

Electronic Supplementary Information (ESI)

for

Microgel-stabilised non-aqueous emulsions

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Experimental:

Materials:

Noigen RN-20 (polyoxyethylene 4-nonyl -2-propylene-phenol) nonionic reactive surfactant (Daichi Kogyo Seiyaku of Japan manufacture; Montello, distributor) was used as received. Poly(ethylene glycol) having molecular weight 400 (PEG 400), P-toluene sulfonic acid (PTSA), maleic anhydride (MA), toluene (T), formamide (FA), xylene and chloroform were purchased from Aldrich and used as received. *N*-Isopropylacrylamide (NIPAAm) was delivered from Aldrich chemicals Co., recrystallized in toluene:hexane (60:40) mixture, and dried. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) and *N,N*-methylenebis-acrylamide (MBA) were purchased from Merck. Azobisisobutyronitrile (AIBN), and formamide delivered from Alderich chemical Co. ABIN purified by recrystallizing three times from methanol and drying in vacuum at room temperature.

Preparation polyoxyethylene 4-nonyl -2-propyl-phenyl maleic anhydride adducts

Maleic anhydride (2 mol) was reacted with polyoxyethylene 4-nonyl -2-propylene-phenol (Noigen RN-20) (1 mol) in the presence of hydroquinone (0.02 g) at 180°C in a nitrogen atmosphere for 24hrs. The mixture was then poured into chloroform and carefully washed with water (5x50 mL) to remove the unreacted maleic anhydride. The chloroform was evaporated in vacuum, and the reaction yield 94% was obtained as brown oil.

The reaction product between MA and Noigen RN-20 designated as NRN-20-MA. The chemical structure of the prepared surfactants illustrated in Scheme 1.

Preparation polyoxyethylene 4-nonyl -2-propyl-phenyl maleate ester

A mixture of freshly distilled PEG 400 (3 mols), NRN-20-MA (1 mol), PTSA (1%) based on total weight of reactants and 100 ml xylene were placed in 0.5 L round-flask fitted with Dean Stark apparatus. The mixture was allowed to heat until the theoretical water was collected through azotropic condensation. Xylene was distilled off from the reaction product by rotary evaporator under reduced pressure. The product was separated by salting out with hot saturated NaCl aqueous solution and extracted with isopropanol using separating funnel. The purified products were isolated after evaporation of isopropanol.

The reaction products between PEG 400 and NRN-20-MA designated as NMA20-(PEG400)₃.

Copolymerization of NIPAAm/AMPS:

Crosslinked N-isopropylacrylamide-co-2-acrylamido-2-methylpropane sulfonic acid microgels, NIPAAm/AMPS, were prepared through a modified temperature programmed in the presence of two immiscible organic solvents; formamide (50: 50 volume %) and toluene and polymerizable surfactant Noigen-MA-PEG400 (0.5 Wt % based on total volume of formamide and toluene). Three different mol ratios of NIPAAm (90, 95 and 98 mol %) were used to copolymerize with AMPS monomers. The NIPAAm monomer was dissolved in 40 ml of formamide and preheated to 40 °C for 30 minute under nitrogen atmosphere. AIBN (0.04 g) and (0.05 g) of NMA-(PEG400)₃ dissolved in 5 ml toluene were injected to initiate the polymerization. The temperature of reaction increased up to 55 °C with rate 5 °C per 15 minutes. The monomers of NIPAAm, AMPS, NMA-(PEG400)₃ and MBA were dissolved in 20 ml of formamide and mixed with AIBN dissolved in 45 ml of toluene and then injected with rate 1 ml/minute by means of a syringe pump under stirring. After the feeding was stopped, the reaction temperature increased and kept at 60 °C for 2 hrs. The resultant nanogels were purified by ultracentrifugation at 20000 rpm and the resultant particles were dispersed in formamide and re-precipitated in 10 fold of acetone.

Characterization of the prepared surfactants

FTIR spectra were analyzed with a Nicolet FTIR spectrophotometer using KBr in a wavenumber range of 4000–500 cm⁻¹ with a resolution accuracy of 4 cm⁻¹. All samples were ground and mixed with KBr and then pressed to form pellets.

The interfacial tension measurements of the prepared NIPAM/AMPS nanogel at oil-oil were carried out at different molar concentrations at temperature 25 °C by means of the pendent drop technique using drop shape analyzer model DSA-100 (Kruss, Germany). In this method the shape of a pendent drop is fitted to the theoretical drop profile according to the Laplace equation, using interfacial tension as one of the adjustable parameters. The error limits of these measurements are on the order of ± 0.1 mN/m. The DSA-100 analysis required accurate density measurements, which were measured as functions of temperature and nanogels concentration with an AP Paar DMA45 MC 1296 densitometer. Pendent drops were formed on the tip of a needle with an outside diameter of 1.83 mm.

High resolution transmission electron microscopy (HR-TEM) images for the prepared nanoparticles were recorded using (JEM-2100F, JEOL, Japan) at an acceleration voltage of 120 kV. The specimens for TEM observation were prepared by the following procedure. The sample was ultrasonically dispersed in ethanol for 5 min, and then a drop of sample suspension was dropped onto a carbon-coated copper grid, which was left to stand for 10 min and transferred into the microscope.

Emulsions were mounted on a glass slide (Matsunami Glass Ind., Ltd.) and examined by using an optical microscope (BX53, Olympus) equipped with a digital camera (XD200,

Flovel Co., Ltd.). The size of the emulsion was determined by calculating the average diameter of 50 droplets.

The FTIR spectrum of NMA20-(PEG400)₃-P(NIPAM-90/AMPS-10) was selected as representative samples and illustrated in **Fig.S1**. **Figure S1** showed absorption bands at 3010, and 3050, 1745, 1610, 850 cm⁻¹ which attributed to the stretching frequency of the aromatic C-H groups, C=O ester, C=C and out of plan bending of CH aromatic at p-position, respectively which indicated the incorporation of NMA20-(PEG400) in the chemical structure of the produced nanogels as illustrated in Scheme 2. The primary amide carbonyl group peaks of AMPS and NIPAM units, and secondary amide N-H deformation bands of microgel units are observed at 1627 and 1545 cm⁻¹, respectively. The bands at 1465.3 cm⁻¹ indicates C-H bending of CH₂ groups, at 1384 cm⁻¹ indicating the vibration of the isopropyl group, at 1216 cm⁻¹, 1078 cm⁻¹, and 1016 cm⁻¹ re indicating the asymmetric and symmetric stretching of S=O bond of SO₃ groups. The appearance of these absorption bands confirms the formation of NMA20-(PEG400)₃-P(NIPAM/AMPS) nanoparticles.

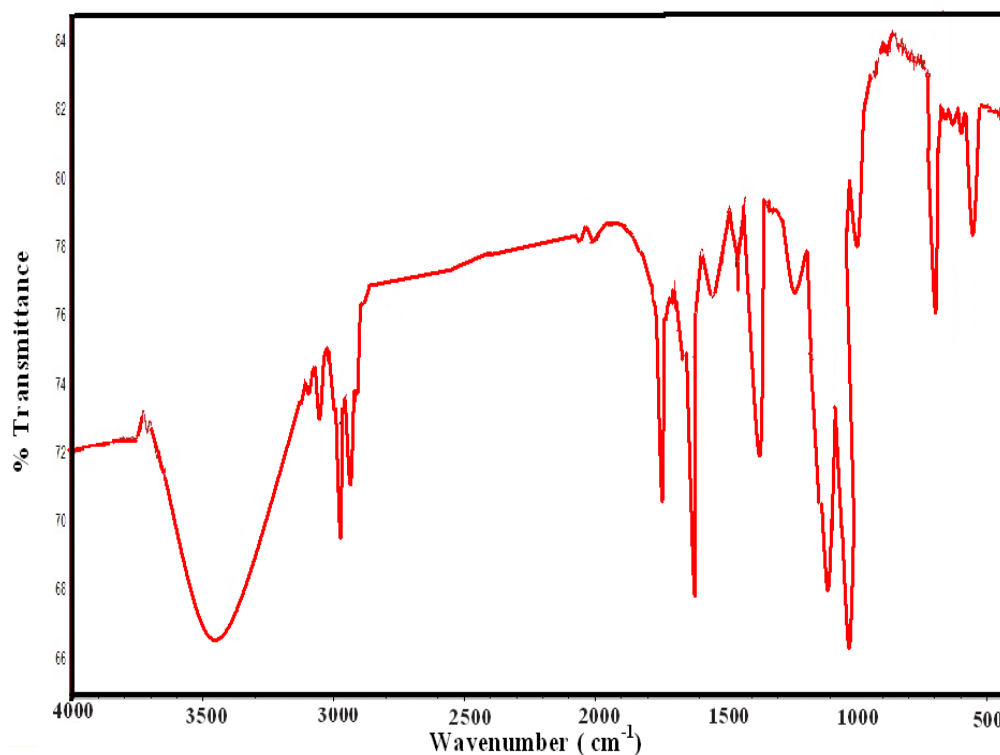
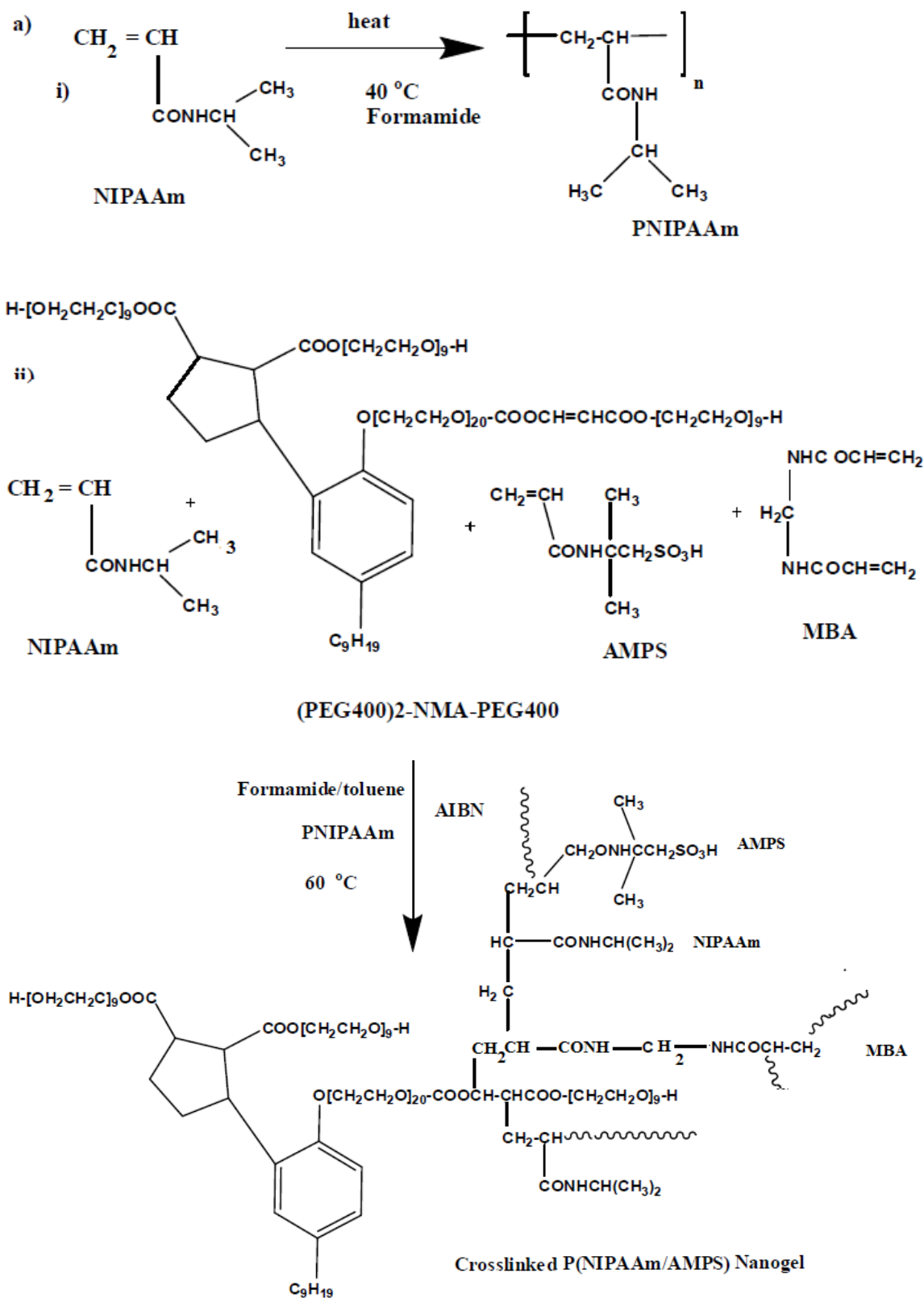


Fig. S1 FTIR of NMA-(PEG400)₃-P(NIPAM/AMPS) 90/10 mol % nanogels.



Scheme 1: Synthesis of NMA20-(PEG400)₃-P(NIPAm/AMPS) nanogels.

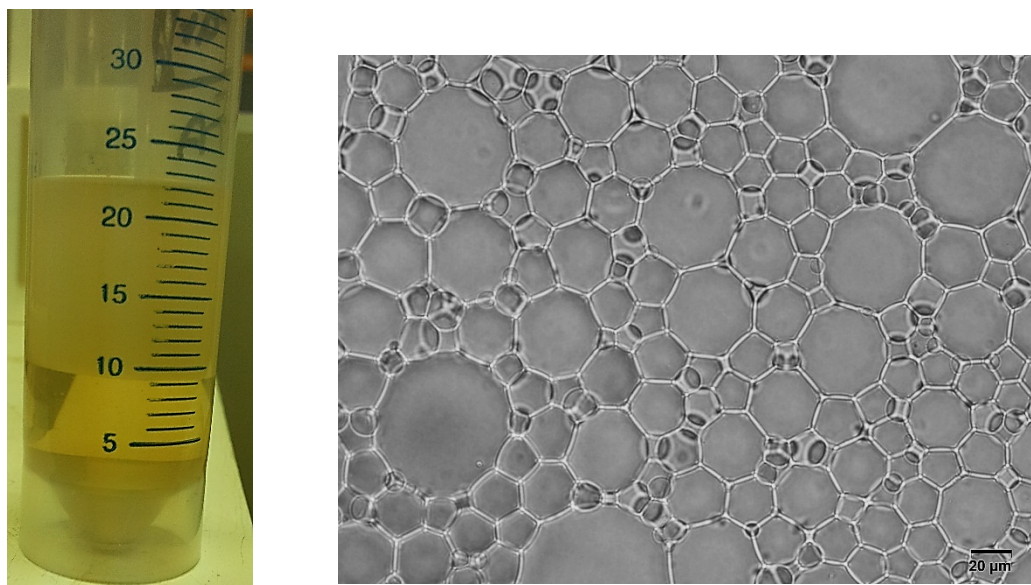


Fig S2. Digital and optical images for equal volumes paraffin oil-in-formamide (o/o) emulsion 6 months after preparation at 25 °C. The emulsion was stabilised by 1 wt.% 90/10 NIPAM/AMPS microgels initially dispersed in formamide, $\phi_{pa} = 0.5$.