Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2017

Electronic Supplementary Information for

Wormlike Micelles versus Water-Soluble Polymers as Rheology-Modifiers: Similarities and Differences

Ji Wang,[a,c] Yujun Feng,*[,a,b] Niti R. Agrawal,[d] Srinivasa R. Raghavan[d]

[a] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, People's Republic of China.

[b] Polymer Research Institute, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, People's Republic of China.

[c] University of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China.

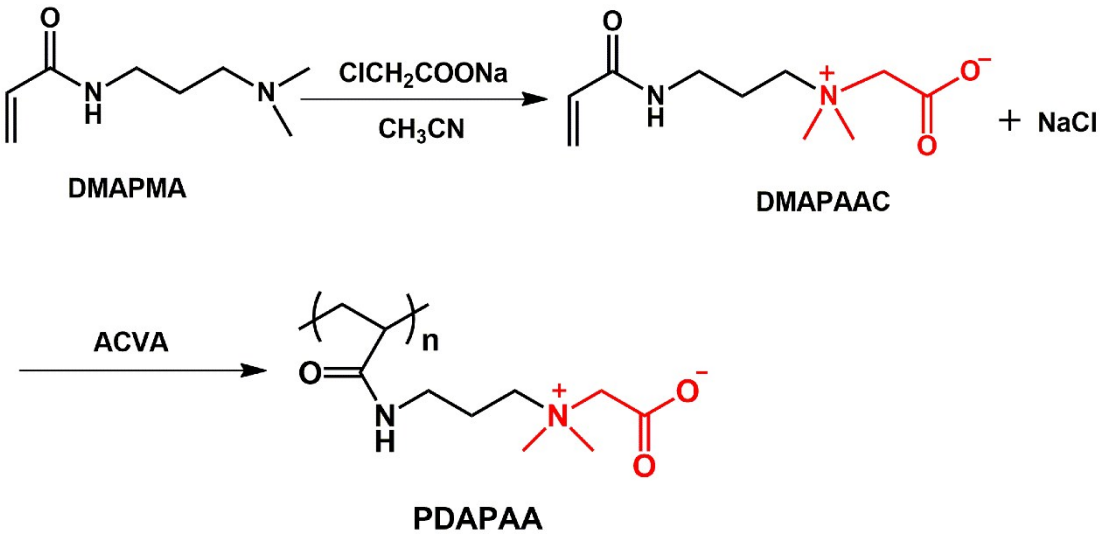
[d] Department of Chemical & Biomolecular Engineering, University of Maryland, College Park, Maryland, 20742-2111, USA

Corresponding authors: e-mail: yjfeng@scu.edu.cn.

Preparation of poly-(2-(dimethyl(3-(acrylamido)propyl ammonium acetate)

Synthesis of Monomer

Following the pathway listed in Scheme S1, the typical experimental procedure for the synthesis is as follows: In a 0.25 L flask equipped with a stirrer, a cooler, and a thermometer, 0.05 mol (8.34 g) *N,N*-dimethylaminopropyl acrylamide and dried acetonitrile were charged under a N_2 atmosphere and the contents were stirred at 55 ºC. Subsequently, 0.08 mol (9.30 g) sodium chloroacetate was added. Following the addition, the mixture was stirred and allowed to stand at the same temperature for 24 h. The solvent was accumulated by filtration, washed with dry ether for several times, and dried under reduced pressure to obtain *N, N*-dimethy ((acrylamido)propyl) ammonium acetate (DMAPAAC). Yield: 9.15 g, 80%.



Scheme S1. The protocol for the synthesis of poly-(2-(dimethyl(3-(acrylamido)propyl ammonium acetate).

Polymerization of Monomer

0.02 mol (4.28 g) The monomer (DMAPAAC) and 0.2 mol % (0.01 g) of 4,4'-azobis(4-cyanovaleric acid) (ACVA) were introduced into a 100 mL ampule. To this, 50 mL of distilled water was added to make a 0.4 M aqueous solution. The ampule contents were then flushed with argon, sealed in vacuum, and then placed in a temperature bath for 24 h. Next, the polymer solutions were precipitated with acetone, lyophilized for 24 h. A dried, brittle, and white solid polymer was subsequently obtained. The structure of the poly-(2-(dimethyl(3-(acrylamido)propyl ammonium acetate) (PDAPAA) was confirmed by ^{1}H NMR spectroscopy (Figure S1), and its molecular weight was determined by gel permeation chromatography (Figure S2).

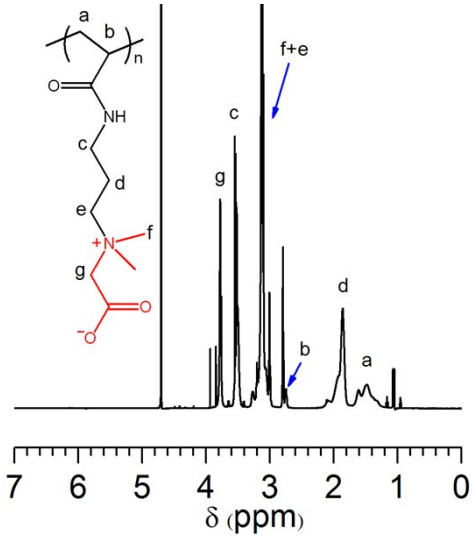


Figure S1. ^{1}H NMR spectrum of poly-(2-(dimethyl(3-(acrylamido)propyl ammonium acetate) in D_2O.

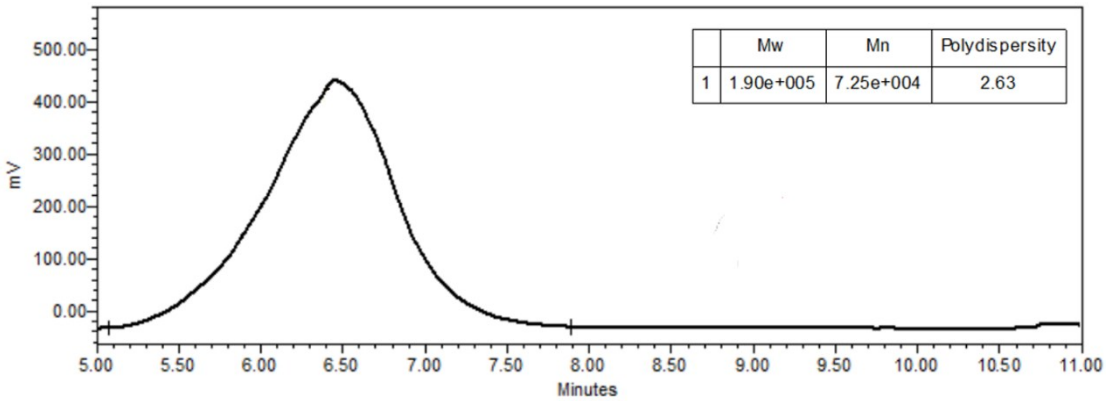


Figure S2. GPC trace of poly-(2-(dimethyl(3-(acrylamido)propyl ammonium acetate).

Characterization of EDAB

The structure and purity of EDAB was confirmed by ^{1}H NMR spectroscopy (Figure S3) and high performance liquid chromatography (HPLC) (Figure S4), respectively.

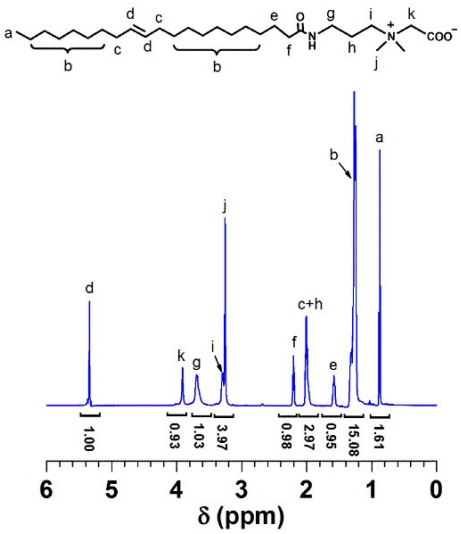


Figure S3. ^{1}H NMR spectrum of erucyl dimethyl amidopropyl betaine (EDAB) in CD_3Cl.

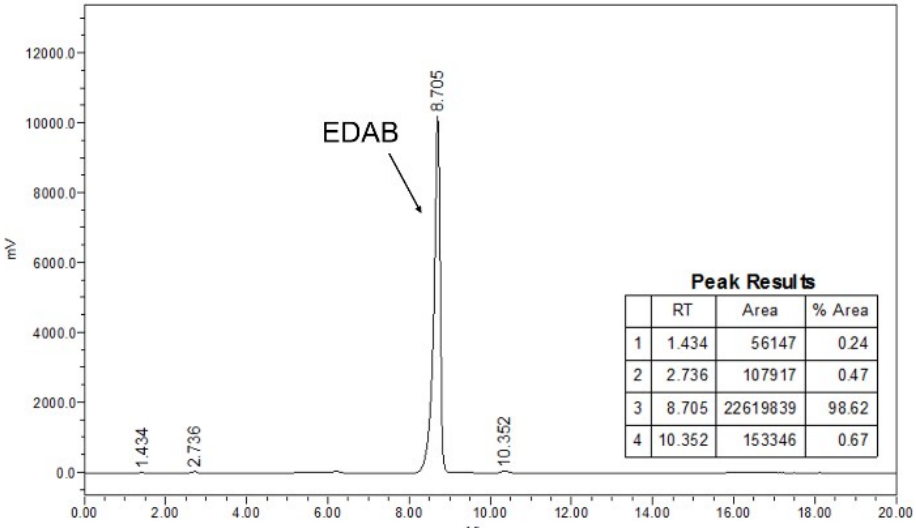


Figure S4. HPLC result of erucyl dimethyl amidopropyl betaine (EDAB).

Determination of chloride ion content in EDAB with ion chromatography

The chloride ion content in EDAB powder was determined by ion chromatography. EDAB solution (0.5 mg·mL^{-1}) was prepared by dissolving surfactant powders in deionized water, followed by gentle agitation while mildly heating. When completely solubilized at high temperatures, the solution was cooled, and then left to stand overnight to measurements.

Ion chromatography (IC) was performed using Dionex Ion Analyzer (Dionex, Sunnyvale, CA, USA) equipped with a GP40 gradient pump, an ED40 electrochemical detector, and an AS40 autosampler. One Dionex, 4 × 210 mm anion-exchange columns was tested: Ion-Pac AS14. 2 mM phthalic acid/10% acetone (pH 5.0) was used as the mobile phase. Flow rate was varied from 1.0 mL/min to 1.2 mL/min. The detector stabilizer temperature was set at 30 °C with temperature compensation of 1.7%/°C. Anion suppressor current was set to 300 mA. The injection volume was 20 μL. A series of standard solutions with increasing values of Cl^- were used for the calibration graph for Cl^- determination. The plot of the peak area versus the chloride concentration was found to be linear up to 100 mg/L of NaCl, with the following linear

regression equation:

$$y = 0.059 + 0.727x \qquad (r^2 = 0.9999)$$

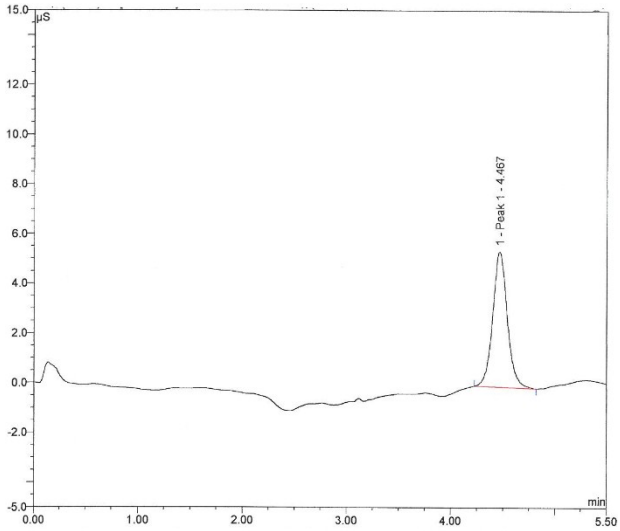


Figure S5. Ion chromatographic result of standard solution of Cl^-.

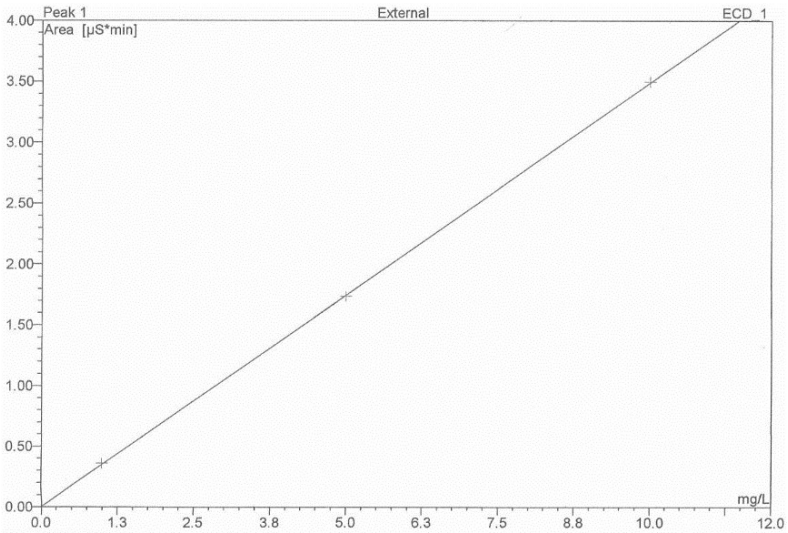


Figure S6. Calibration curves of Cl^- obtained by IC.

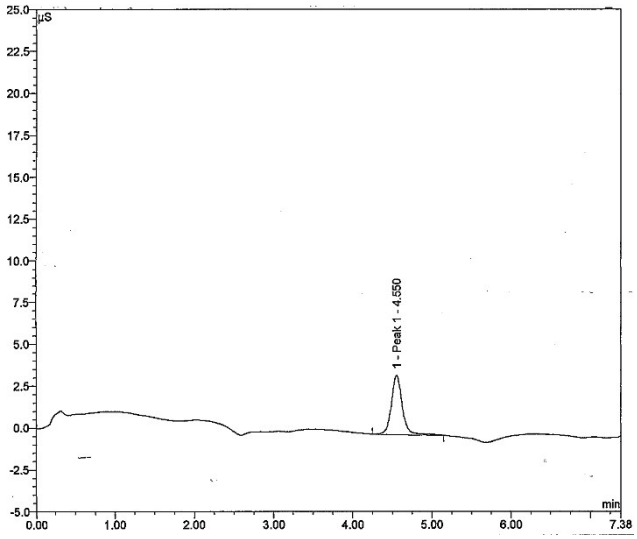


Figure S7. IC result of erucyl dimethyl amidopropyl betaine (EDAB).

Additional Rheological results

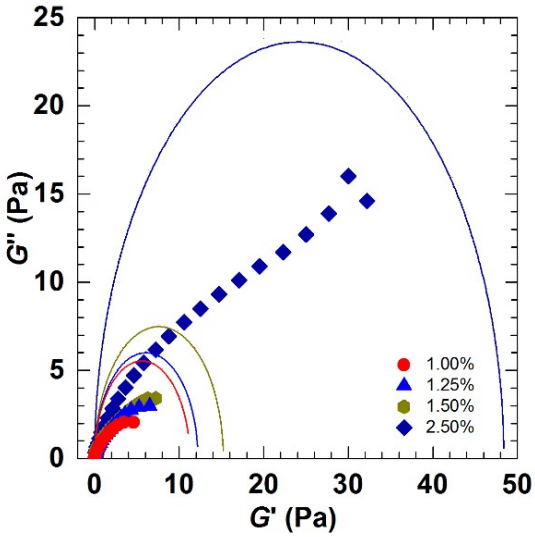


Figure S8. Experimental Cole-Cole plots for PAM saline aqueous solution at different concentrations. The solid line represents the osculating semicircle at the origin.

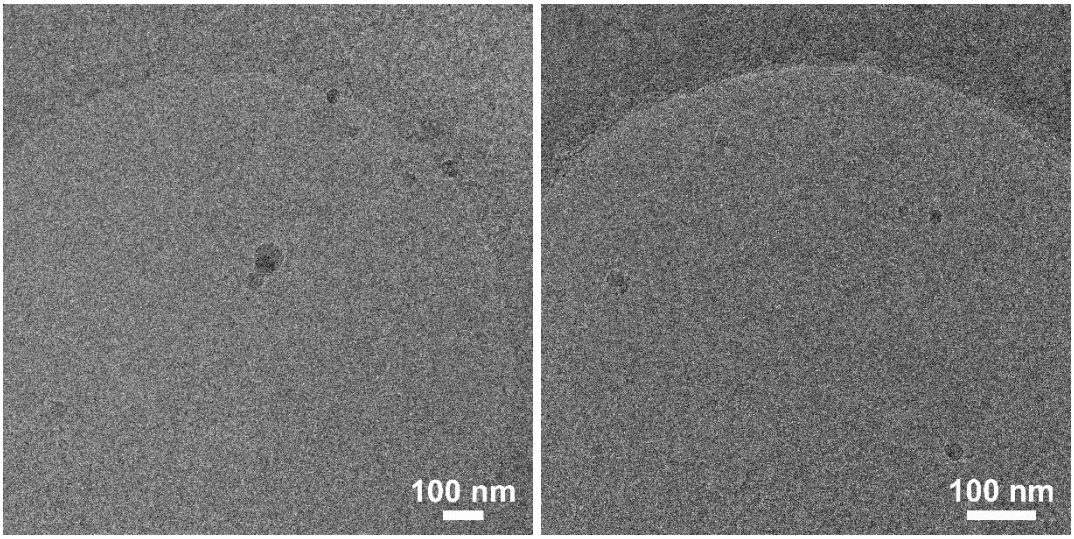


Figure S9. Cryo-TEM micrographs of 2.50 wt % PAM saline aqueous solution at 25 ºC (A) and 85 ºC (B).

Static light scattering

The radius of gyration (R_g) of samples were measured in 0.5 M NaCl by static light scattering with a Brookhaven Instrument equipped with BI-200SM goniometer and a BI-TurboCorr digital correlation. A solid-state laser polarized at the vertical direction (532 nm, 100 mW) was used as light source. The light scatting measurements were carried out at 25 ºC. Toluene was used as a reference standard. The scattering angle θ was varied from 30 to 150°. The experiments were carried in a dilute polymer concentration where intermolecular associations can be neglected. Solvents were filtered through Durapore (Millipore) 0.20 μm membrane, polymer solutions were filtered through Durapore 0.45 μm membrane. The refractive index increment was measured at the same wavelength on a brice-Phoenix differential refractometer.

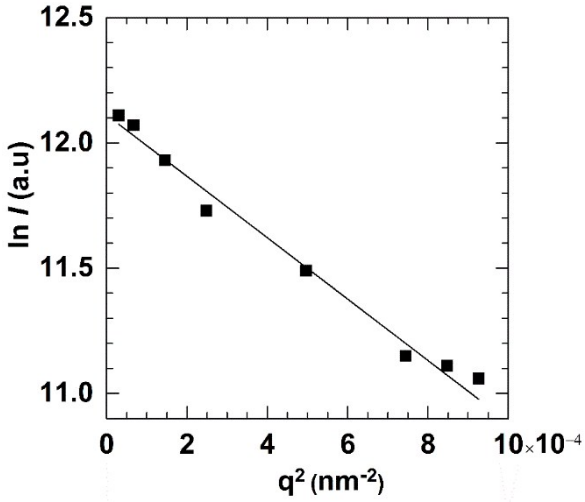


Figure S10. Guinier plot of PAM in 0.5 M NaCl at 25 °C. R_g of a single PAM chain is about 61 nm.