

Electronic Supplementary Information

Bergman Cyclopolymerization within the Channels of Functional Hybrid Nanocomposite Formed by Co-assembly of Silica and Polymerizable Surfactant Monomer

Chetan Jagdish Bhongale, Chung-He Yang and Chain-Shu Hsu*

Department of Chemistry, National Chiao Tung University, Hsinchu,
Taiwan 30050

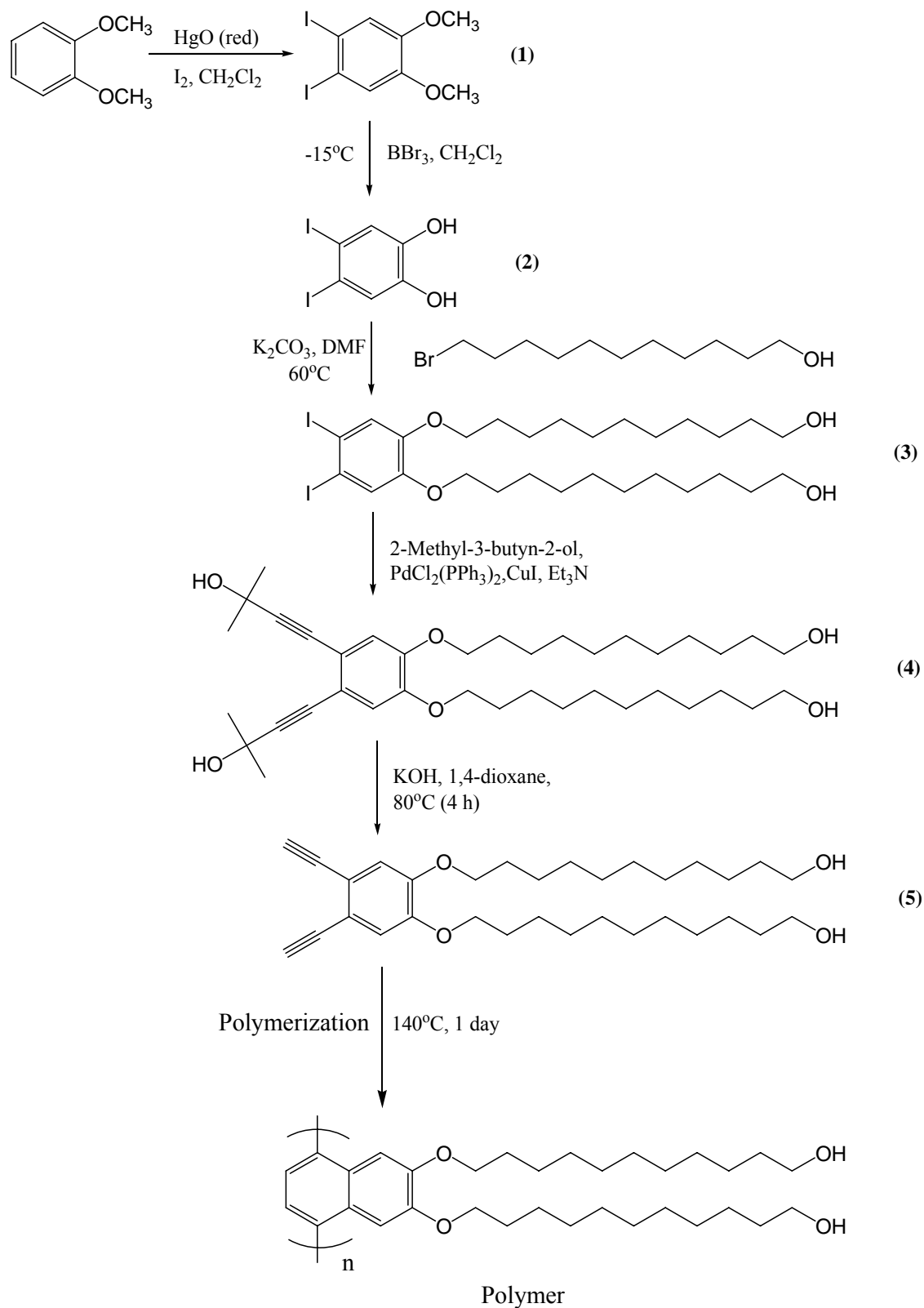
*To whom correspondence should be addressed

E-mail: cshsu@mail.nctu.edu.tw

Instrumental Techniques:

^1H NMR spectra were recorded (Unity 300 spectrometer at 300 MHz) in CDCl_3 solutions. EI-MS data was obtained from MICROMASS TRIO-2000 spectrometer. SEM images were acquired on a field-emission scanning electron microscope (JSM-6500 F, JEOL); to enhance the conductivity of the specimen, a layer of platinum was sputtered (duration 30 s, current 30 mA, pressure 4 Pa). TEM micrographs and EDS experiments were carried under AEM/EDS JEOL, JEM-2010. X-ray diffraction measurements for nanocomposite films were done with a diffractometer (Bede D1 type) with $\text{Cu}_{\text{K}\alpha}$ radiation at $\lambda = 1.54056 \text{ \AA}$. UV-vis absorption spectra (Hewlett-Packard HP8453 spectrometer) and fluorescence spectrometer (SpectraPro-150 with Muller SVX 1450 xenon lamp) were measured in a standard manner. FT-IR spectra were recorded on PerkinElmer Spectrum One instrument.

Scheme S1:



Synthesis of the surfactant monomer:

1,2-diiodo-4,5-dimethoxybenzene (1)

Iodine crystals 39.67 g (156.31 mmols) and dry CH₂Cl₂ (50 mL) were taken in round bottom flask, sonicated and stirred for few minutes. 16.92 g HgO (red) powder (78.15 mmols) was added slowly for about 20 minutes. Then added 1,2-dimethoxybenzene 9.0 g (65.13 mmols) from side arm slowly. The reaction was stirred at room temperature for 20 hours. Filtered the solution and discarded the scarlet red precipitate formed. The filtrate was washed with 5% sodium thiosulphate, saturated NaCl and then extracted with ethyl acetate (EA). The organic layer was dried over MgSO₄, filtered; the ethyl acetate was removed on rotar to get the solid crude. Recrystallization of the crude from ethyl acetate gave white product. ¹H NMR: (300 MHz, CDCl₃): δ= (300 MHz, CDCl₃): δ=7.23 (s, 2H; ArH), 3.83 (s, 6H; OCH₃).

4,5-diiodo-1,2-benzenediol (2)

1,2-diiodo-4,5-dimethoxybenzene (7 g, 17.94 mmols) was dissolved in about 40 mL CH₂Cl₂ and maintained the reaction temperature at -15°C. Then 12 mL of BBr₃ solution (1M in CH₂Cl₂) was added slowly by syringe under N₂ atmosphere while stirring. The reaction was monitored by TLC. Reaction completed after 6 hours. The reaction mixture was extracted with CH₂Cl₂ and water, saturated NaCl, organic layer separated and dried over MgSO₄. The organic layer was filtered and solvent evaporated on rotar to get the solid crude. The compound was purified on column with EA/Hexane (3:7) as an eluent, to get pink white solid. ¹H NMR (300 MHz, CDCl₃): δ=7.34 (s, 2H; ArH), 5.45 (s, 2H, -OH).

S4

11-2-[(11-hydroxyundecyl)oxy]-4,5-diiodophenoxy-1-undecanol (3)

3 g (8.2 mmols) of compound **2** was dissolved in little DMF and to it was added 2.8 g (20.7 mmols) K_2CO_3 . The mixture was stirred and heated at 60-70°C, on which solution was turned reddish after about 45 minutes and then added 4.16 g (16.5 mmols) of 11-bromo-1-undecanol to the reaction mixture. Heating continued for about three hours under N_2 atmosphere. Then the reaction mixture was poured into the water, acidified by dilute HCl, extracted with EA/water and washed two times with saturated NaCl. The organic layer was separated and dried over $MgSO_4$. After evaporating EA on rotar, pink solid obtained. Decanting several times with EA, yellowish solid product was obtained. 1H NMR: (300 MHz, $CDCl_3$): δ =7.24 (s, 2H; ArH), 3.92 (t, 4H, $-OCH_2$), 3.63 (t, 4H, $-\underline{CH}_2OH$), 1.78-1.29 ppm (m, 36H, $-CH_2$).

4-2-(3-hydroxy-3-methyl-1-butynyl)-4,5-di[(11-hydroxyundecyl)oxy]phenyl-2-methyl-3-butyn-2-ol (4)

Compound **3** (3 g, 4.2 mmols) was dissolved in three neck round bottom flask containing about 50 mL triethylamine by sonication. Then added $PdCl_2(PPh_3)_2$ (0.06 g, 0.03 mmols), PPh_3 (0.16 g, 0.6 mmols) and CuI (0.02, 0.34 mmols) to it. The mixture was stirred and heated at about 70°C for 45 minutes. Then was added 2-methyl-3-butyn-2-ol (0.86 g, 10.02 mmols) to it from the side arm. Yellowish gel was formed. Heating and stirring continued for one day. Reaction was monitored by TLC. Filtered the reaction mixture and triethylamine was removed on rotar; extracted with EA and water, washed with saturated NaCl. Organic layer was separated and dried over $MgSO_4$, filtered and EA was removed on rotar to get the solid crude. Recrystallization of the crude from EA/Hexane gave fine yellowish

S5

crystals. $^1\text{H NMR}$: (300 MHz, CDCl_3): δ =6.86 (s, 2H; ArH), 3.97 (t, 4H, $-\text{OCH}_2$), 3.63 (t, 4H, $-\text{CH}_2\text{OH}$), 2.81 (s, 2H, $\text{HO}-\text{C}(\text{CH}_3)_2$), 1.62 (s, 12H, $-\text{CH}_3$), 1.80-1.28 ppm (m, 36H, $-\text{CH}_2$).

11-4,5-di(1-ethynyl)-2-[(11-hydroxyundecyl)oxy]phenoxy-1-undecanol (5)

Compound **4** (1.2 g, 1.95 mmols) was dissolved in a little amount of 1,4-dioxane. KOH pellets (0.52 g, 9.3 mmols) were crushed and added to it. Mixture was stirred and heated at about 80-90°C for about four hours. Dean-Stark apparatus was attached to it to collect the acetone formed during the reaction. Then the reaction mixture was poured into water and was acidified with dilute HCl, extracted with EA, water and washed by saturated NaCl. The organic layer was separated, dried over MgSO_4 , filtered and EA was removed on rotar. Recrystallization from EA/Hexane gave **5** as off-white solid. $^1\text{H NMR}$: 6.92 (s, 2H, ArH), 3.98 (t, 4H, $-\text{OCH}_2$), 3.63 (t, 4H, $-\text{CH}_2\text{OH}$), 3.22 (s, 2H, $\equiv\text{C}-\text{H}$), 1.81-1.26 ppm (m, 36H, $-\text{CH}_2$). IR (KBr): 3360, 3280, 2920, 2850, 2107, 1705, 1595, 1506, 1460, 1388, 1340, 1260, 1205, 1093, 1055, 850, 720 and 610 cm^{-1} .

Polymerization of surfactant monomer (5):

Benzene solution of surfactant monomer (0.3 g, 0.6 mmols) was taken in thick-walled screw cap glass tube which was capped in the glove box under nitrogen atmosphere prior to heating at 140°C for one day. After cooling, polymer was collected by filtration and washed with diethyl ether. The polymer was dried *in vacuo* to yield 0.22 g of insoluble red-brown solid. IR (KBr): 3425, 2913, 2845, 1625, 1505, 1457, 1378, 1250, 1050, 847 and 719 cm^{-1} .

S6

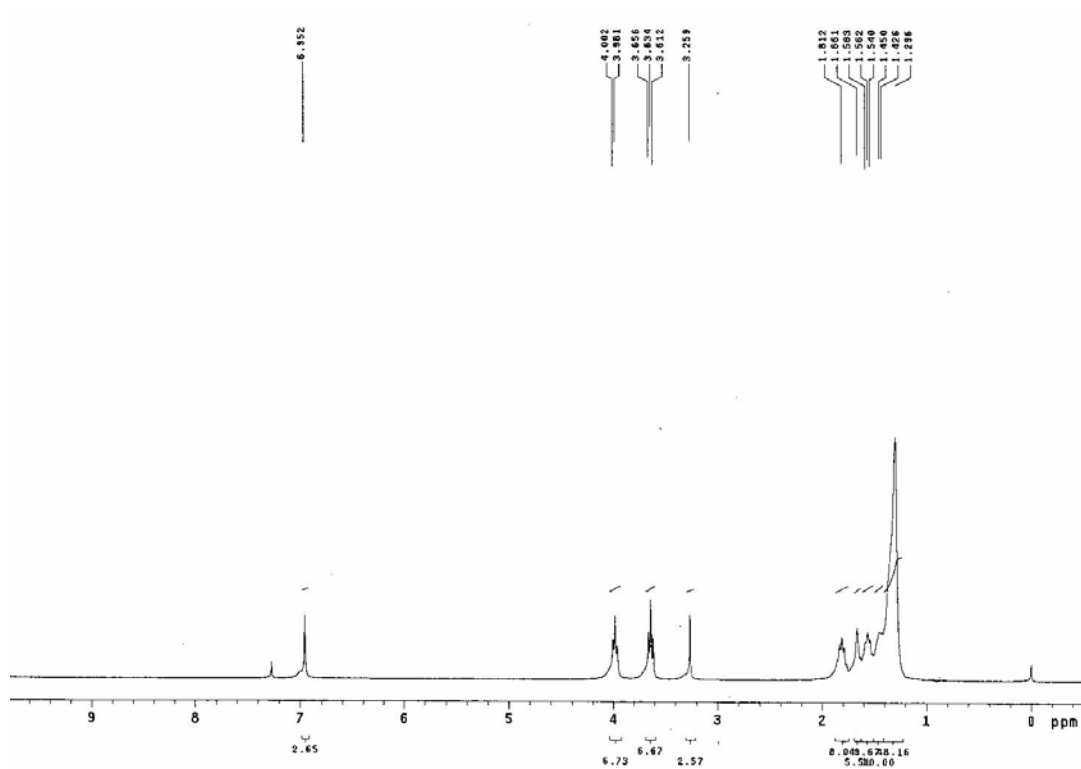


Fig. S1 ¹H NMR of monomer (5):

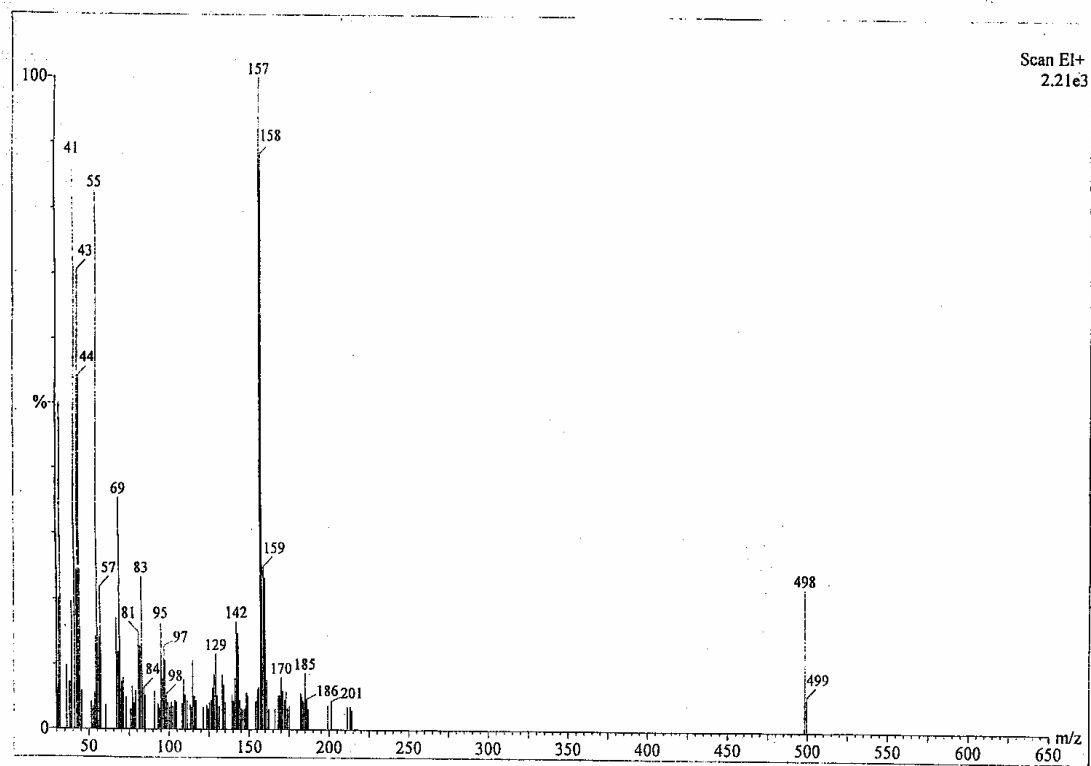


Fig. S2 EI-MS data of monomer (5):

Formation of the hybrid nanocomposite by self-assembly:

Precursor solutions were synthesized from tetraethyl orthosilicate (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$), surfactant monomer, and HCl catalyst prepared in ethanol/water solvent. The final reactant mole ratio for nanocomposites prepared from surfactant monomer was 1 TEOS: 30 ethanol: 5 H_2O : 0.1 HCl: 0.5 monomer. In a typical preparation, TEOS, ethanol, water and dilute HCl were stirred and heated at 35°C for half an hour. To this solution was added the surfactant monomer in ethanol and stirred for three hours. Films were prepared on quartz by evaporative spin-coating (1,500 r.p.m.), or dip-coating (at a rate of 30 cm min^{-1}). During deposition, preferential evaporation of ethanol concentrates the depositing film in water and nonvolatile silica and surfactant monomer. The progressively increasing surfactant concentration drives self-assembly of surfactant monomer/silica micelles and their further organization into ordered liquid crystalline mesophases. These films were vacuum-dried for overnight and kept immersed in benzene in thick-walled screw cap glass tubes which were capped in the glove box under nitrogen atmosphere prior to heating at 140°C for one day.