Experimental Methods

Synthesis: Ludox Silica (Sigma Aldrich) was functionalized with sulfonic acid using 3-(trihydroxysilyl)-1-propanesulfonic acid (Gelest). To ensure dense surface coverages, the silane was added dropwise, in a large excess at pH 2. These conditions favor the anchoring reaction. The excess (un-tethered) silane was removed after completion of the reaction using dialysis (Snake skin Dialysis tubings, Pierce Scientific) against deionized water[13]. The functionality of the resultant sulfonic acid-derivatized SiO_2 nanoparticles was determined by titrating against a standard solution of NaOH. Nearly monodisperse Amine terminated PEG (Polymer source, Canada) was added stoichiometrically according to the functionality calculated using titration, and the linking reaction was allowed to proceed to completion over several days. Water was removed by evaporation in a convection oven and the product was dried extensively under vacuum and stored in the dried form at room temperature. The efficiency of the sulfonic acid/amine linking reaction was evaluated by dissolving the dried samples in chloroform and dialyzing them against pure chloroform for extended periods of time. Thermal gravimetric analysis (TGA) results in Fig. S1 reveal no change in the polymer weight fraction even after two days of dialysis, confirming that the linking reaction goes to completion under the synthesis conditions.

Rheology: Rheological measurements were performed using controlled strain (Rheometric Scientific/TA, ARES) and stress controlled (Paar Physica, MCR 301) rheometers outfitted with cone and plate fixtures. Prior to each experiment, the history of sample loading was removed by continuously shearing the materials at large strains, ie. well above the yield strain.

TEM images were obtained at 120 kV with TEI Technie T12 TEM/STEM by dissolving the sample in water, coating a few drops of the resultant suspension on a copper grid, and subsequently evaporating the solvent.

Supplementary Figures

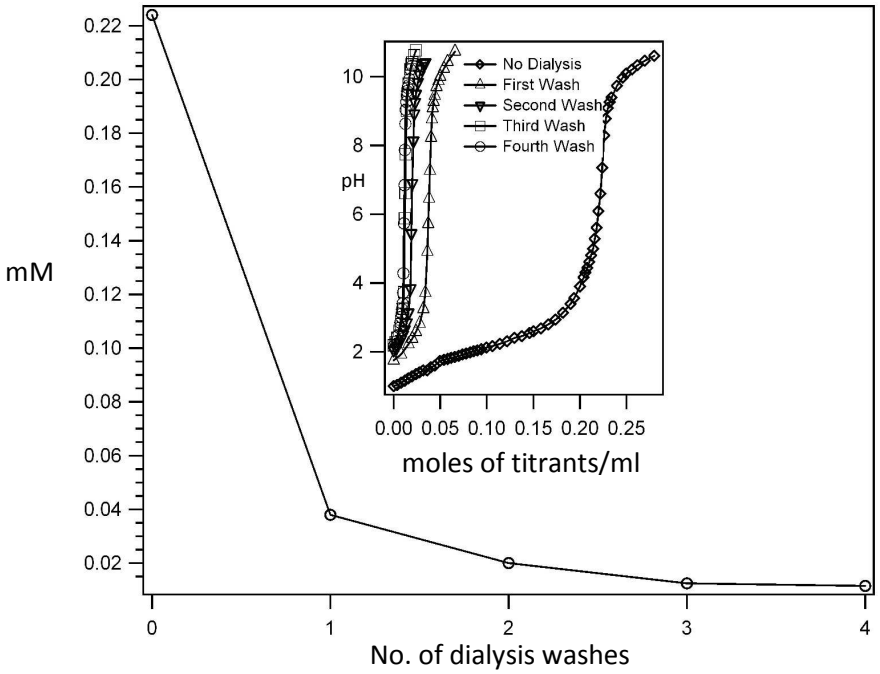

Fig. S1 Functionality of sulfonic acid functionalized particles as a function of the number of dialysis cycles. The functionality reaches a plateau value after 3 washes, confirming removal of excess silane. Inset shows the corresponding pH curves.

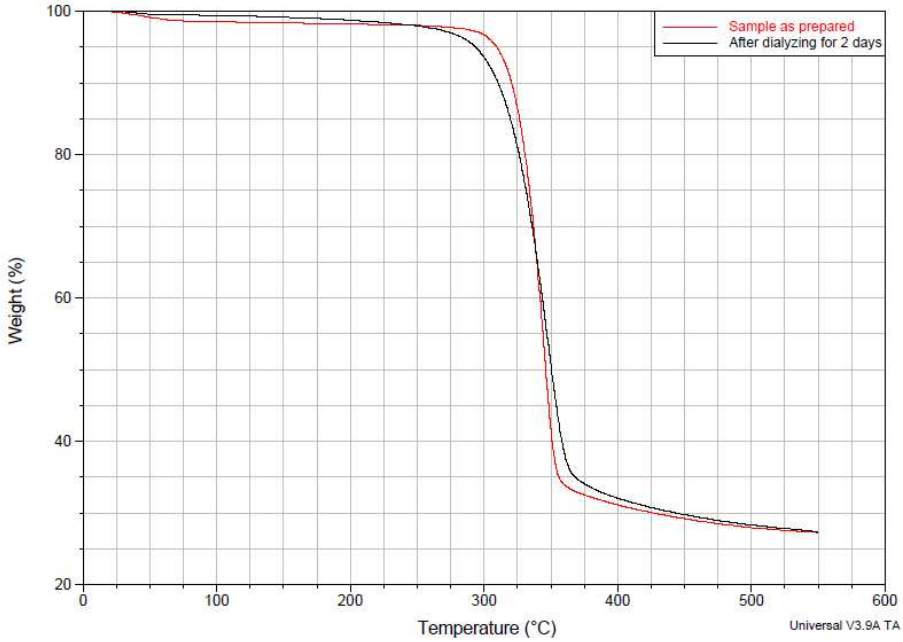

Fig. S2 TGA characterization of PEG(2k)-SiO_2 NIMs material before and after dialysis in chloroform for 2 days. Dialysis was performed using a membrane with a 10,000 g/mol molecular weight cut-off.

(a)

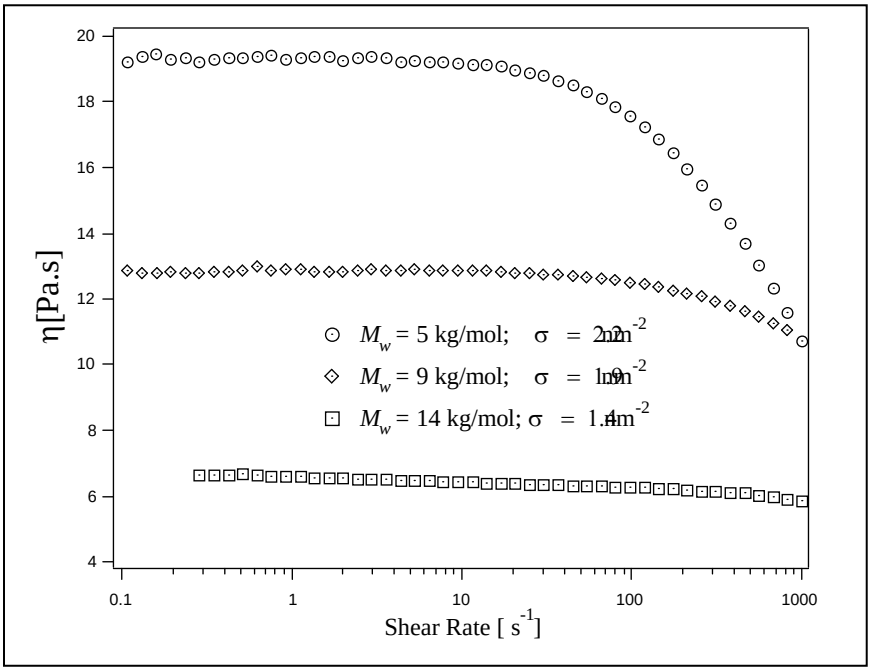

Fig. S3 Steady-state flow curve for several NIMs materials at 80 °C from controlled-stress rheology measurements.

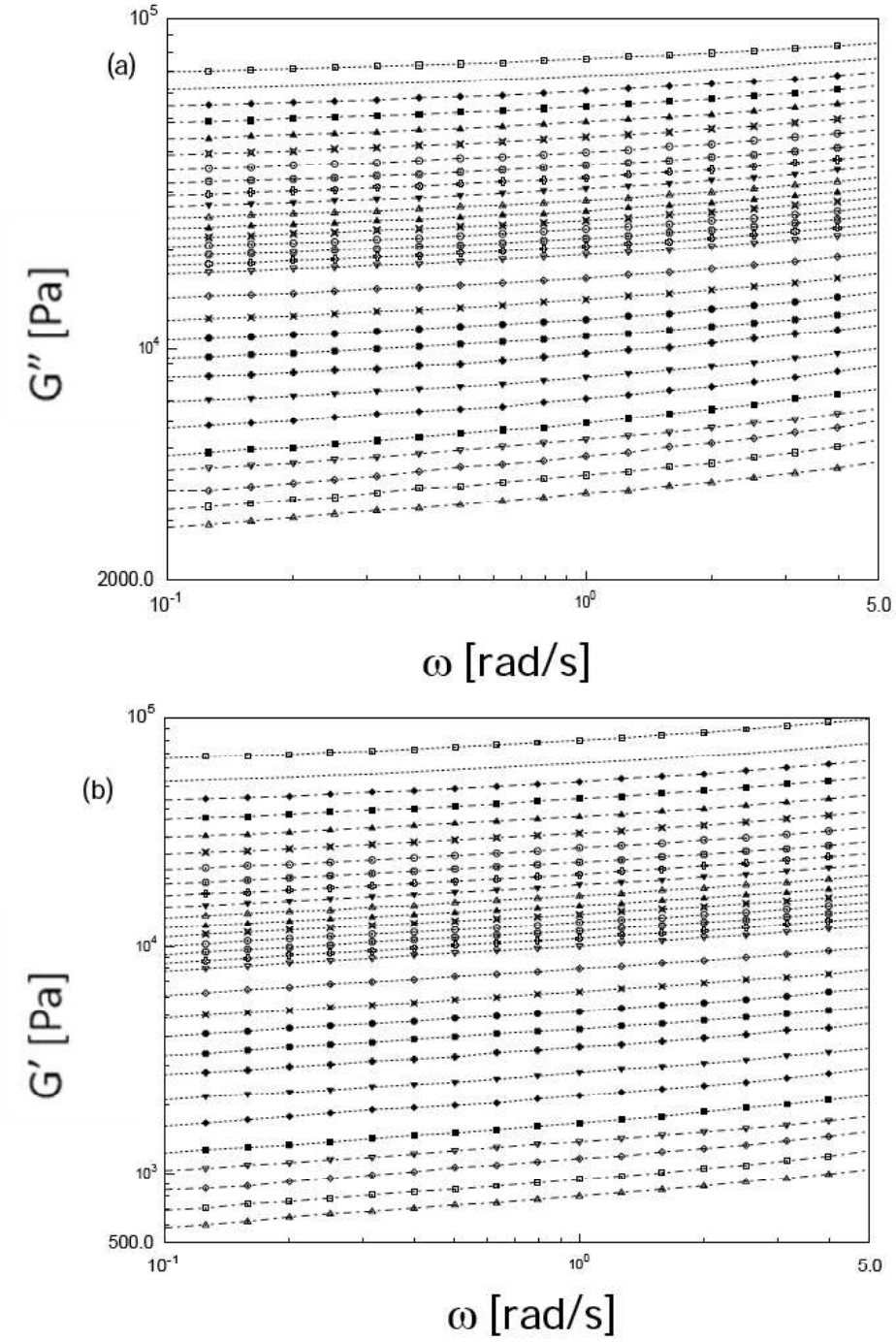

Fig. S4 (a) Loss modulus G'' and **(b)** storage modulus G' vs. frequency ($0.1\ s^{-1} < \omega < 5s^{-1}$) for NIMs with ϕ = 12.2 % at various discrete values of shear strain. Strain values are. from top to bottom: 0.15, .20, .25, .30, .35, .40, .45, .50, .55, .60, .65, .70, .75, .80, .85, .9, .95, 1, 1.2, 1.4, 1.6, 1.8, 2, 2.4, 2.8, 3.2, 3.6, 4, 4.5 and 5. All measurements were performed at a temperature of 70 °C.

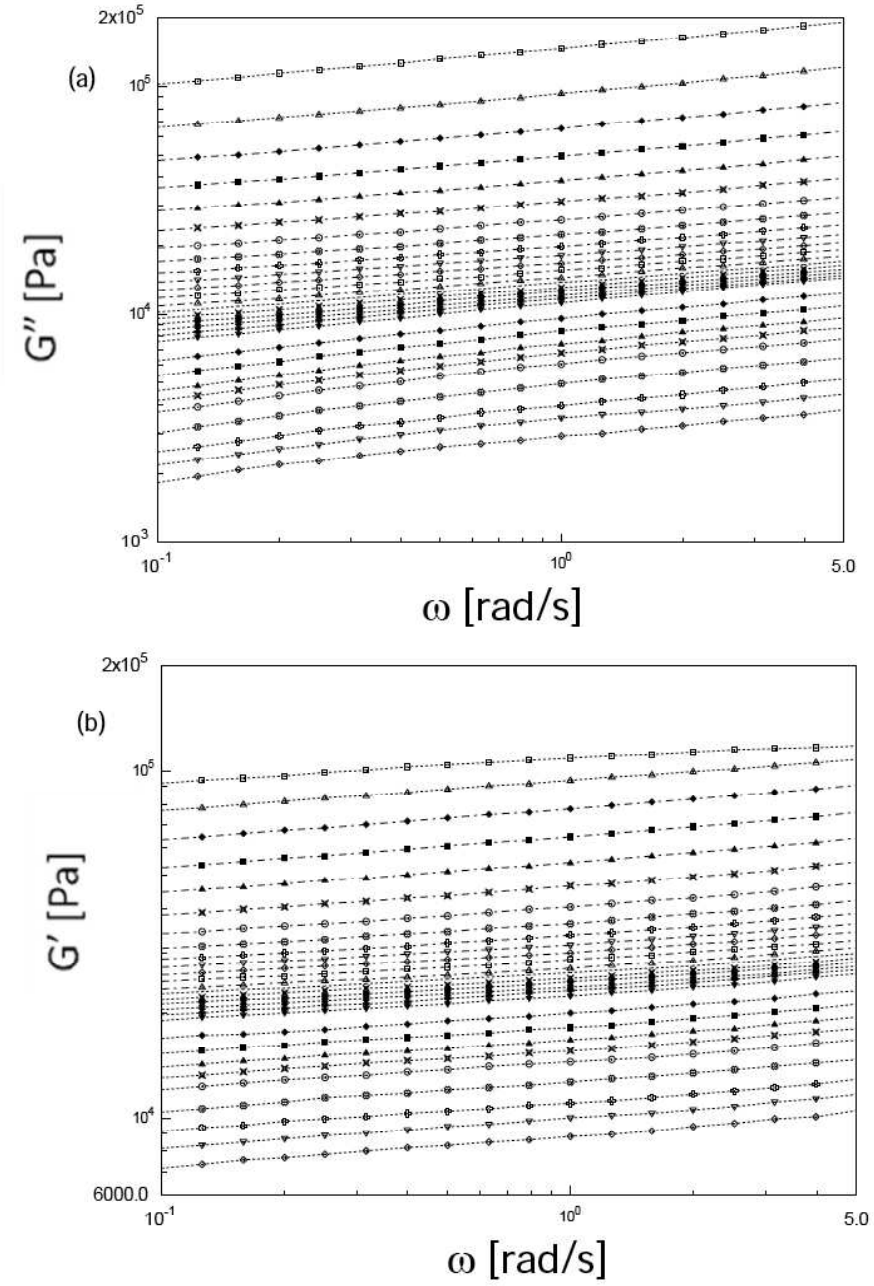

Fig. S5 (a) Loss modulus G'' and **(b)** storage modulus G' vs. frequency ($0.1\ s^{-1} < \omega < 5\ s^{-1}$) for NIMs with ϕ = 16.1 % at various discrete values of shear strain. Strain values are, from top to bottom: 0.10, .15, .20, .25, .30, .35, .40, .45, .50, .55, .60, .65, .70, .75, .80, .85, .9, .95, 1, 1.2, 1.4, 1.6, 1.8, 2, 2.4, 2.8, 3.2, 3.6 respectively from top to bottom. Measurements were taken at a temperature of 70 °C.