Supporting Information

Synthesis of Comb-like Polymeric Surfactants with a Tricyclic Rigid Core and Their Use as Dispersantin Pymetrozine Water Suspension Concentrates

Xinyan Yan [1]， Zhaolan Zhai [1]， Zhanqian Song [1]，

Shibin Shang [1, 2], Xiaoping Rao [1, 2*]

1. Institute of Chemical Industry of Forest Products, CAF; National Engineering Lab. for Biomass Chemical Utilization；Key and Open Lab. of Forest Chemical Engineering, SFA; Key Lab. of Biomass Energy and Material, Jiangsu Province, Nanjing 210042, China.

2. Institute of Forestry New Technology, CAF; Beijing 100091, China.

Corresponding author:

*(X. Rao) Tel: + 86-25-85482452; Fax: + 86 25-85413445, E-mail: rxping2001@163.com;

This Supporting Information contains 5 Figures in 5 pages.

The RGMA and comb-like polymeric surfactants poly-(RGMA-co-MAPEG) were prepared successfully. IR spectrum of Rosin, RGMA and poly-(RGMA-co-MAPEG) were shown in Figure S1. IR spectrum showed that RGMA was synthesized successfully by appearance of the characteristic absorption bands assigned to C=O in the ester group at 1723.82 cm^{-1} and disappearance of the characteristic absorption bands assigned to the C=O in carboxyl acid group at 1694.96 cm^{-1} of the rosin. The IR spectrum of RGMA also gave the typical peaks for C=C of GMA at a wave number of 1637 cm^{-1}. The IR spectrum of poly-(RGMA-co-MAPEG) showed C=C peak at wave number at 1637 cm^{-1} of RGMA almost disappeared completely after copolymerization.

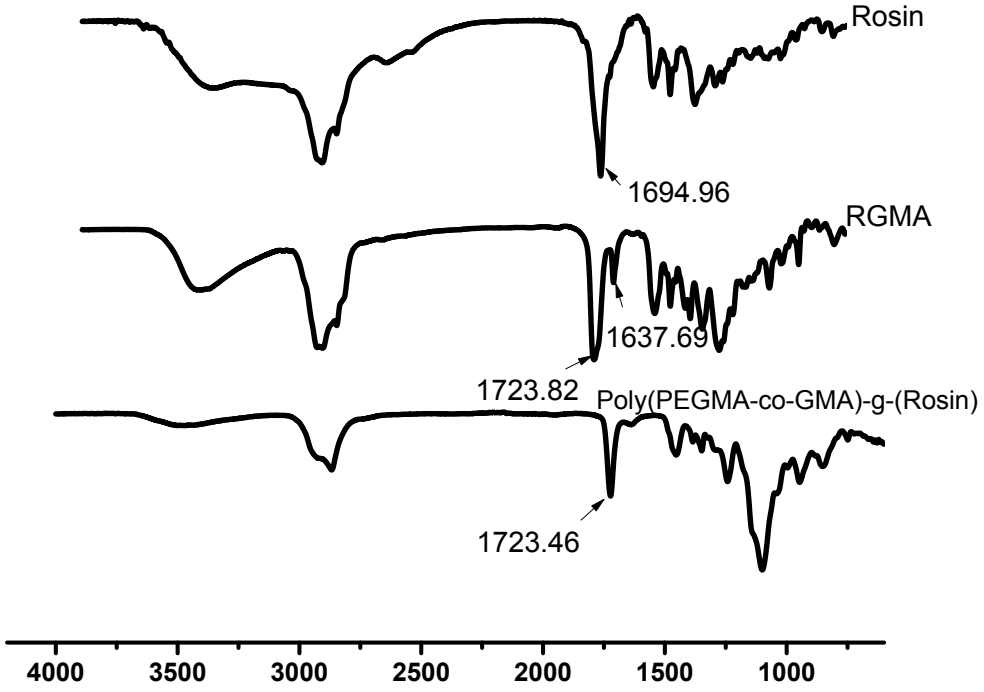

Fig.S1 FT-IR spectra of Rosin, RGMA and poly-(RGMA-co-MAPEG)

The ^1H NMR spectrum of 950CA and 950AA were shown in Fig.S2. ^1H NMR ($CDCl_3$) δ (ppm) 5.75(s,1H), 5.31 (m, 1H), 3.65(m, 2H), 3.58(s,1H), 3.34(s,3H), 2.52 (m,1H), 2.17(m,2H), 2.04(m,2H), 2.01(m,2H), 1.93 (m,1H), 1.21(d,3H).

Compared with poly-MAPEG, the peak at δ5.31ppm(c in Fig.S2), δ2.52ppm (b in Fig.S2) and δ1.21ppm (a in Fig.S2) in 950CA could prove the introduction of tricyclic rigid core to products successfully. The peak δ5.31ppm was the resonance peak of ethylene protons of rosin in

RGMA units in the backbone, while the peak at δ2.52ppm corresponded to methylene proton peak. Similarly, the peak at δ1.21ppm was the resonance peak of methyl protons.

The IR and ^{1}H NMR analyses indicated that the free radical copolymerization between RGMA and MAPEG was successful under this condition.

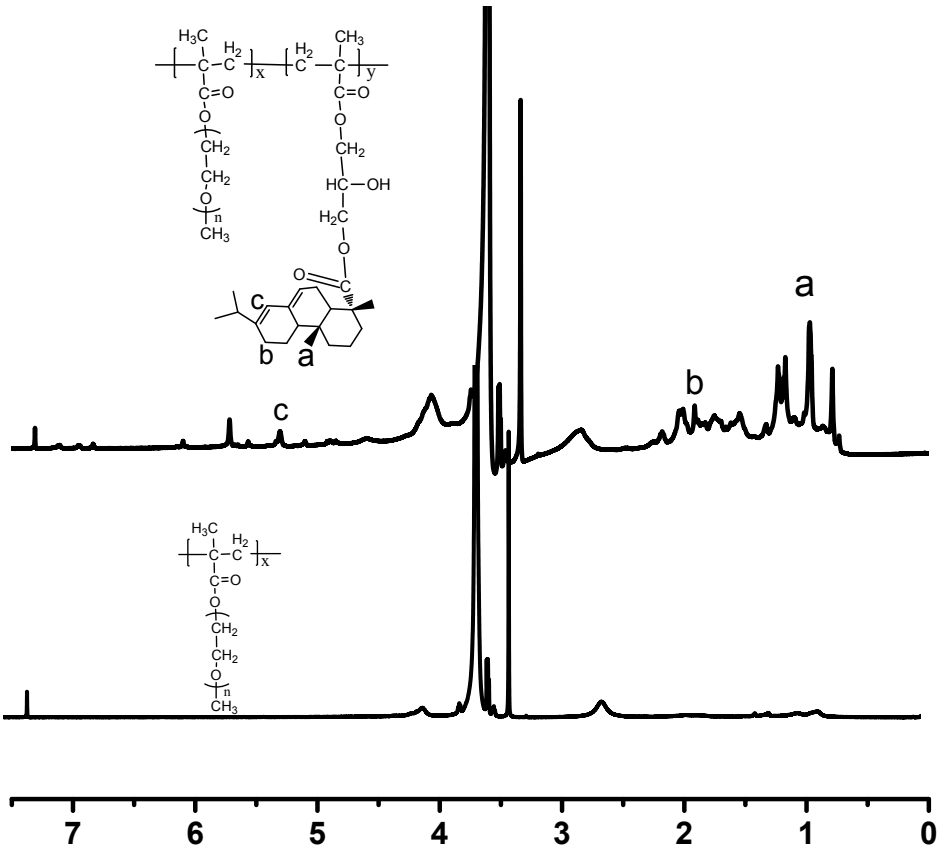

Fig.S2 ^{1}H NMR spectrum of poly-(RGMA-co-MAPEG) and poly-MAPEG

Their GPC traces of poly-(RGMA-co-MAPEG) and poly-MAPEG were shown in Fig.S3. It was found that the higher the content of hydrophobic group in comb-like surfactants increased, the wider the distribution of molecular weight. That maybe because the special structure of rosin. The steric hindrance of tricyclic rigid structure was larger.

The values of Mw/Mn of the graft copolymers after purification were lower than before purification because the crude products were purified by re-precipitation and dialysis to remove unreacted monomers and some polymers with lower molecular weight. Take 950CA as an example. As shown in Fig.S4, the value of Mw/Mn of the graft copolymers before dialysis was 2.38. But as shown in Fig.S3, the values of Mw/Mn of the graft copolymers was down to 1.28 after dialysis, because the crude products were purified by re-precipitation and dialysis to remove

unreacted monomers and some polymers with lower molecular weight. That is the same to others.

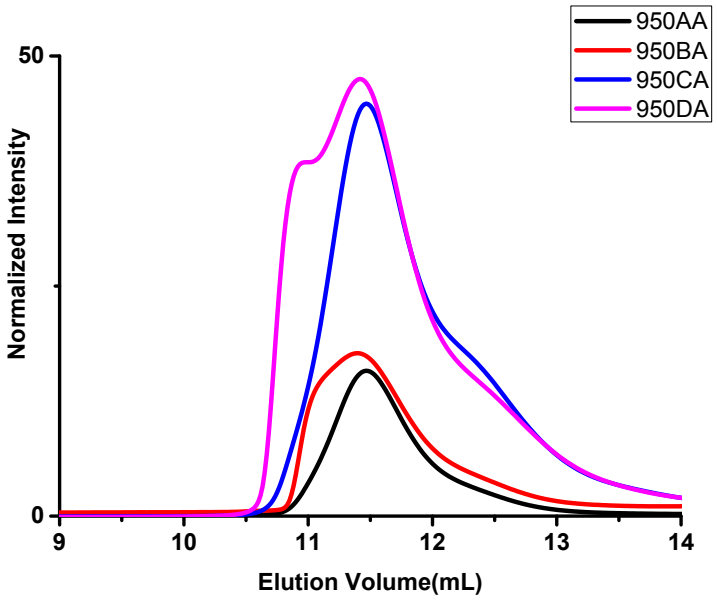

Fig.S3 GPC traces of poly-(RGMA-co-MAPEG) and poly-MAPEG

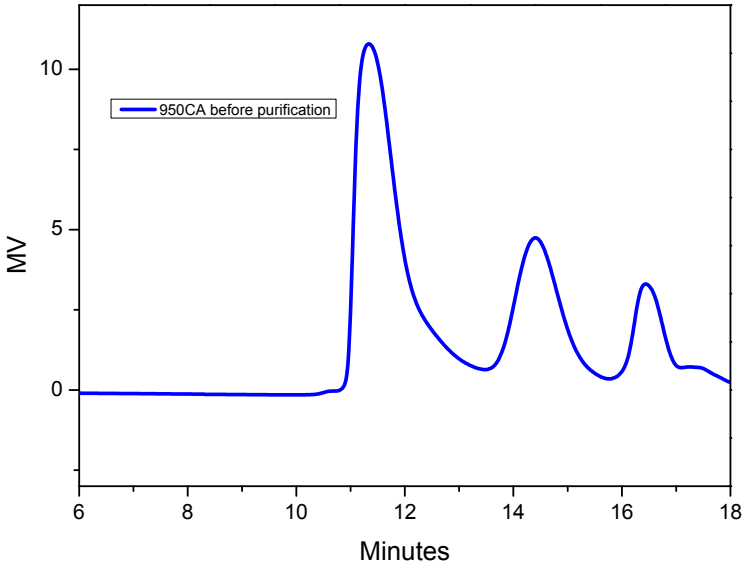

Fig.S4 GPC curves of 950CA before purification

Particle size dispersity of suspension when 950 BA was used as dispersant, and was displayed in Fig.S5. All particle size was less than 10 μm and most parts ranged from 0.1 μm to10 μm. Average particle size (d_{43}/μm) was 1.21 μm. That is the same to others.

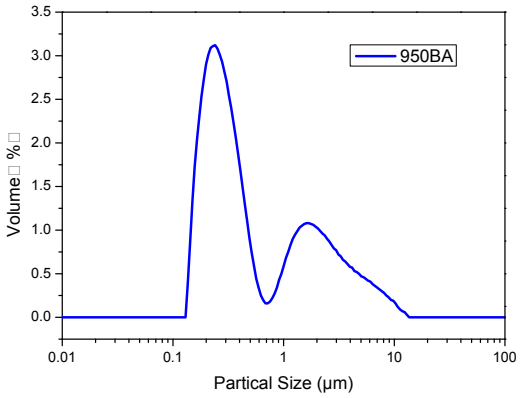

Fig.S5. Particle size dispersity of suspension when 950 BA was used as dispersant.