What Causes the Anomalous Aggregation in Pluronic Aqueous Solutions?

(Supporting Information)

Kuo-Chih Shih[1], Zhiqiang Shen[2], Ying Li[2], Martin Kröger[3], Shing-Yun Chang[1], Yun Liu[4, 5],Mu-Ping Nieh[6, 7, 8]*, Hsi-Mei Lai[1]*

[1]Department of Agricultural Chemistry, National Taiwan University, Taipei, 10617, Taiwan

[2]Department of Mechanical Engineering, University of Connecticut, Storrs, Connecticut 06269, United States

[3]Department of Materials, Polymer Physics, ETH Zürich, CH-8093 Zurich, Switzerland

[4]Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

[5]Chemical & Biomolecular Engineering Department, University of Delaware, Newark, DE 19716, United States

[6]Polymer Program, Institute of Materials and Science, [7]Department of Chemical and Biomolecular Engineering, [8]Department of Biomedical Engineering, University of Connecticut, Storrs, Connecticut 06269, United States

***Correspondence to:**

Dr. Hsi-Mei Lai (E-mail: hmlai@ntu.edu.tw)

Telephone: +886-2-33664816

Fax: +886-2-23633123

***Co-Correspondence to:**

Dr. Mu-Ping Nieh (E-mail: mu-ping.nieh@uconn.edu)

Telephone: +1 8604868708ABSTRACT

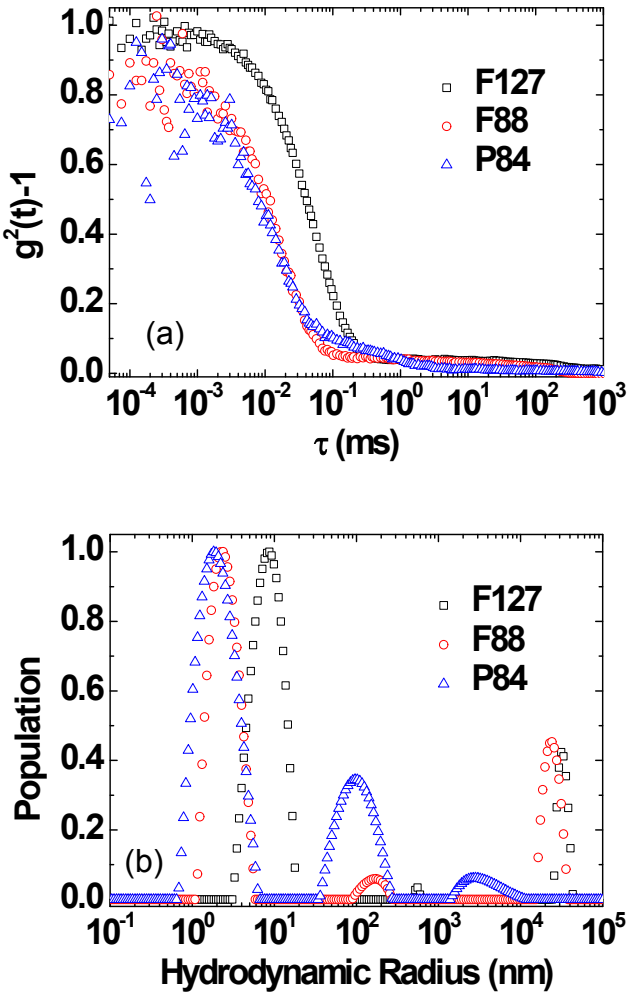


Fig. S1. The autocorrelation functions (a) and R_H histograms(b) of 0.5% F127 (black square), 1% F88 (red circle) and 1% P84 (blue triangle) in H_2O, respectively.

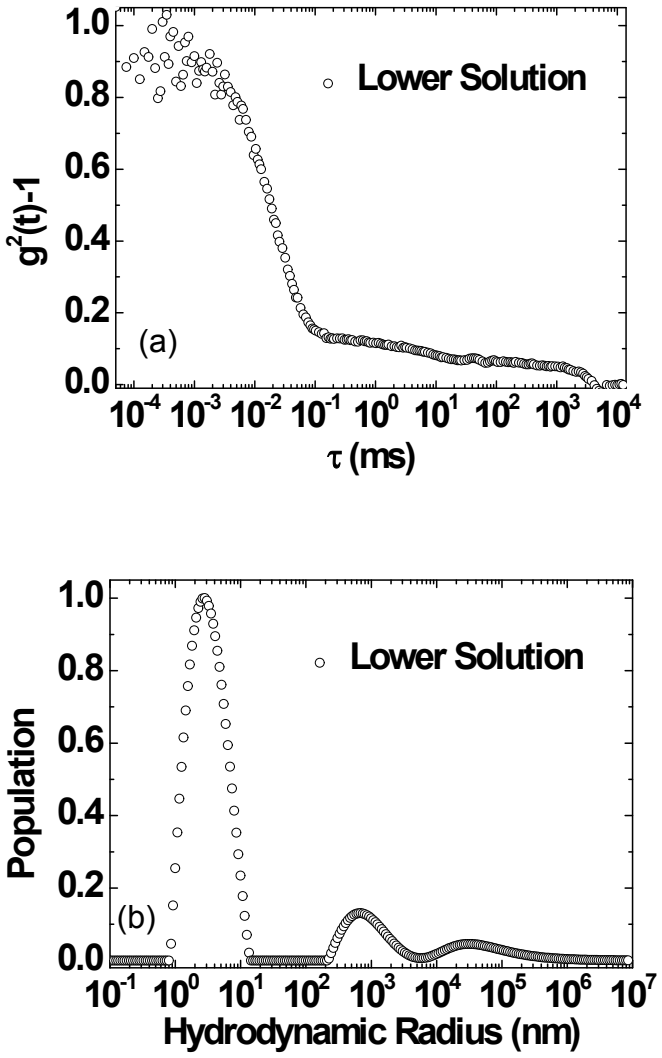


Fig. S2. The autocorrelation function (a) and R_H histogram (b) of lower half solution after centrifugation.

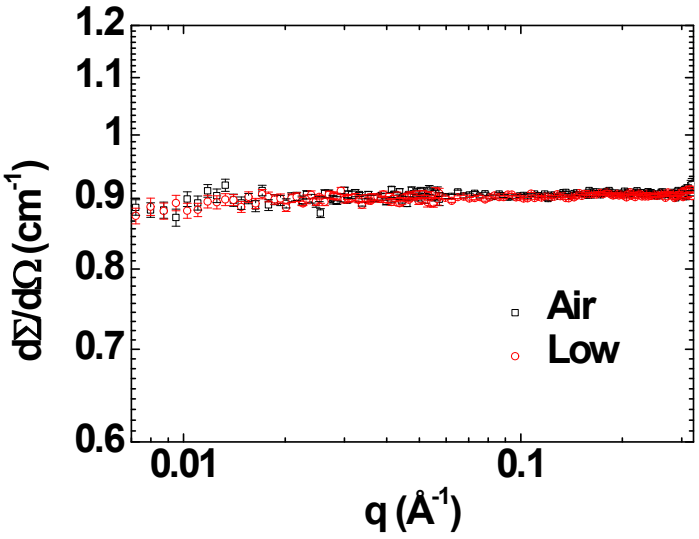


Fig. S3. The SANS data ofagitated sample (black square)and centrifuged lower half solution (red circle) afteragitation in H_2O/D_2O solvent whose neutron SLDcontrast-matches with that of F108.

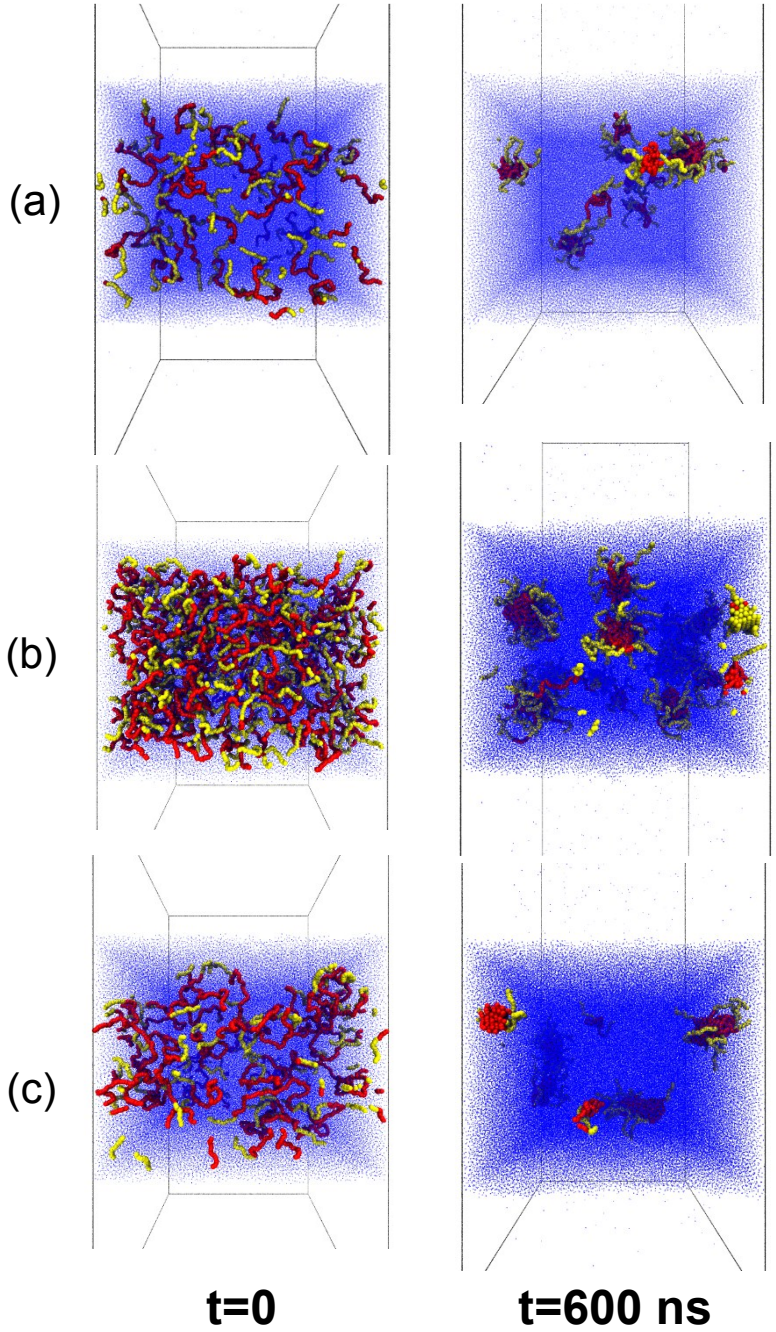


Fig. S4.Polymers chains in the water with volume of 3.67×10^4 nm^3;Snapshots of 40 chains of PEO_{19}-PPO_{44}-PEO_{19}(P84)(a),80 chains of P84(b),and 40 chains of PEO_{19}-PPO_{88}-PEO_{19}(c). Beads of PEO,PPO and water are colored in yellow, red and blue, respectively.

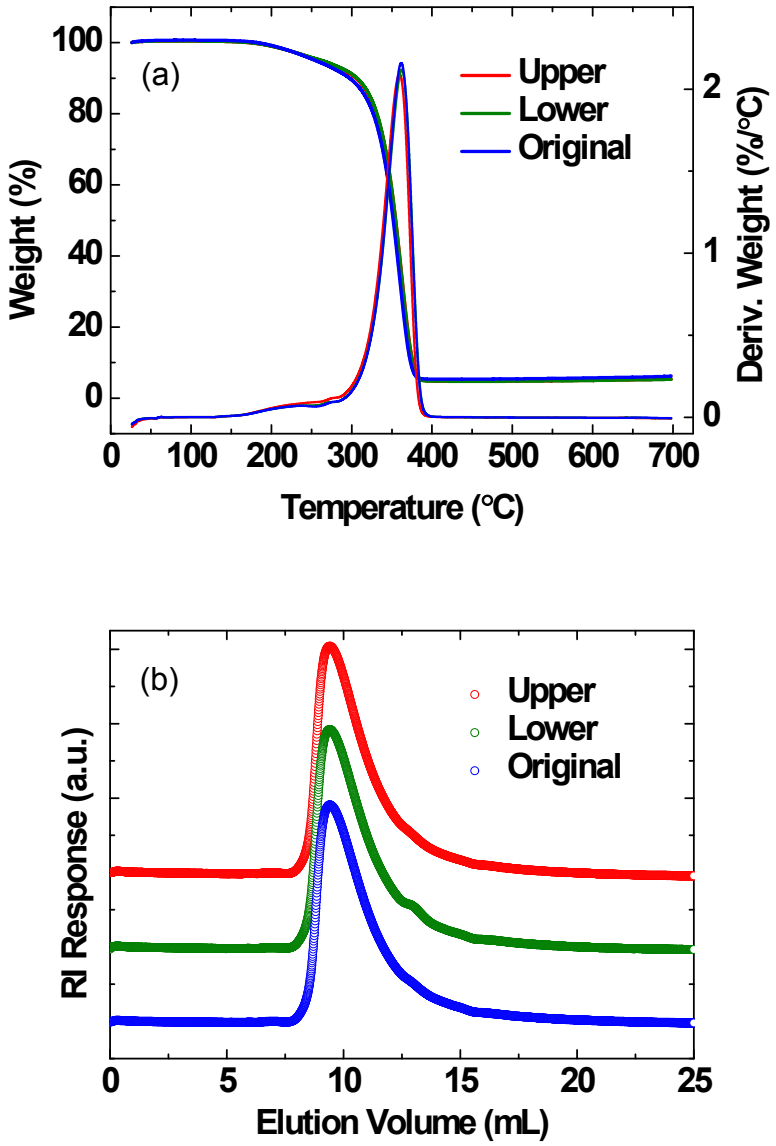
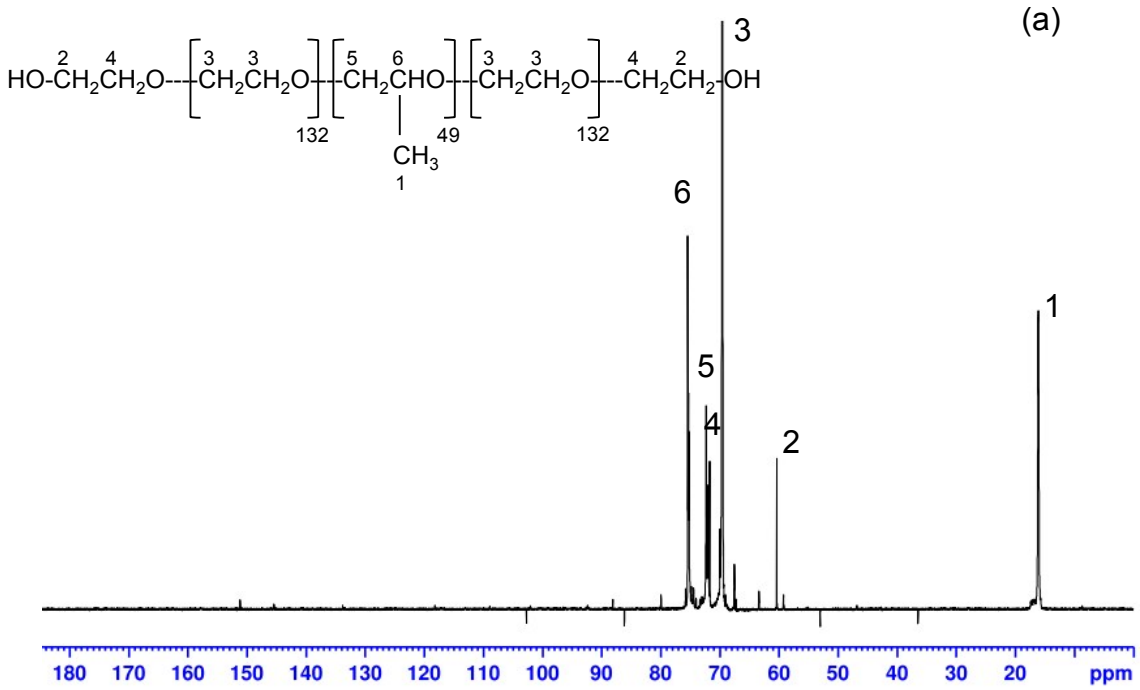
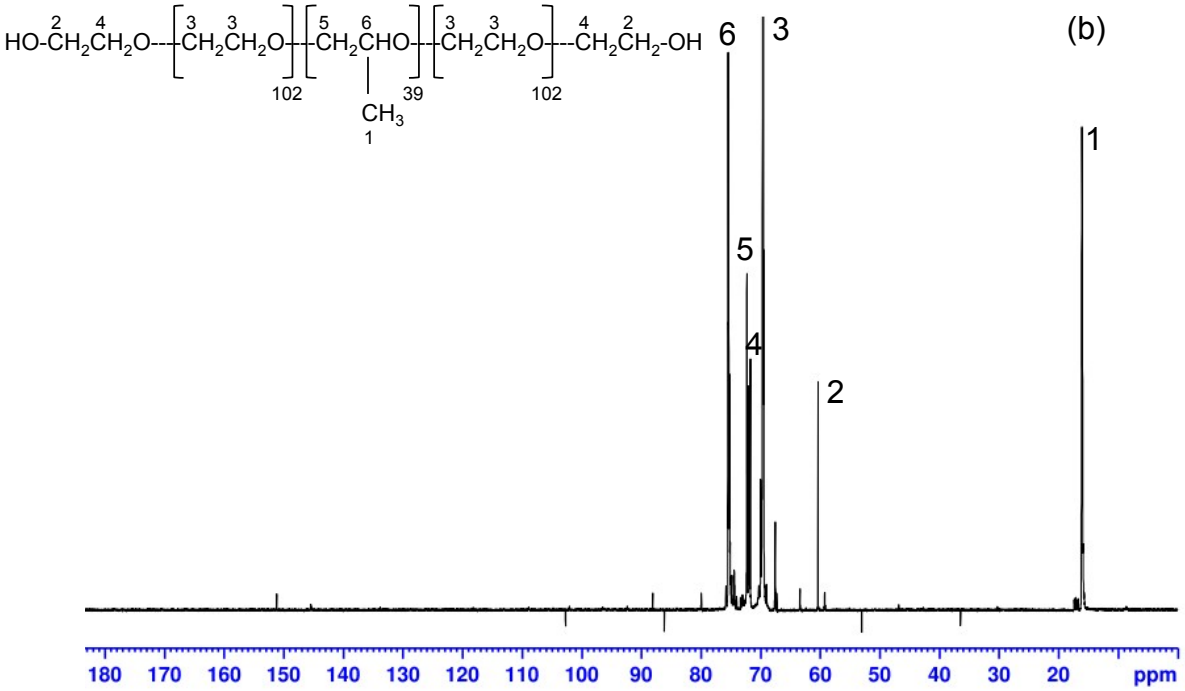


Fig. S5. TGA (a) and GPC(b) results for the upper (red), lower (green) layer solution and the original solution (blue triangle) of 1% F108 solution.


(a)
HO-CH2CH2O---CH2CH2O---CH2CHO---CH2CH2O---CH2CH2-OH
132
49
132
CH3
1
2
3
4
5
6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


(b)
HO-CH2CH2O---CH2CH2O---CH2CHO---CH2CH2O---CH2CH2-OH
102
39
102
CH3
1
2
3
4
5
6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

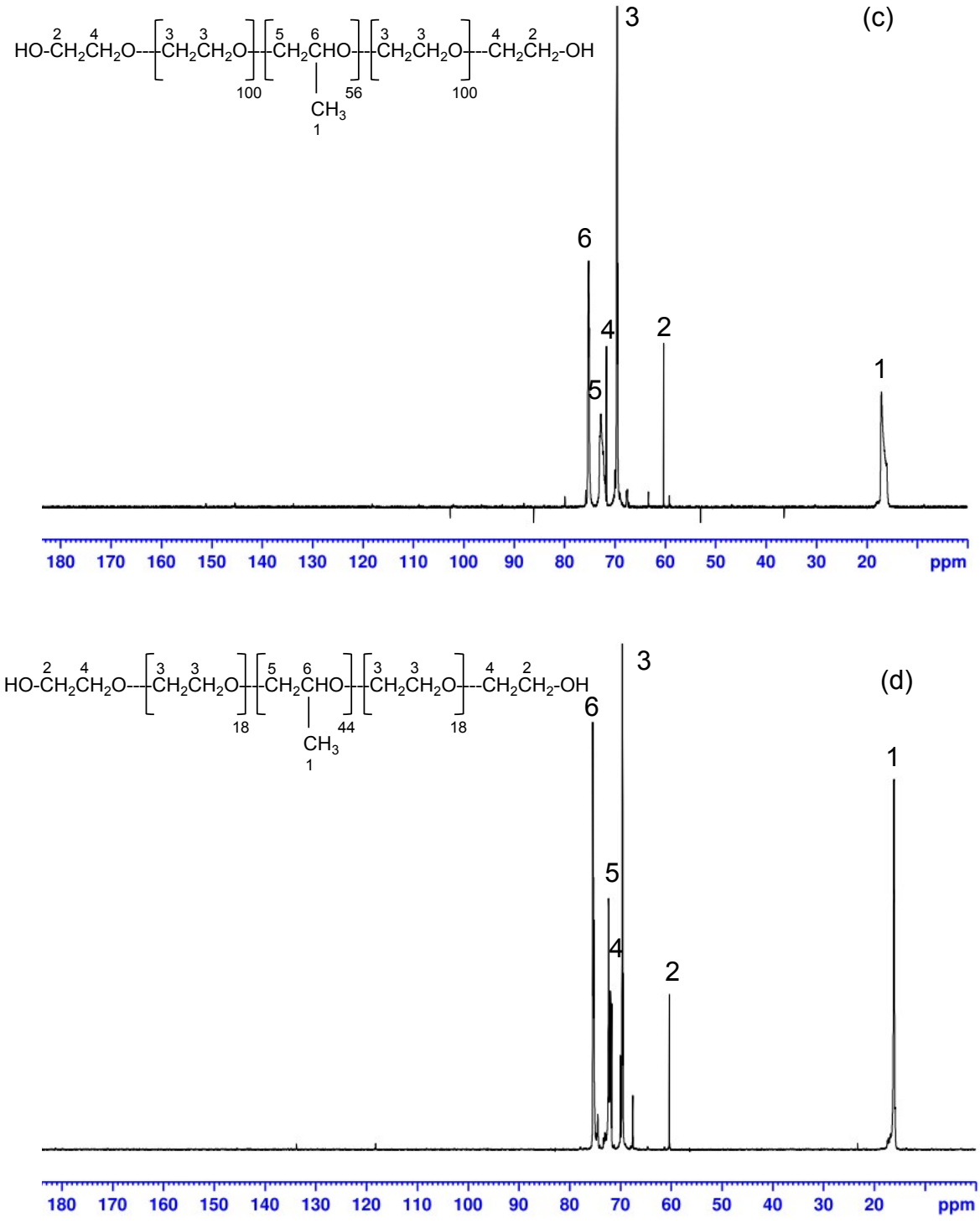


Fig. S6. 125.76 MHz ^{13}C NMR spectra of 10% w/w solutions of F108 (a), F88 (b), F127 (c) and P84 (d) in D_2O at 298 K.

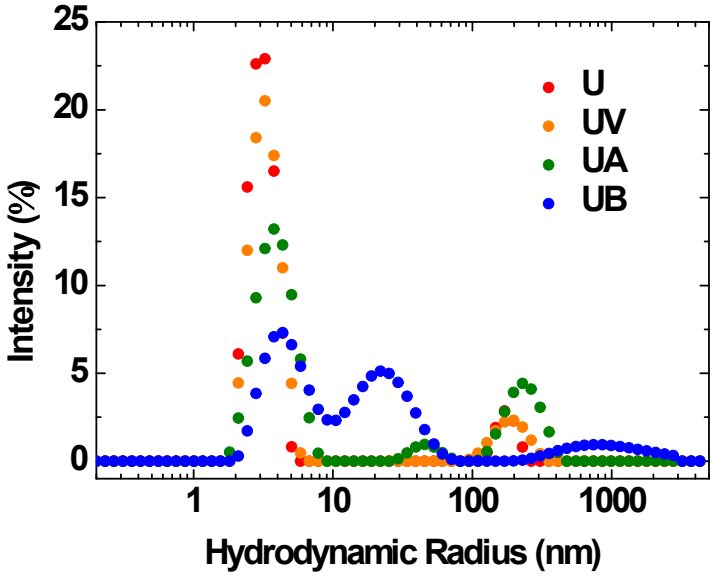


Fig. S7. The R_H histogramsof the upper half solution stored for 2 days (U) and the same sample after vortexing, adding acid and base (UV, UA and UB).

Sample U represent the centrifuged upper layer solution stored for 2 days. UV, UA and UB are prepared by the U sample with vortexing, addition of citric acid and sodium hydroxide, respectively. The size of the PL unimer remains ~ 3 nm after each of the treatments. For particles whose$R_H$is larger than ~ 40 nm are considered as large aggregates while particles with R_H~ 20 nm after the additionof sodium hydroxide are F108 micelles. In short, after the formation of large aggregations, neithervortexingnor addition acids/bases of use could dissociate the aggregates. The inhibition mechanisms are different from the dissociation mechanism of aggregates.

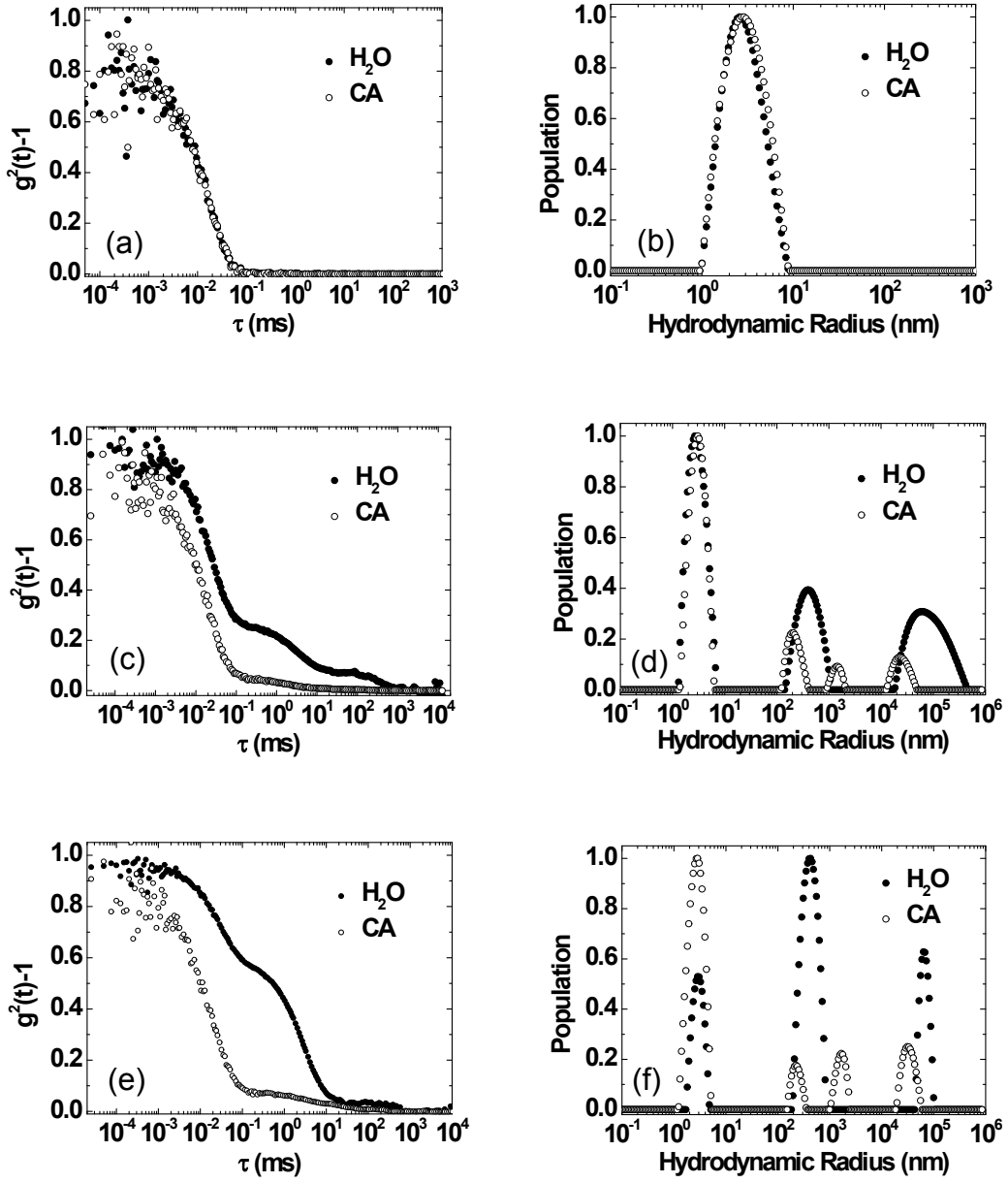


Fig. S8. The autocorrelation functions (a, c & e) and R_H histograms (b, d & f) of the upper half solution of F127 stored for 0 (a & b), 2 (c & d) and 20 (e & f) days, respectively.

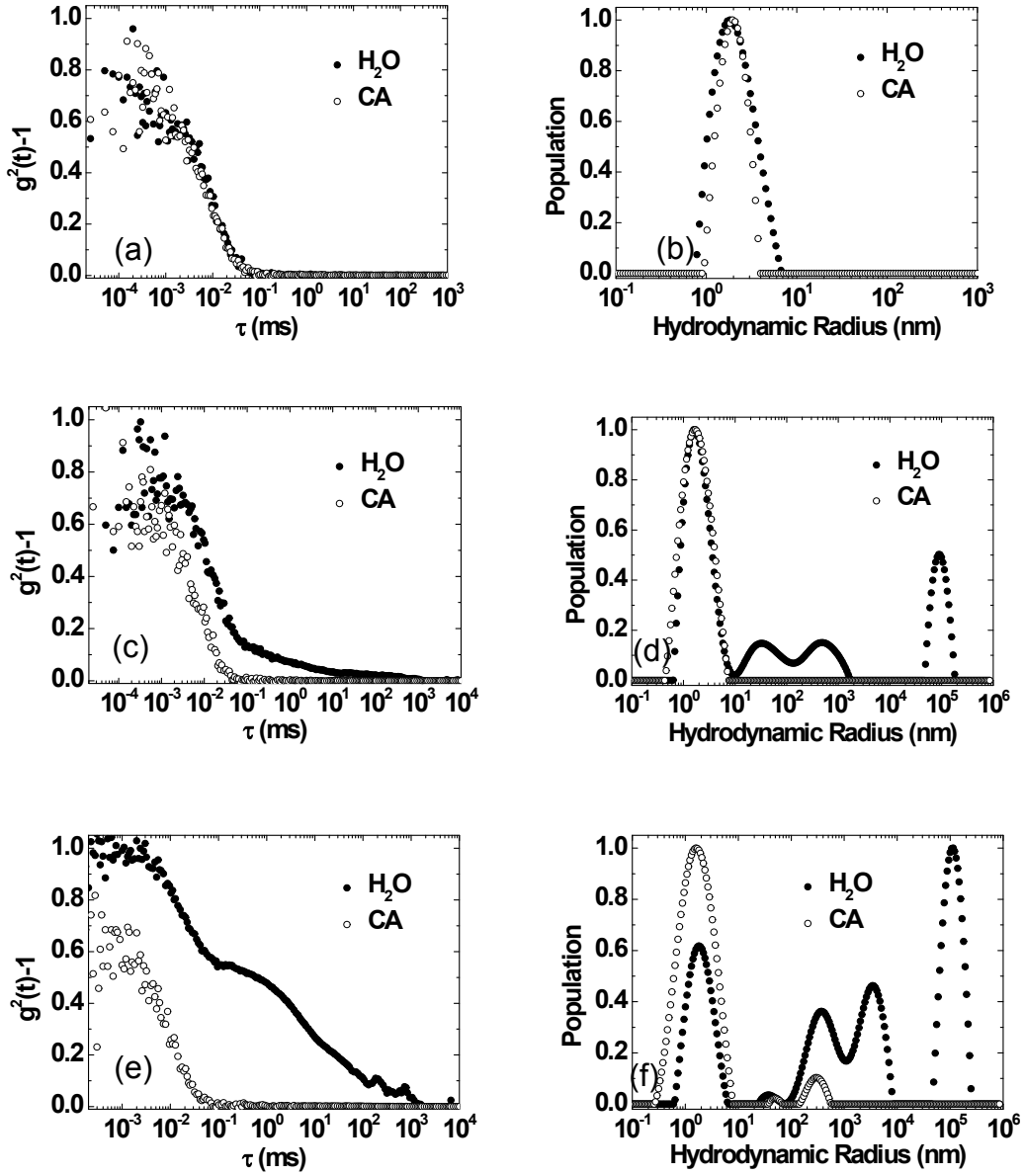


Fig. S9. The autocorrelation functions (a, c & e) and R_H histograms (b, d & f) of the upper half solution of F88 stored for 0 (a & b), 2 (c & d) and 20 days(e & f), respectively.

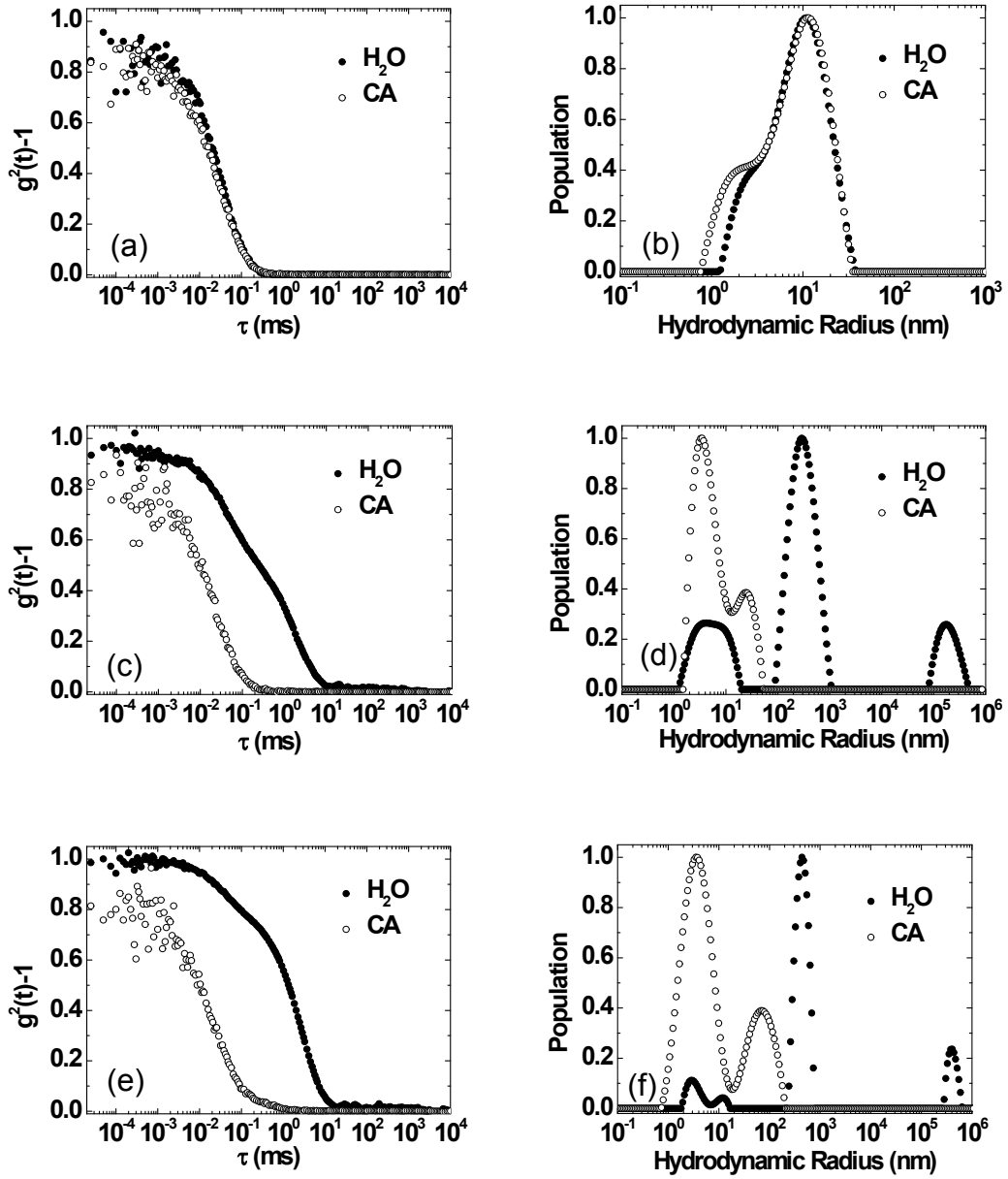


Fig. S10. The autocorrelation functions (a, c & e) and R_H histograms (b, d & f) of the upper half solution ofP84 stored for 0 (a & b), 2 (c & d) and 20 days(e & f), respectively.