

Water Soluble Core-Shell Hyperbranched Polymers for Enhanced Oil Recovery

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Surface modification of nano-sized silica by APTES. 5g dried nano-sized silica was dispersed in 100ml dry toluene. After 30min of ultrasonication, 2.0 mmol of APTES was added with magnetic stirring and the mixture was stirred for 24h at 80°C. The resulted mixture was recovered by filtration, washed with methanol five times repeatedly and dried in vacuum at room temperature. The product was functional core nano-sized silica labeled SG. The number of surface-grafted amino groups was scaled by 1mol/L hydrochloric acid aqueous with thymol blue as indicator.

Synthesis of PAMAM hybrid nano-SiO₂. (Michael addition of MA to amine groups): Into a 250ml flask, 5g SG with 100ml methanol was added, and the mixture was sonicated for 30min in order to produce completely dispersed materials. 5ml MA in 40ml methanol was added drop wisely into stirring solution at 0°C under N₂ atmosphere over a period of half hour. Subsequently, the mixture was then allowed to rise to room temperature (approximately 25°C) with mildly stirring. After 48h, the resulting material was recovered by filtration and washed with excess methanol five times repetitively. The obtained product was labeled PAMAMSG (G0.5).

(Amidation of resulting ester with EDA): 80ml methanol with 4g PAMAMSG 0.5 was added into a 250ml flask, and treated with ultrasonic for 30min in order to produce finely dispersed colloid. The mixture was stirred by magnetic stirrer under N₂ atmosphere. Afterwards, 6ml of EDA (highly than that of methyl ester group) in 40ml methanol was added drop wisely into solution at 0°C over a period of half hour. The mixture was then allowed to rise to room temperature (approximately 25°C) with slowly stirring. After 48h, the resulting material was recovered by filtration and rinsed with excess methanol five times repetitively. The obtained product was labeled PAMAMSG (G1.0).

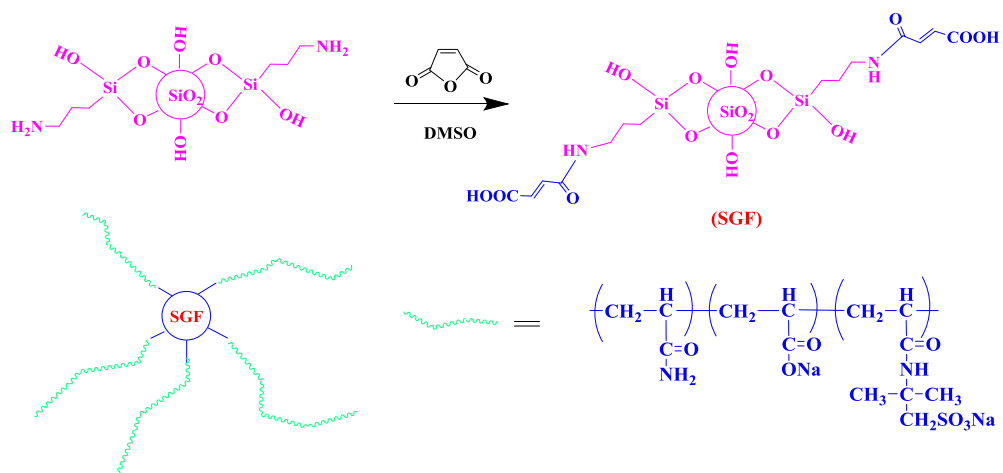
The second round synthesis was then repeated as mentioned above, noted that two times higher volume of MA or EDA was reasonable than that in the first round to obtain PAMAMSG (G1.5) and PAMAMSG (G2.0).

Synthesis of PAMAM hybrid nano-SiO₂ monomer. 3.5g PAMAMSG (G1.0) or PAMAMSG (G2.0) was gradually added into 35ml dimethylsulfoxide (DMSO), the mixture was treated with ultrasonic for 30min, then stirred for 1 h in a water bath at 18.5°C. 2g MAH in 20ml DMSO was added drop wisely into solution over a period of 2 h. The temperature of the mixture was allowed to rise to 70°C with stirring. After 6h, the product was cooled to room temperature, filtered, and poured into excessive ethanol to obtain the precipitate. The precipitate was washed five times with methanol and dried in a vacuum to obtain yellow product, namely PAMAMSGF (G1.0) or PAMAMSGF (G2.0). MAH functionalized SG namely SGF, was synthesized under identical procedure mentioned above.

Synthesis of water soluble hyperbranched polymers (HBPAMs). A 100 mL three-necked round-bottom flask is equipped with a mechanical stirrer, nitrogen inlet, and a thermometer. 0.075g PAMAMSGF, 8.5g AM, and 2.5g AA, 1.5g AMPS are dissolved in a certain volume of deionized water and the pH of the mixture was tuned to 7.0-7.2 using sodium hydroxide solution. Then some volumes of deionized water were supplement to obtain 12.5% mass concentration for total monomer. The procedure of synthesis and purification of HBPAMs is consistent with the method reported previously.⁷

Rheological Measurements. Polymer solutions were prepared by dissolution of a known amount of polymer powder in water and NaCl solution. The apparent viscosity of samples solution was determined by a Brookfield DV-III rheometer equipped with different size of spindles (different diameter depending on solution

viscosity) at 25°C. Rheological experiments were carried out with a Haake RS600 controlled-stress rheometer equipped with a cone plate geometry (angle 1°, diameter 35mm).



Scheme 1S. Synthesis procedure of poly(AM/AA/AMPS)/SiO₂.

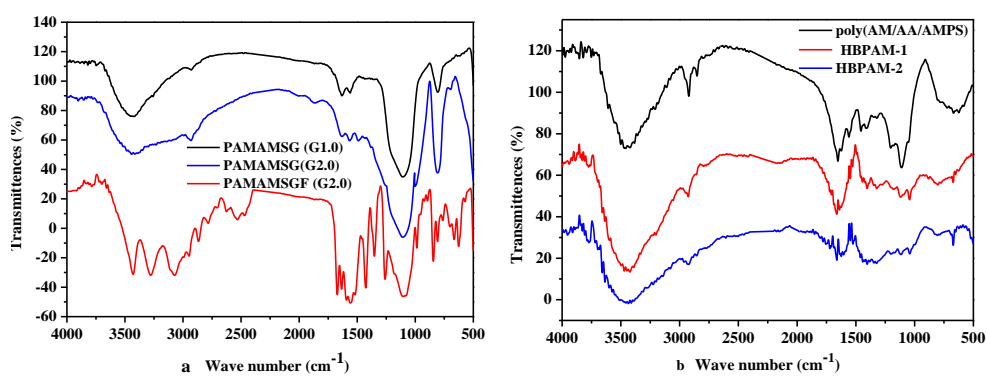


Figure S1. IR spectrum of (a) PAMAMSGs, PAMAMSGF (G2.0) and (b) polymers.

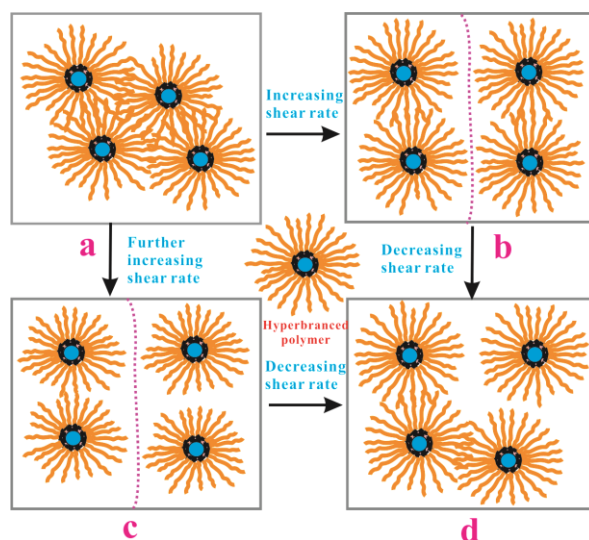


Figure S2. Schematic representation of morphology for hyperbranched polymer under shear force ($T=25^{\circ}\text{C}$); (a) entanglement of hydrophilic multiple-branch chains to form entire network structure in low shear stress (7.34s^{-1}), (b) partial entanglement of multiple-branch hydrophilic chains to form partial network structure in higher shear force (167s^{-1}), (c) dynamic balance of entanglement and disentanglement of multiple-branch hydrophilic chains in highest shear force (500s^{-1}), (d) reformed entire network due to entanglement of multiple-branch hydrophilic chains in low shear stress (7.34s^{-1}).

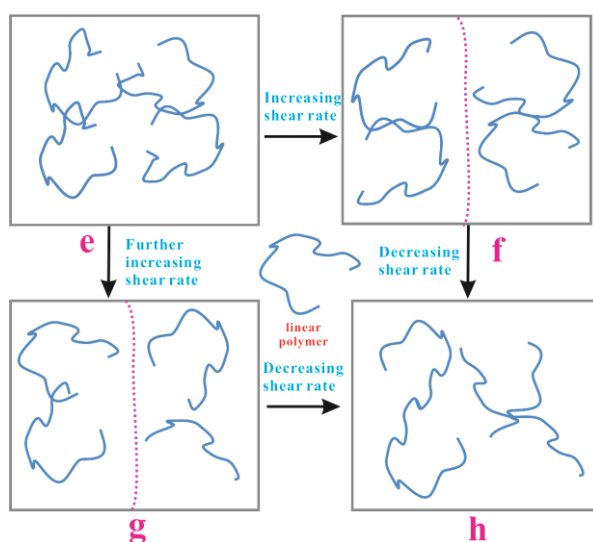


Figure S3. Schematic representation of morphology of poly(AM/AA/AMPS) under shear force ($T=25^{\circ}\text{C}$); (e) entanglement of linear chains to form network structure in low shear stress (7.34s^{-1}), (f) partial entanglement of linear hydrophilic chains to form partial network structure in higher shear force (167s^{-1}), (g) dynamic balance of entanglement and disentanglement of linear chains and a small proportion of degradation of polymer chains in highest shear force (500s^{-1}), (h) reformed partial network due to entanglement of linear chains at low shear stress (7.34s^{-1}).