

## Formation of Hybrid Micelles from Poly(ethylene glycol)-*block*-poly(4-vinylpyridinium) Cations and SO<sub>4</sub><sup>2-</sup> Anions in an Aqueous Milieu

Kai Wu, Linqi Shi,\* Wangqing Zhang, Yingli An, Xiao-Xia Zhu\*, Xu zhang, Zhanyong Li  
[\*]

K. Wu, Prof. L. Shi, W. Zhang, Y. An.

Institute of Polymer Chemistry, Nankai University, Tianjin, 300071, China

E-mail: shilinqi@nankai.edu.cn.

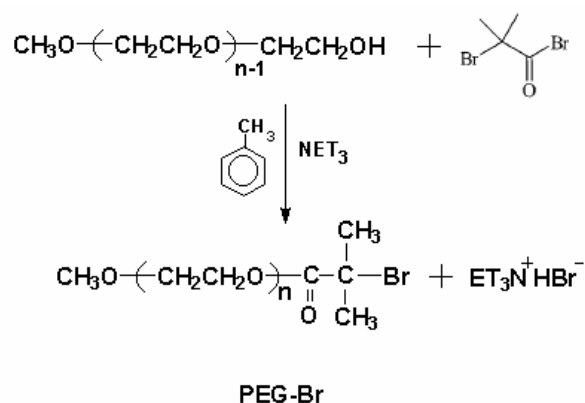
Prof. X.X. Zhu

Département de chimie, Université de Montréal, Pavillon Bombardier, C.P. 6128, succ.

Centre-ville, Montreal, QC, H3C 3J7, Canada

E-mail: julian.zhu@umontreal.ca

**Preparation of the Macroinitiator PEG<sub>112</sub>-Br.** 25.0 g CH<sub>3</sub>O-PEG<sub>112</sub>-OH was dissolved in 300 mL of toluene in a 500 mL three-neck flask. After azeotropic distillation of about 60 mL toluene at reduced pressure to remove traces of water, 2.5 mL triethylamine was added and the solution mixture was cooled to 0°C. Then 2.0 mL 2-bromoisobutyryl bromide was added dropwise via syringe over 1 hour, and the reaction mixture was stirred overnight at room temperature. The stirred solution was treated with charcoal, which was subsequently removed by filtration, and most of the toluene was removed by rotary evaporation prior to precipitation into a 10-fold excess of cold ether. The crude polymer was dried under vacuum, dissolved in water at pH 8-9, and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were collected and dried over MgSO<sub>4</sub>, and removal of the solvent under vacuum led to isolation of the purified macroinitiator (PEG<sub>112</sub>-Br). The procedure can be seen in Scheme S1.



Scheme S1 Preparation of the Macroinitiator PEG<sub>112</sub>-Br

## Supporting Figures

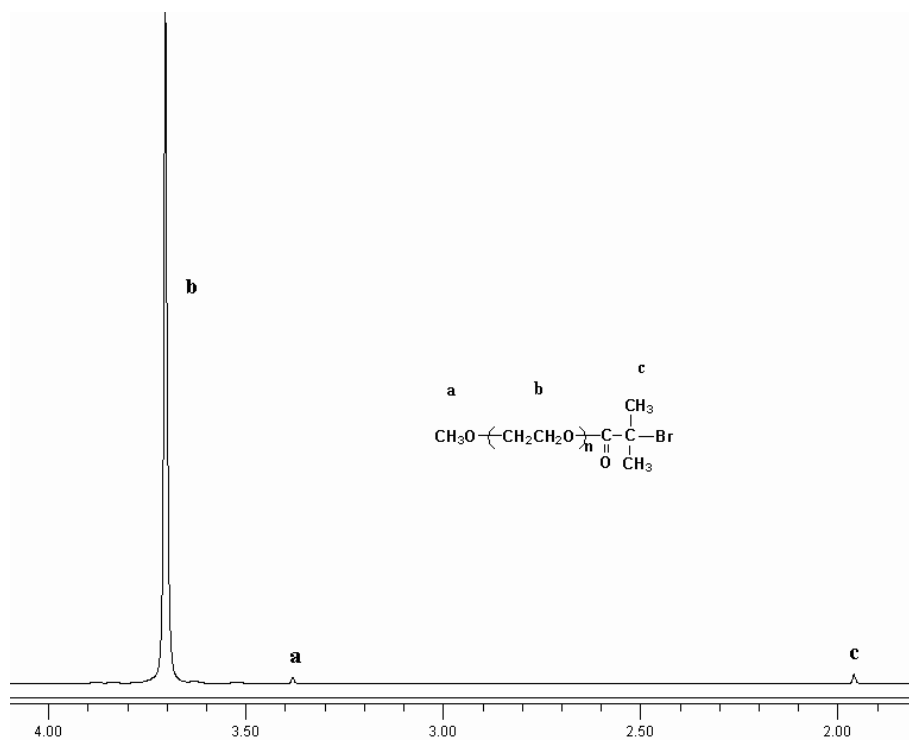


Figure S1. The <sup>1</sup>H NMR spectrum of PEG<sub>112</sub>-Br.

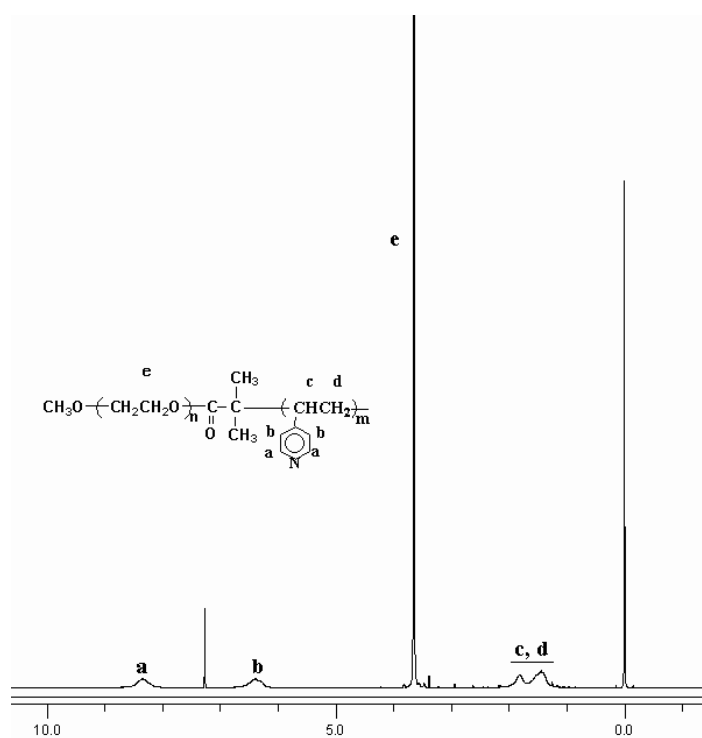


Figure S2. The <sup>1</sup>H NMR spectrum of PEG<sub>112</sub>-b-P(4-VP)<sub>55</sub>.

The composition of the block copolymer PEG<sub>112</sub>-b-P(4-VP)<sub>55</sub> was determined by the <sup>1</sup>H NMR spectrum in Figure S2.

The following Figures S3 to S5 show the dependence of the hydrodynamic radius  $R_h$  (S3, circles), apparent radius of gyration  $R_g$  (S3, triangles), ratio of  $R_g/R_h$  (S4), and excess Rayleigh ratio at the scattering angle  $90^\circ$   $R_{90}$  (S5) of the  $\text{PEG}_{112}\text{-}b\text{-P(4-VPH}^+)_{55}/\text{SO}_4^{2-}$  micelles on the  $\text{Na}_2\text{SO}_4$  concentration, where the  $\text{PEG}_{112}\text{-}b\text{-P(4-VP)}_{55}$  concentration is 0.50 mg/mL.

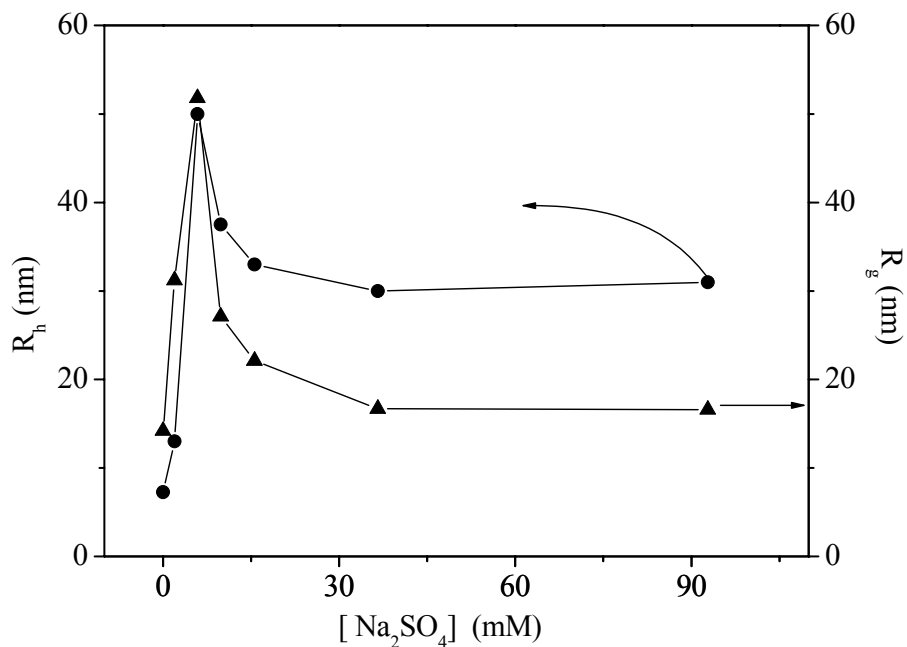


Figure S3

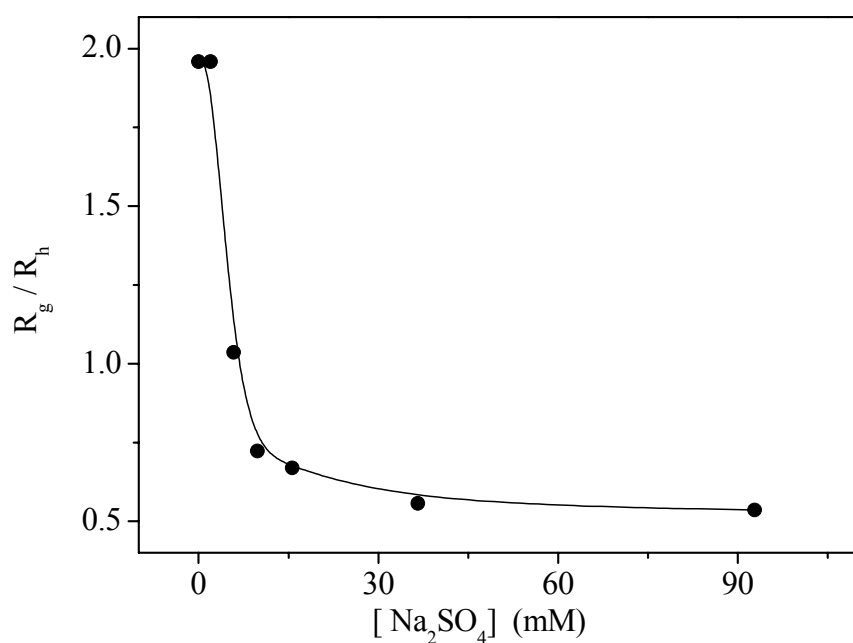


Figure S4

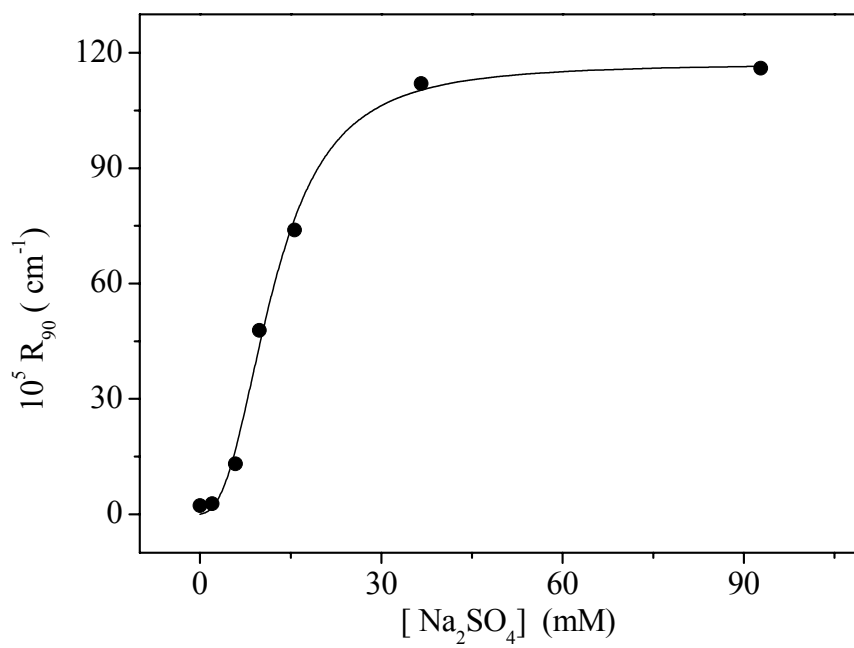


Figure S5