Supporting Information “Rheology and Structure of Surface crosslinked Surfactant-Activated Microgels”

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S.I.1 Synthesis of Microgel Particles.

The conventionally crosslinked SAM microgel was prepared as follows. A monomer premix was made by combining 140 grams of water, 5 grams of SDS, 175 grams of EA, 75 grams of n-BA, 33.3 grams of BEM and 225 grams of HEMA. Initiator A was made by mixing 2.86 grams of 70 wt% TBHP in 40 grams of water. Reductant A was prepared by dissolving 0.13 grams of erythorbic acid in 5 grams of water. Reductant B was prepared by dissolving 2 grams of erythorbic acid in 100 grams of water. A 3 liter reaction vessel was charged with 800 grams of water, 13.3 grams of 30 wt% SDS and 25 grams of poly (vinyl alcohol). The reaction vessel was heated to 60ºC under a nitrogen blanket and proper agitation. Initiator A was then added to the reaction vessel followed by the addition of reductant A. After about 1 min, the monomer premix was metered into the reaction vessel over a period of 150 minutes. About 3 min after the start of monomer premix metering, reductant B was metered into the reaction vessel over a period of 180 minutes. About 90 minutes after the start of monomer premix metering, 0.43 grams of 70 wt% APE crosslinker was added to the monomer premix. After completion of reductant B feed, the temperature of the reaction vessel was maintained at 60ºC for 60 minutes. The reaction vessel was then cooled to 55ºC. A solution of 1.79 grams of 70 wt% TBHP and 0.58 grams of 30wt% SDS in 25 grams of water was added to the reaction vessel. After 5 min, a solution of 1.05 grams of erythorbic acid and 0.1 grams of 30wt% SDS in 25 grams of water was added to the reaction vessel. The reaction
vessel was maintained at 55ºC. After 30 min, a solution of 1.79 grams of 70 wt% TBHP and 0.3 grams of 30 wt% SDS in 25 grams of water was added to the reaction vessel. After 5 minutes, a solution of 1 gram of erythorbic acid and 0.17 grams of 30 wt% SDS in 25 grams of water was added to the reaction vessel. The reaction vessel was maintained at 55ºC for about 30 min. The reaction vessel was then cooled to room temperature and the contents filtered through a 100 micron cloth. A stable suspension was obtained containing about 30 wt% solids with particle size of 100 nm. The polymer had weight fractions of EA, n-BA, BEM, HEMA and APE of 35, 15, 5, 45 and 0.06% respectively.

The surface self-crosslinked SAM microgel was prepared as follows. A monomer premix was made by combining 140 grams of water, 5 grams of PEO(15)GESPS22, 175 grams of EA, 75 grams of n-BA, 33.3 grams of BEM and 225 grams of HEMA. Initiator A was made by mixing 2.86 grams of 70 wt% TBHP in 40 grams of water. Reductant A was prepared by dissolving 0.13 grams of erythorbic acid in 5 grams of water. Reductant B was prepared by dissolving 2 grams of erythorbic acid in 100 grams of water. A 3 liter reaction vessel was charged with 800 grams of water, 13.3 grams of 30 wt% SDS and 25 grams of poly (vinyl alcohol). The reaction vessel was heated to 60ºC under a nitrogen blanket and proper agitation. Initiator A was then added to the reaction vessel followed by the addition of reductant A. After about 1 min, the monomer premix was metered into the reaction vessel over a period of 150 minutes. About 3 min after the start of monomer premix metering, reductant B was metered into the reaction vessel over a period of 180 minutes. After completion of reductant B feed, the temperature of the reaction vessel was maintained at 60ºC for 60 minutes. The reaction vessel was then cooled to 55ºC. A solution of 1.79 grams of 70 wt% TBHP and 0.58 grams of 30 wt% SDS in 25 grams of water was added to the reaction vessel. After 5 min, a solution of 1.05 grams of erythorbic acid and 0.1 grams of 30 wt%
SDS in 25 grams of water was added to the reaction vessel. The reaction vessel was maintained at 55ºC. After 30 min, a solution of 1.79 grams of 70 wt% TBHP and 0.3 grams of 30 wt% SDS in 25 grams of water was added to the reaction vessel. After 5 minutes, a solution of 1 gram of erythorbic acid and 0.17 grams of 30 wt% SDS in 25 grams of water was added to the reaction vessel. The reaction vessel was maintained at 55ºC for about 30 min. The reaction vessel was then cooled to room temperature and the contents filtered through a 100 micron cloth. A stable suspension was obtained containing about 30 wt% solids with particle size of 119 nm. The polymer had weight fractions of EA, n-BA, BEM, HEMA and PEO(15)GESPS22 of 35, 15, 5, 45 and 1% respectively.

**S.I.2 Characterization of Polymer Film Softness**

The two microgels were compared by the solvent swelling study. 8 g of latex suspension was carefully poured into a Petri dish and dried at 25 ºC with controlled humidity for over 48 hrs to make sure water was completely evaporated. The polymer film was carefully cute into a 19 𝑚𝑚 × 19 𝑚𝑚 square (thickness is 0.32 ± 0.02 𝑚𝑚). The fresh cut films were then transferred to the center of a clean Petri dish. 15 g of ethanol (>99%) was added and the changes of the diagonal length were recorded up to 3 hrs after ethanol addition. Five independent repeats were carried out. The film area was calculated and plotted in Fig. SI.1 as a function of swelling time. The surface crosslinked SAM polymer film swells faster and expands much more than the conventionally crosslinked SAM polymer film. The results indirectly support the proposal that a softer microgel in bulk was created through the novel surface crosslinking chemistry.
Fig. SI.1: SAM polymer film swelling in ethanol: film area as a function of swelling time (top); and photo taken during experiment (bottom)