Waist Cross-linked Micelles Synthesized via Self-assembly Guiding Radical Polymerization

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Supplementary Information

Materials Maleic anhydride (MA), polyethylene glycol 600 (PEG-600), *p*-toluene sulphonic acid (TSA) and octadecyl alcohol (OA) were purchased from Aldrich. Azoisobutyronitrile (AIBN) was supplied by Alfa Aesar and recrystallized from methanol before use. N,N'-methylene bis(acrylamide) (MBA), *n*-heptane, pyrene, potassium persulphate ($K_2S_2O_8$) and methylbenzene were analytical grade and used as received from Shanghai Chemical Reagent Industry.

Synthesise of O-Be, O-B-EG, O-B-EG micelles, WCMs and RWCMs

O-Be 13.5 g of Maleic anhydride (0.05 mol) and 4.9 g of octadecyl alcohol (0.05 mol) were dissolved in methylbenzene (0.5 mol, 53 ml). The reaction mixture was refluxed 4h, the disappearance of peaks at 1850 and 1780 cm^{-1} (C=O stretch vibration of Maleic anhydride)in IR spectrum indicated that the reaction was carried out completely. After evaporating methylbenzene by rotary evaporator, O-Be was obtained (18.1 g , 98%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 0.89 (—CH_3, 3H), 1.20-1.42 ((—CH_2—)$_{15}$, 30H), 1.78 (—CH_2, 2H), 4.30 (—OCH_2, 2H), 6.40 (=CH, 1H), 6.50 (=CH, 1H); IR (KBr, cm^{-1}) 3426, 3064, 2954, 2917, 2847, 1732, 1719, 1640, 1473, 1421, 1360, 1219, 1165.

O-B-EG 7.5 g of PEG-600 (0.0125 mol) and *p*-toluene sulphonic acid (0.172g, 1 mmol) was dissolved in methylbenzene (0.3 mol, 31.8 ml), and 4.6 g of O-Be (0.0125 mol) was dissolved in 21.2 ml of methylbenzene (0.2 mol). O-Be solution was dropwised into PEG-600 solution under a stirring condition, the reaction mixture was refluxed 6h, and a water segregator was used to remove the generated water. Then methylbenzene was evaporated by rotary evaporator. The product was dialyzed in water using a dialytic-bag (molecular weight cutoff 3500) to remove unreacted materials (O-B-EG can form micelles in water and can not pass though the dialytic-bag). Final product (O-B-EG) was obtained after drying at a temperature of 60 ^OC for several days (9.6 g, 79%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 0.89 (—CH_3, 3H), 1.20-1.40 ((—CH_2—)$_{15}$, 30H), 1.68 (—CH_2, 2H), 3.60-3.80 ((—OCH_2)$_{27}$, 54H), 4.18 (—OCH_2, 2H), 4.35 (—OCH_2, 2H), 6.28 (=CH, 2H). IR (KBr, cm^{-1}) 3457, 2920, 2851, 1732, 1637, 1460, 1351, 1113, 948, 848.

O-B-EG micelles 0.1 g of O-B-EG (0.103 mmol) was dispersed in 100 ml of water (5.56 mol). After stirring for 4 h, the O-B-EG micelles was obtained.

WCMs 0.1 g of O-B-EG (0.103 mmol) was dispersed in 100 ml of water (5.56 mol). After 4 h stirring, $K_2S_2O_8$ (0.005 g, 0.018 mmol) and MBA (0.005 g, 0.033 mmol) was added simultaneously in N_2 atmosphere. The reaction mixture was stirried 6 h at a temperature of 68^OC, the disappearance of the peak at 1640 cm^{-1} in IR spectrum indicated that O-B-EG was polymerized completely, and the WCMs was obtained. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 0.89 (—CH_3, 3H), 1.20-1.40 ((—CH_2—)$_{15}$, 30H), 1.60 (—CH_2, 2H), 3.52-3.88 ((—OCH_2)$_{27}$, 54H), 4.05 (—OCH_2, 2H), 4.25 (—OCH_2, 2H). IR (KBr, cm^{-1}) 3347, 2923, 2853, 1735, 1680, 1527, 1463, 1351, 1115, 948, 850, (absorption peak at 1680 is attributed to the C=O stretch vibration from MBA).

RWCMs 0.1 g of O-B-EG (0.103 mmol) was dispersed in 100 ml of n-heptane (0.66 mol). After 4 h stirring, AIBN (0.005 g, 0.031 mmol), deionized water (0.18 ml, 0.01mol) and MBA (0.005 g, 0.033 mmol) was added simultaneously in N_2 atmosphere. The reaction mixture was stirried 6 h at a temperature of 60 ^{O}C, the disappearance of the peak at around 1640 cm^{-1} (C=C stretch vibration) in IR spectrum indicated that O-B-EG was polymerized completely, and the RWCMs was obtained.

^{1}H NMR, FT-IR, DLS, FE-SEM, TEM , UV transmittance and Fluorescence spectroscopy analysis

The ^{1}H NMR spectra of O-Be, O-B-EG, O-B-EG micelles, WCMs and RWCMs were measured on a Bruker ARX 400MHz spectrometer with 1000 scans at a relaxation time of 2 s. Fourier-transform infrared (FT-IR) spectroscopy (Nicolet Avatar 360) was also used to confirm the structures of the obtained products.

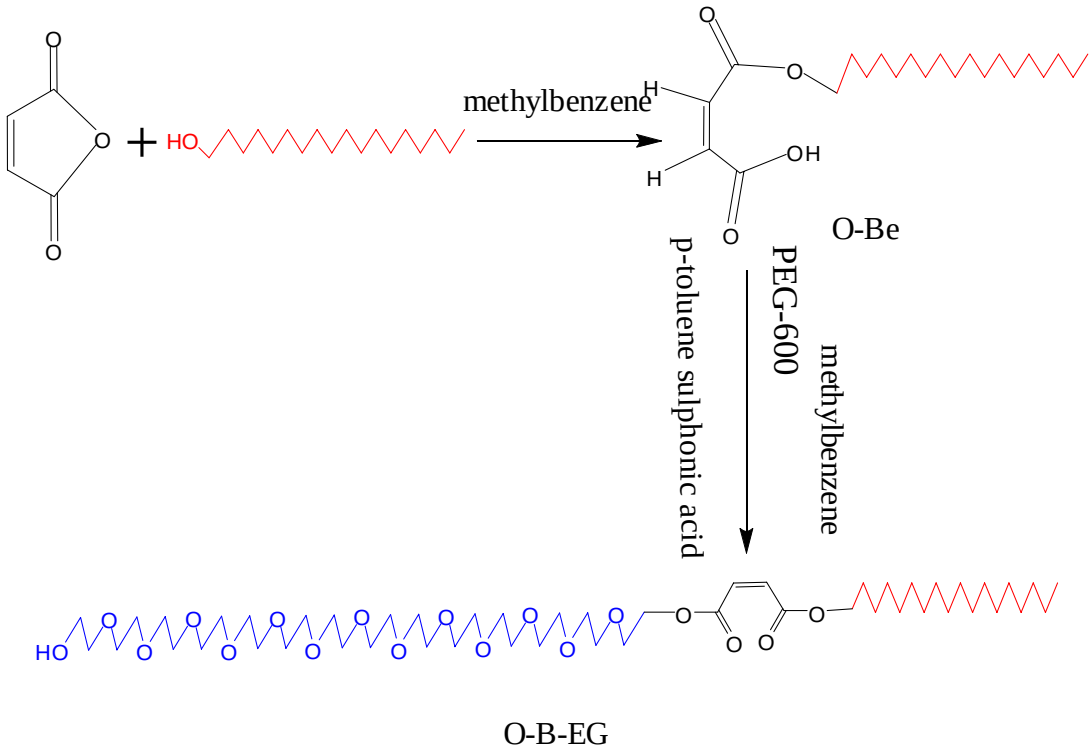
After the micelles were dispersed in aqueous solution, the particle size of micelles was characterized by dynamic light scattering (DLS) on a ZetaPALS. For the study of temperature-dependence of particle size, diameter of the samples were measured by DLS at a predetermined temperature between 30 and 50 ^{O}C, and each temperature was remained at least 15min.

To obtain microscope images of micelles, samples were dispersed in deionized water, and dropwised on aluminium sheets. After air-drying for 10 days at room temperature, the samples were gold sputtering treated, and field emission scanning electron microscope (FE-SEM, LEO-1530) was used to observe the surface morphology of micelles.

Transmission electron microscopy (TEM) measurements and electron diffraction experiment were performed with a JEM2100 at an acceleration voltage of 200 kV. To prepare the TEM samples, a small drop of WCMs solution was deposited onto a carbon-coated copper electron microscopy (EM) grid and then dried under room temperature at atmospheric pressure. The energy dispersion spectroscopy analysis was also carried out on a energy dispersive spectrdmeter (ZNCA Energy TEM 100 x-ray energy spectrum) assembled on JEM2100.

The UV transmittance of micelles in aqueous solutions was measured by UV spectrophotometry (Unico UV/vis 2802PCS) at a predetermined temperature between 30 and 50 ^{O}C, and each temperature was also remained at least 15 min.

As so-called pyrene 1:3 ratio (I_1/I_3) method is one of the most popular procedures for the determination of the critical micelle concentration (CMC) of surfactant solutions. The CMC of O-B-EG in aqueous solution was measured by fluorescence spectrophotometry on HITACHI F-7000 using pyrene as fluorescence indicator (stimulation slit width: 1 nm, emission slit width: 2.5 nm, scanning speed: 60 nm/min). The CMC of O-B-EG in aqueous solution is defined as the concentration of O-B-EG that I_1/I_3 exhibiting sharp change.



Scheme 1S. Synethetic pathway of O-Be and O-B-EG.

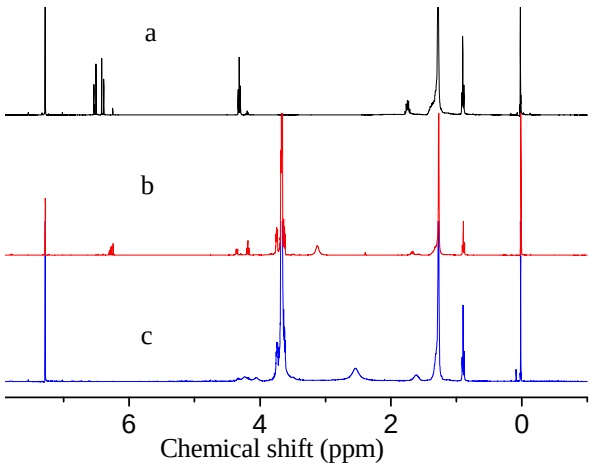


Figure 1S. ^{1}H NMR spectra of (a) O-Be, (b) O-B-EG and (c) WCMs in $CDCl_3$.

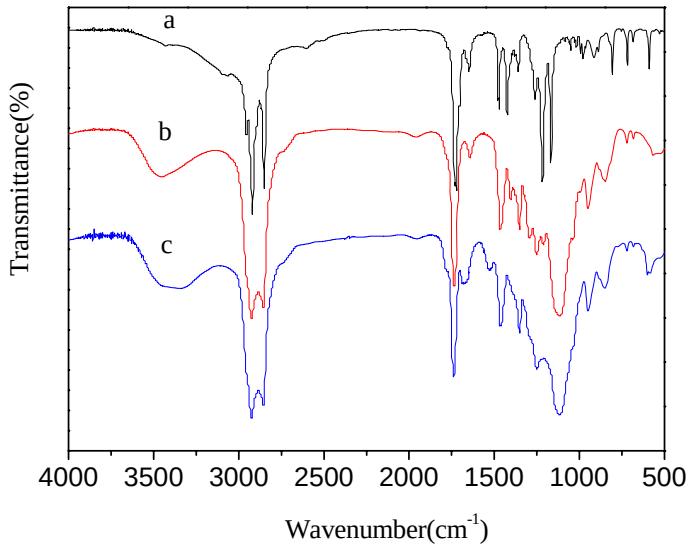


Figure 2S. FT-IR spectra of (a) O-Be, (b) O-B-EG and (c) WCMs.

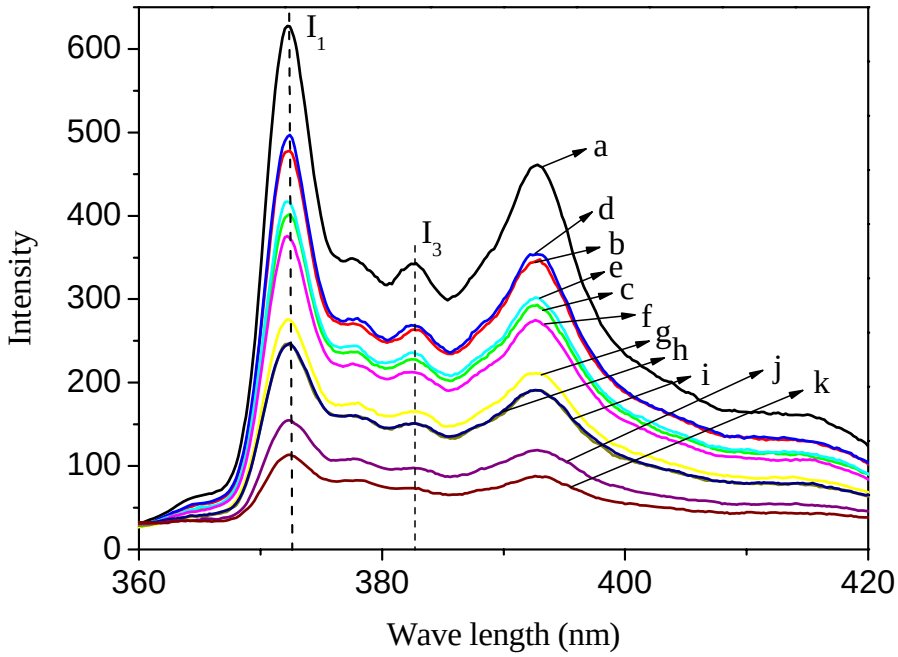


Figure 3S. Fluorescence spectra of pyrene in different concentration of O-B-EG aqueous solutions (a: 0.005 mg/mL, b: 0.01 mg/mL, c: 0.02 mg/mL, d: 0.04 mg/mL, e: 0.08 mg/mL, f: 0.1 mg/mL, g: 0.15 mg/mL, h: 0.2 mg/mL, i: 0.3 mg/mL, j: 0.4 mg/mL, k: 0.5 mg/mL).

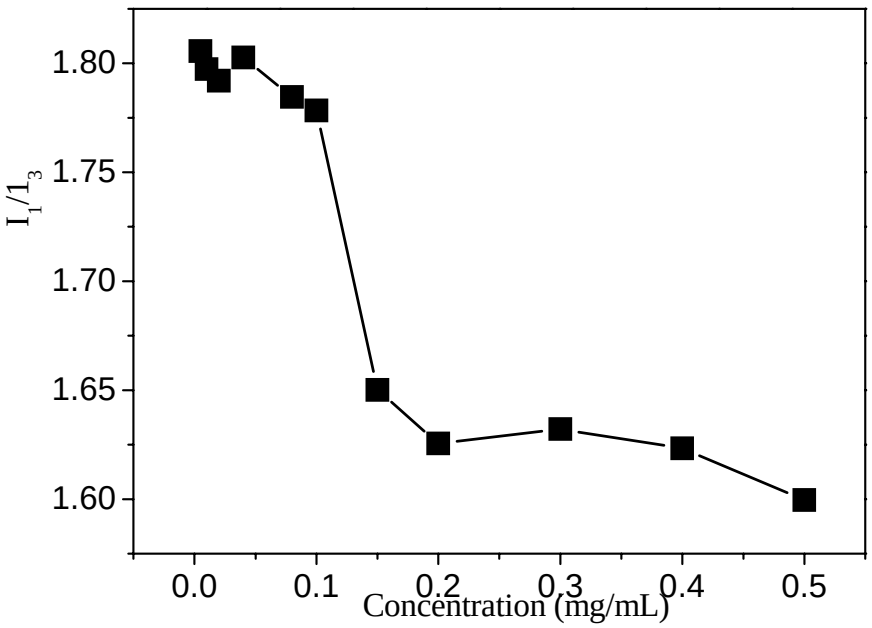
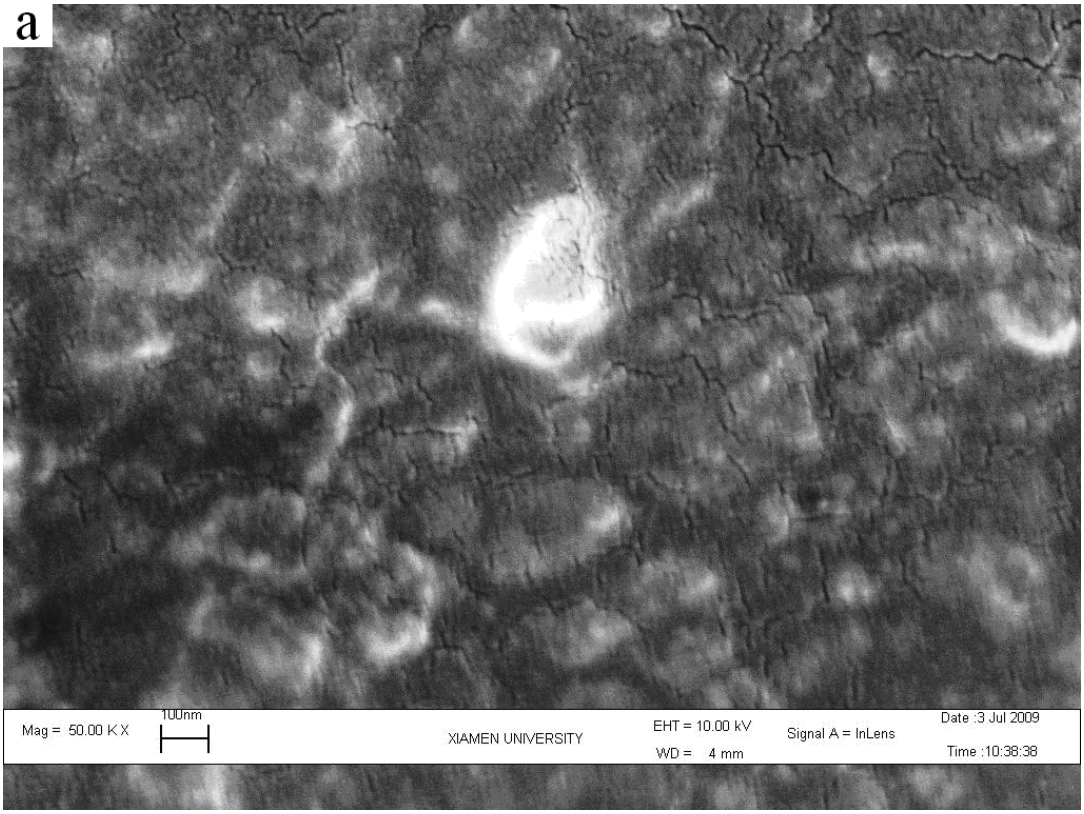


Figure 4S. Plot of pyrene 1:3 ratio (I_1/I_3) versus concentration of O-B-EG in aqueous solutions (a sharp change of I_1/I_3 can be observed at the concentration of O-B-EG approximate to 0.15 mg/mL, this concentration is the CMC of O-B-EG in aqueous solutions).



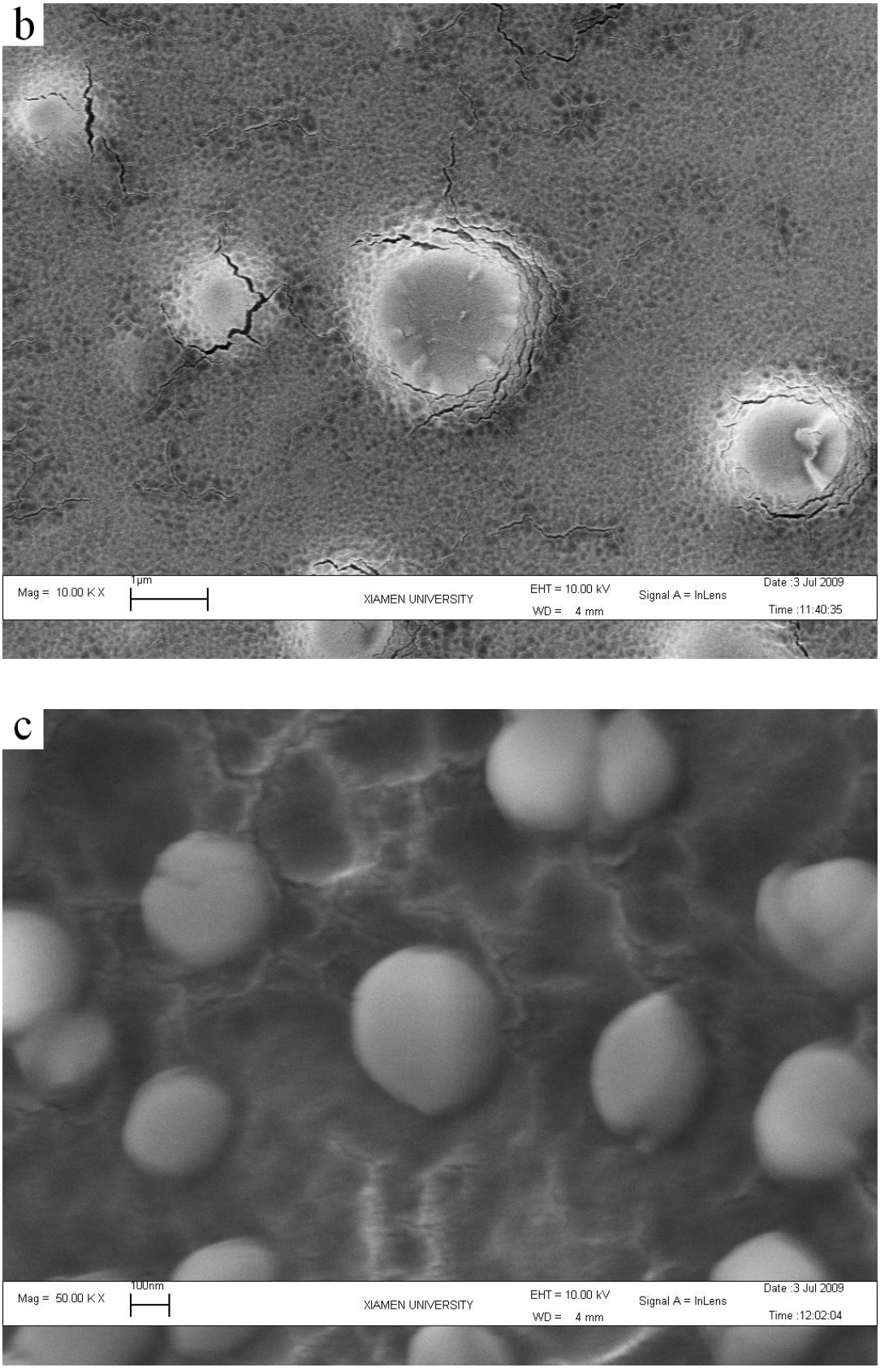
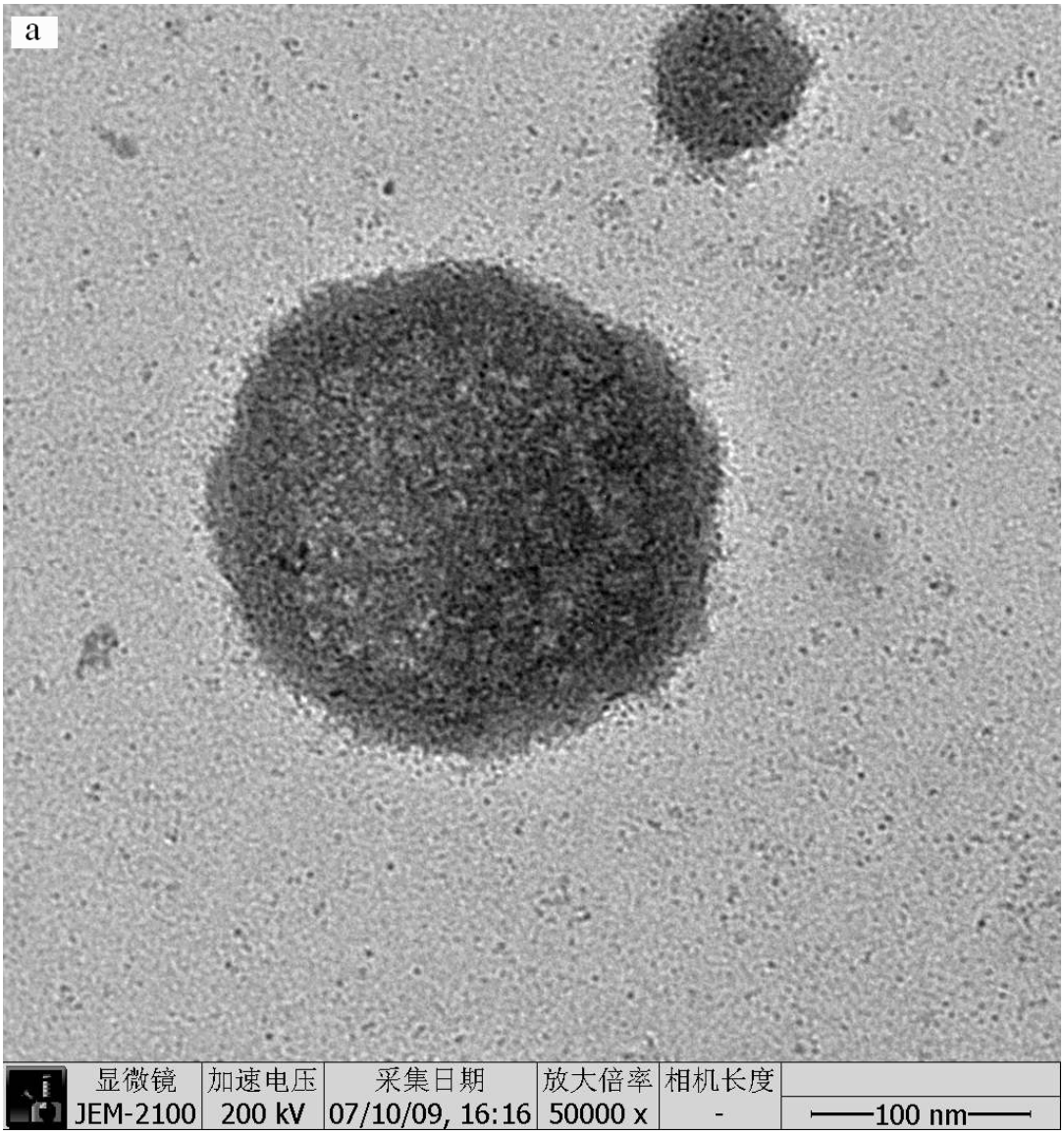


Figure 5S. FE-SEM original images of O-B-EG micelles (a), collapsed WCMs (b) and non-collapsed WCMs (c).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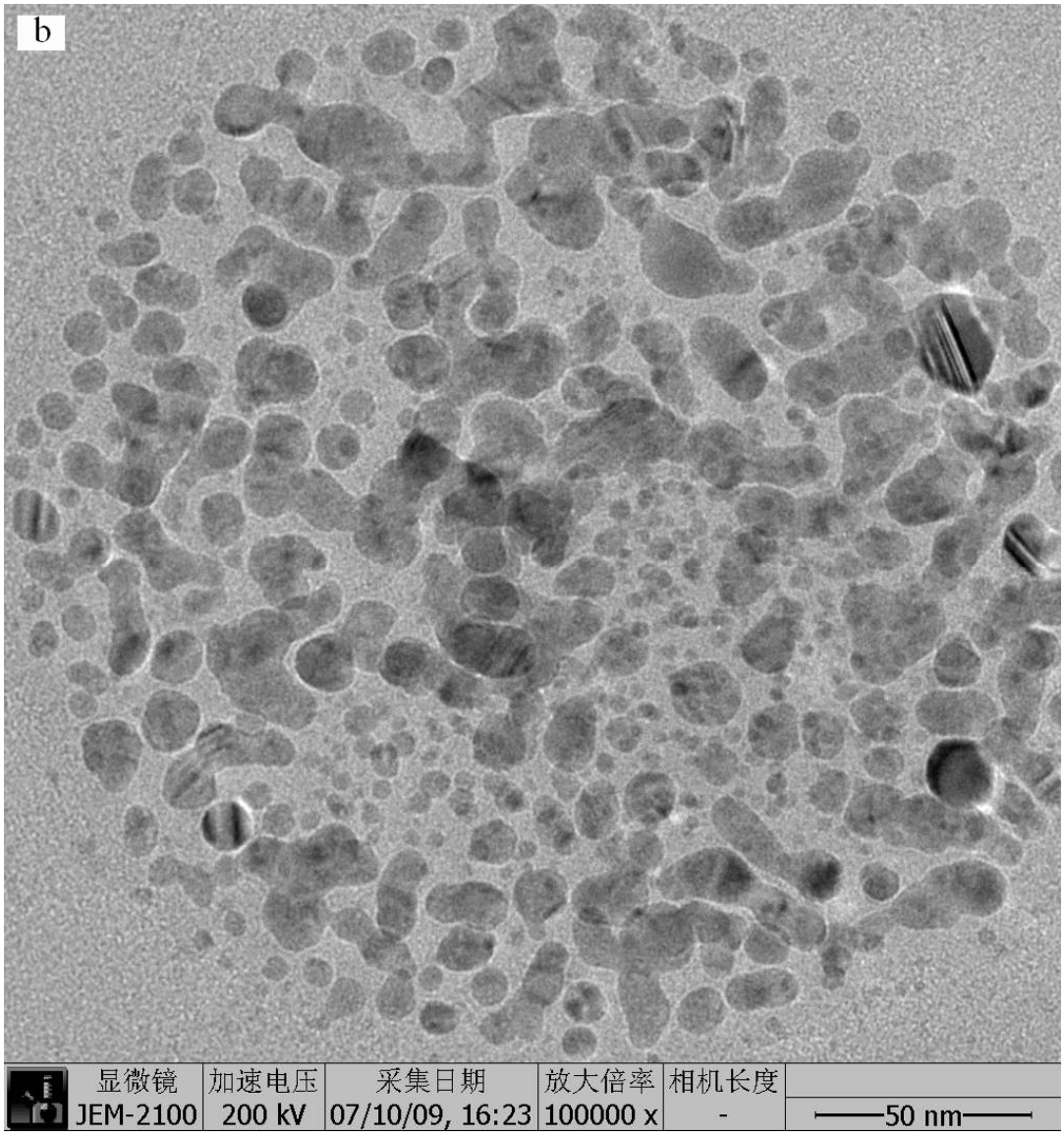
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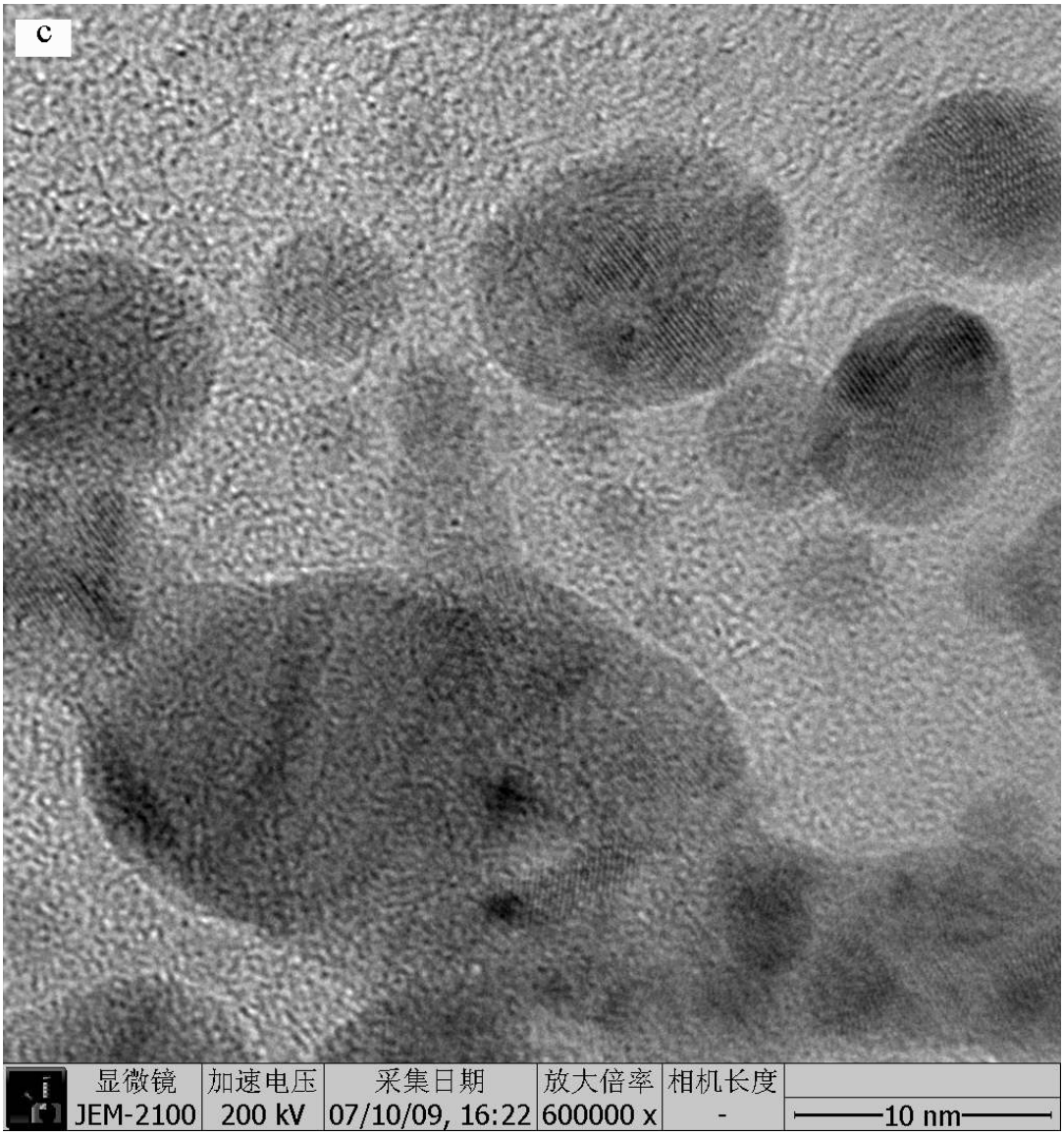

Figure 6S. TEM original images of WCMs (a), electron beams bombarded WCMs (b) and WCMs fragments (c)

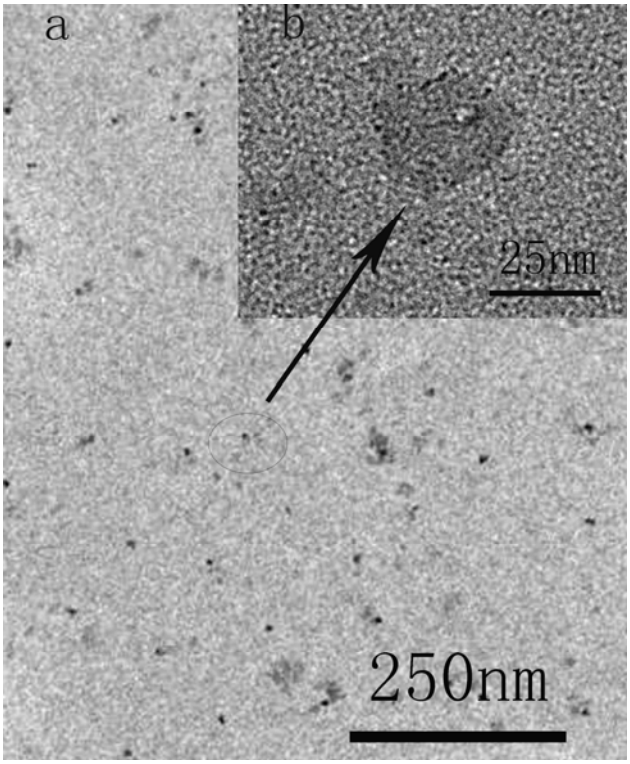

Figure 7S TEM images of monomolecular layer O-B-EG micelles.

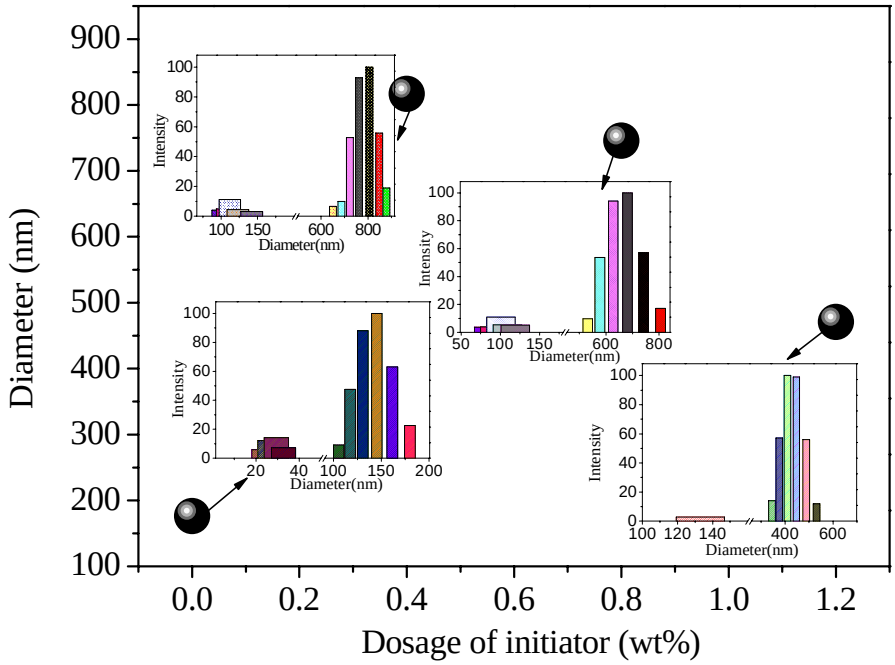

Figure 8S. Diameter of O-B-EG micelles (non-polymerized micelles, dosage of initiator: 0%) and influence of the dosage of initiator on the Diameter of WMCs.

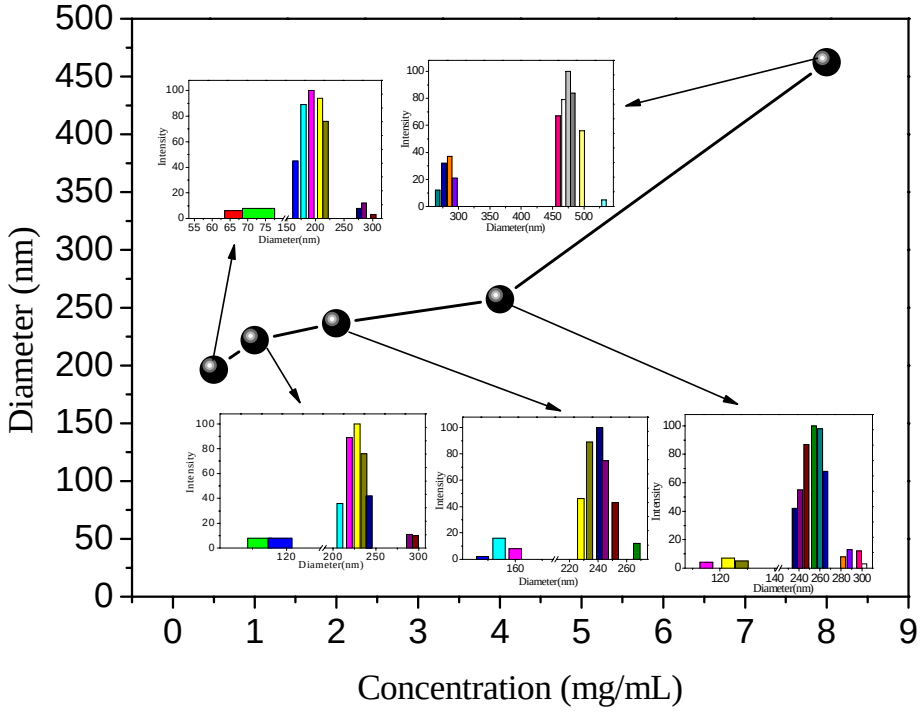

Figure 9S. Effect of the concentration on the diameter of O-B-EG micelles.

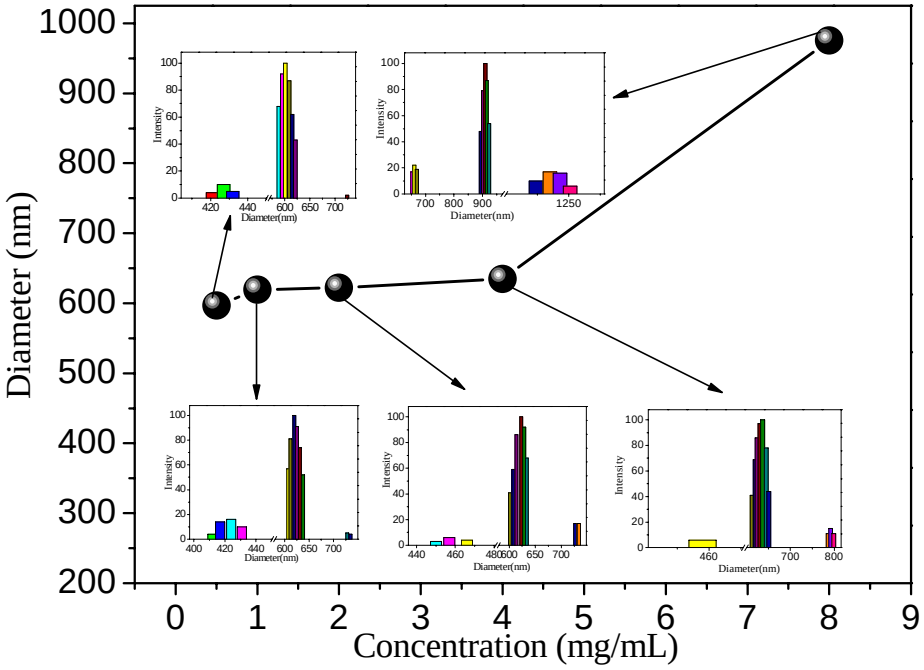

Figure 10S. Influence of the concentration on the diameter of WCMs micelles.