

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 60°C 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 60°C for 60 minutes. The reaction vessel was then cooled to 55°C. 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 55°C. 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 30wt% SDS in 25 grams of water was added to the reaction vessel. The reaction vessel was maintained at 55°C 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 60°C 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 60°C for 60 minutes. The reaction vessel was then cooled to 55°C. 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 55°C. 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 30wt% SDS in 25 grams of water was added to the reaction vessel. The reaction vessel was maintained at 55°C 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 °C with controlled humidity for over 48 hrs to make sure water was completely evaporated. The polymer film was carefully cut into a $19\text{mm} \times 19\text{mm}$ square (thickness is $0.32 \pm 0.02\text{ mm}$). 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.

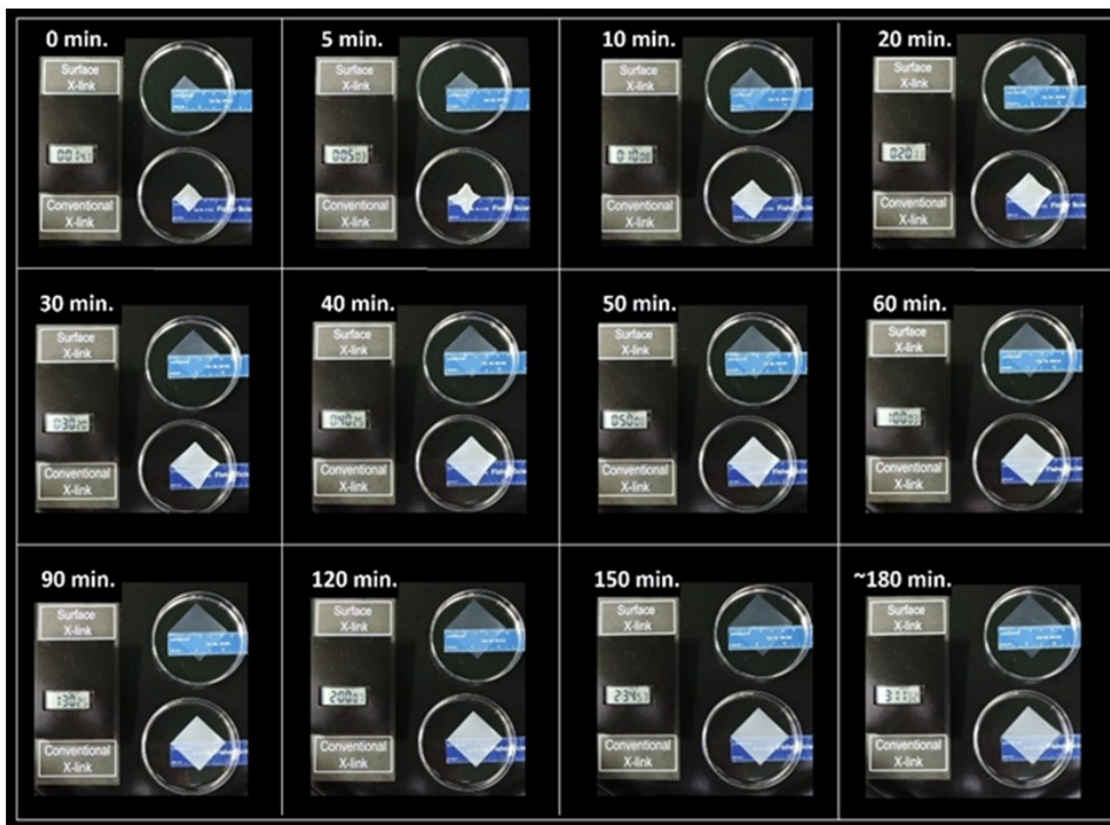
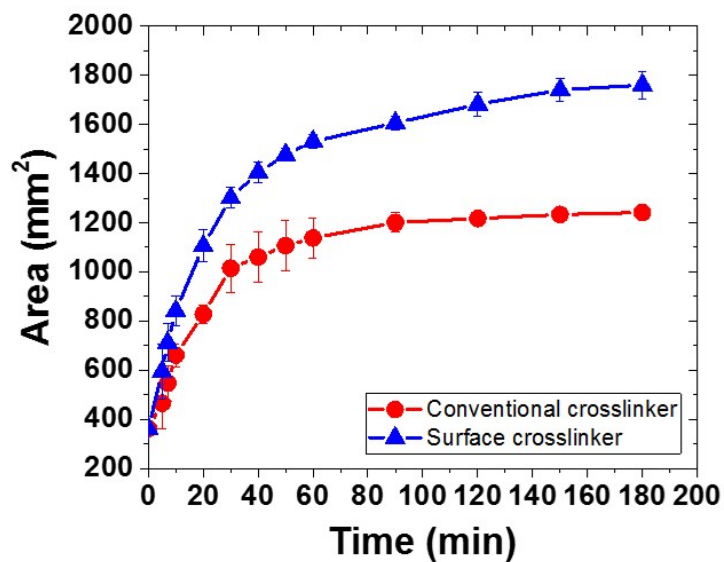


Fig. SI.1: SAM polymer film swelling in ethanol: film area as a function of swelling time (top); and photo taken during experiment (bottom)