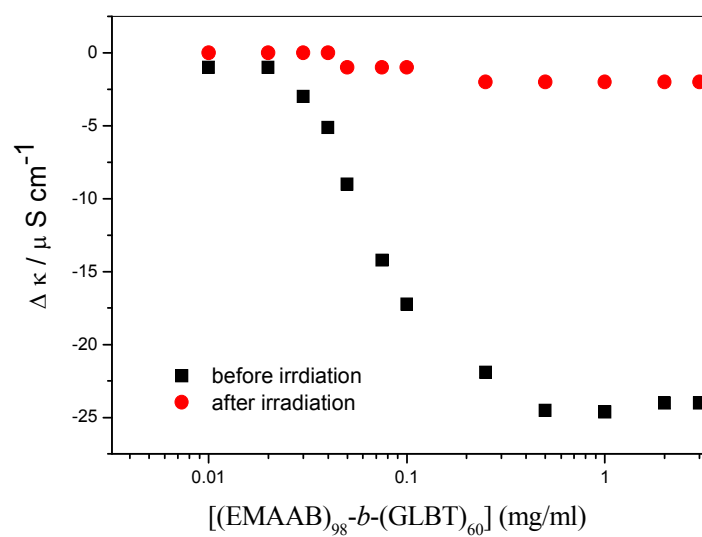


Figure S4 Variation of $\Delta\kappa$ with [surfactant] in solution containing and 0.1 mM KCl with varying $[(\text{EMAAB})_{98}\text{-}b\text{-(GLBT)}_{60}]$ in pH 2 buffer.

Conductivity of poly(GLBT) vs pH

The conductivity pure buffer solution was subtracted from conductivity of polymer solution to plot the graph.

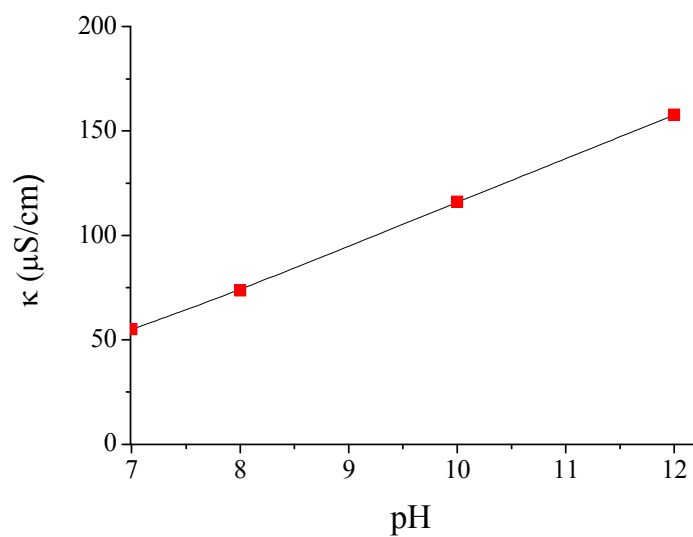


Figure S5 Plot of electric conductivity with pH of 1.7 mg/ml buffer solution of poly(GLBT).

Reference

1. Zhao, Y.; Tremblay, L.; Zhao, Y., Doubly photoresponsive and water-soluble block copolymers: Synthesis and thermosensitivity. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, 48, (18), 4055-4066.