

Supporting Information

High-Frequency Mechanical Behavior of Pure Polymer-Grafted Nanoparticle Constructs

Connor R. Bilchak,¹ Yucheng Huang,² Brian C. Benicewicz,²
Christopher J Durning,¹ Sanat K. Kumar^{1*}

¹Department of Chemical Engineering, Columbia University, New York, NY, 10027

²Department of Chemistry & Biochemistry, University of South Carolina, Columbia, SC, 29201.

*Correspondence to: sk2794@columbia.edu

Materials and Methods: All chemicals were obtained from either Fisher or Acros and used as received unless otherwise specified. The RAFT agent 2-(dodecylthiocarbonothioylthio)propanoic acid (DoPAT) was purchased from Boron Molecular, Inc. 4-Cyanopentanoic acid dithiobenzoate (CPDB) was purchased from Strem Co. Ltd. Spherical silica nanoparticles (14 ± 4 nm diameter) in methyl ethyl ketone were obtained from Nissan Chemical. 3-Aminopropyldimethylethoxysilane was purchased from Gelest, Inc. and used as received. Methyl acrylate (99%, Acros) and methylmethacrylate (99%, Acros) were purified by filtration through an activated basic alumina column. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol twice before use.

Poly(methylacrylate) [PMA] grafted spherical silica particles were synthesized by surface initiated reversible addition-fragmentation chain transfer polymerization (SI-RAFT) technique by following our previous publications.^{27,37} Molecular weights and dispersities were determined using gel permeation chromatography (GPC) equipped with a Varian 290-LC pump, a Varian 390-LC refractive index detector, and three Styragel columns (HR1, HR3 and HR4, molecular weight range of 100-5000, 500-30000, and 5000-500000, respectively). Tetrahydrofuran (THF) was used as the eluent for GPC at 30°C and a flow rate of 1.0 mL/min. The GPC was calibrated with poly (methyl methacrylate) (PMMA) standards obtained from Polymer Laboratories.

The pure PMA and PMA GNPs were dissolved in a 95/5 mixture of tetrahydrofuran (THF) and chloroform at a concentration of 20-40mg/ml. .25wt% of the antioxidant Irganox 1010 (BASF, Germany) was added to all samples to minimize degradation effects. Solid samples were prepared by solvent casting the material into Teflon petri dishes at atmospheric conditions. The samples were then covered with aluminum foil and left to dry in a fume hood for 6 hours, or until the samples were solid enough to be handled with tweezers. The samples were then placed in a vacuum oven and allowed to dry for a further 6 hours under vacuum at room temperature. After drying, the samples were thermally annealed by heating to 70°C under vacuum for at least 24 hours.

Weight percent loadings are calculated via thermogravimetric analysis (TGA) using a Q500 TGA (TA Instruments, New Castle DE, USA). Approximately 5-10mg of dry, annealed sample were loaded into pre-weighed aluminum TGA pans and the samples were heated at a rate of 10.00°C/min in air to 700°C. NP core volume fractions were calculated from $\phi = \frac{\omega \rho_c}{\rho_{\text{SiO}_2}}$ where ρ_{SiO_2} and ρ_c are the density of bare silica nanoparticles and the PMA composites, respectively.

Small Angle X-Ray (SAXS) experiments on bulk samples were conducted on a SAXSLab BioNordic Instrument with a Cu-K α source ($\lambda=1.54\text{\AA}$). Samples for SAXS were prepared by drying ~50-60mg of sample mass from a solution of 95/5 THF/Chloroform in atmospheric conditions, and then annealing in the manner described above. The samples were then molded into cylindrical discs (~ 8mm diameter, 1mm thickness) using a Hot Press (Carver, Wabash, IN) and the thicknesses were measured to the nearest 1 μm . The solid samples were then adhered to the sample holder using double-sided tape, taking care to not place the tape in the path of the beam. Data were collected at four different detector positions and stitched together to create master curves, providing an available q-range from $.005\text{\AA}^{-1}$ to $\sim 2\text{\AA}^{-1}$. Data at each detector position was collected for at least 3 minutes. The 2-dimensional SAXS patterns were azimuthally averaged to produce 1-dimensional scattering curves (a mask was applied to the X-ray beam stop and spaces between detectors). The scattering of the empty beam (i.e., the scattering measured by the instrument without any sample in the beam) was subtracted from the data file to remove the contribution from the beam. Fits to the data were performed using Sasfit software. Each SAXS curve is fit to a single scattering contribution that consists of a polydisperse sphere form factor (to account for the shape of the NP cores; average core radius $\bar{r}=6.8\text{nm}$, dispersity breadth $\beta=.29$) and a Perkus-Yevick hard sphere structure factor (to model the average spacing between the NPs).

Small-amplitude oscillatory shear (SAOS) measurements in the linear flow regime were conducted on neat PMA ($M_n=135\text{kDa}$) over a wide range of temperatures. Data were collected using an AR2000ex rheometer (T.A. Instruments, New Castle, DE). Samples were dried into disks 4mm in diameter and $\approx 1\text{mm}$ thick. Frequency sweeps between

0.1 and 100Hz were collected at the various temperatures and a master curve was generated using Time-Temperature Superposition.

Quartz Crystal Microbalance with Dissipation (QCM-D): AT-cut quartz crystal sensors pre-coated with gold electrodes (14mm diameter, .37mm thickness, fundamental frequency $\approx 5\text{MHz}$) were purchased from Biolin Scientific (Paramus, NJ). Before use, the sensors were cleaned using basic piranha solution (5:1:1 by volume mixture of deionized water, ammonium hydroxide, and hydrogen peroxide) at 70°C for 5 minutes. The sensors were removed from the piranha, immediately washed with deionized water and methanol three times, and then placed in a UV/Ozone chamber for 15 minutes to grow a surface oxide layer. The sensors were individually loaded into the QCM-D flow cell and were exposed to a 100sccm/min flow rate of dry N_2 —this was done to be consistent with gas transport experiments on the materials. The resonant frequency and dissipation at the fundamental frequency and the first six harmonic overtones (f_n and D_n where n is the overtone number) were then collected at $T=35^\circ\text{C}$ (again, to be consistent with the gas transport experiments), essentially “taring” the sensor for use as a microbalance. GNP films were deposited on the sensors by spin-casting concentrated (60-80mg/ml) solutions of GNPs in THF at 800-100rpm for 60 seconds, ensuring that the sensor surface was completely covered before spinning. After 1-2 hours of drying at ambient conditions, the films were annealed under vacuum at 70°C for at least 24 hours. Sensors were then individually reloaded into the QCM-D flow cell, and the f_n ’s and D_n ’s for the coated sensor were measured (again under 100sccm/min dry N_2 gas and at 35°C). Film thicknesses were measured with spectroscopic ellipsometry (J.A., Woollam, α -SE) using the Cauchy model. In all cases the film thicknesses were $3-5 \pm 0.05\mu\text{m}$, which is in the film thickness range for accurate QCM-D rheology measurements as recommended by Shull et al for soft materials such as PMA (for reference, G' of pure PMA as measured by rheology on bulk material is $\sim 1\text{ GPa}$).³² The data for the bare sensor and the dry film were then “stitched” together (Figure S1) for modelling.

A number of QCM-D data fit protocols have been developed to relate the viscoelastic properties of the film to the sensor oscillatory response, many of which make an

inherent assumption regarding the viscoelastic property dependence on frequency. We use Johannsmans' equations for the perturbation of thin viscoelastic films at each overtone to describe the complex frequency shift Δf^* relative to the fundamental f_F as:^{S1}

$$\frac{\Delta f^*}{f_F} = -\frac{2f_n}{Z_q} m_f \left[1 + \frac{1}{3} \left(J_f \frac{Z_q^2}{\rho_f} - 1 \right) \left(\frac{2f_n m_f}{Z_q} \pi n \right)^2 \right] \quad (S1)$$

$$\Delta \Gamma = \frac{8}{3\rho_f Z_q} f_f^4 m_f^3 n^3 \pi^2 J'' \quad (S2)$$

Where Z_q is the acoustic impedance of quartz, m_f is the film mass, ρ_f is the density of the film, $\Delta \Gamma$ is the change in bandwidth (related to the dissipation by $D_n = 2\Gamma_n/f_n$), and f_n is the frequency shift at overtone n . This equation depends on three quantities for each overtone—the real and imaginary parts of the complex compliance, and the film mass. We approximate the film mass (constant for all overtones) using the thickness measured using ellipsometry and the known area of the film, which then allows us to estimate G' and G'' at each overtone. This equation is typically fit with at least two overtones of data to accurately determine G' and G'' (typically the 3rd and 5th overtones are used; results for fitting the data with the 5th and 7th overtones are shown below). Fits to this data are referred to as “J-Fit”. We also employ the Voight-Kelvin Model as part of Q-Tools Software (Q-Sense, Biolin Scientific), which predicts the frequency and dissipation changes and then recursively fits G' and G'' to minimize the mean square error. This fitting requires frequency and dissipation data to be measured for a minimum of two overtones. Fits to this data are referred to as “EVK-Fit”.

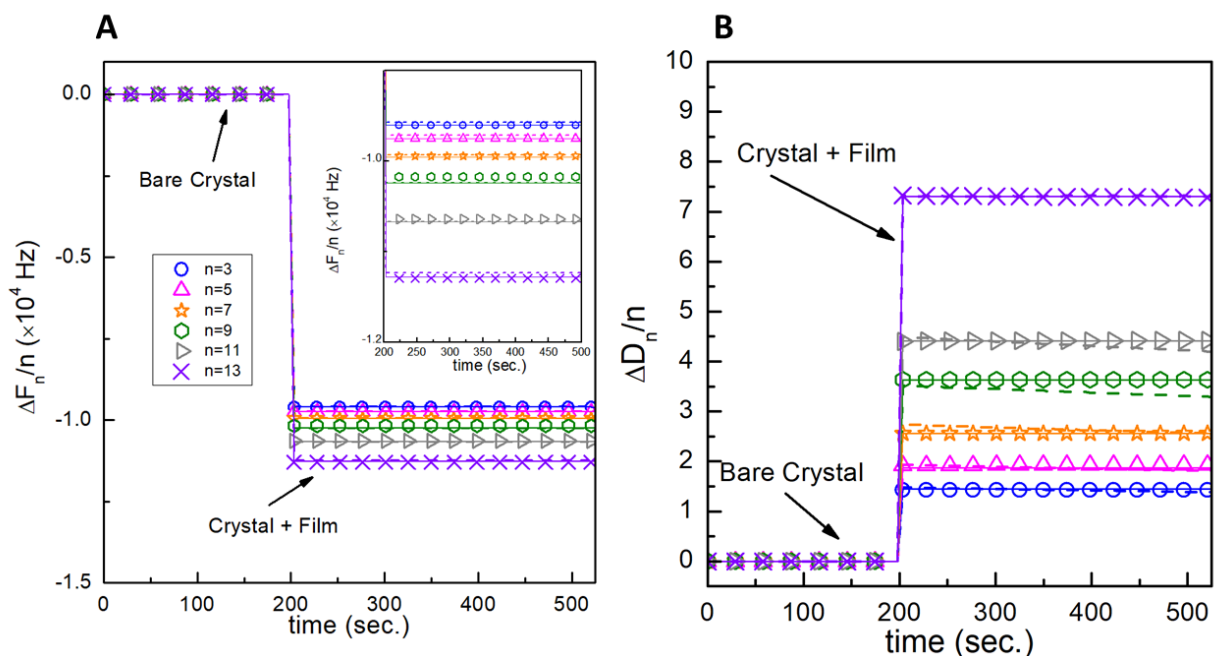


Figure S1: Measured and modeled shifts in (A) resonant frequency and (B) energy dissipation terms for PMA-grafted NPs ($\sigma=0.47$ chains/nm², $M_n=100$ kDa) with thickness $3.51\pm0.04\mu\text{m}$. (inset) resonant frequency shifts of the various overtones across a smaller frequency window to highlight the spread in the frequency data as a function of n . The systematic increase in Δf_n with increasing n is clearly visible on this smaller scale. In all graphs, the points represent the collected data. The solid lines represent the time-resolved J-Fits, and the dashed lines are the time-resolved EVK-Fits; both agree with the data well, with the J-Fits having slightly better agreement. The portions of the graph that correspond to the bare crystal measurement and the film measurement have been highlighted. For clarity, only every 50th data point is shown. These data are representative of the shifts in f_n and D_n seen for all GNPs.

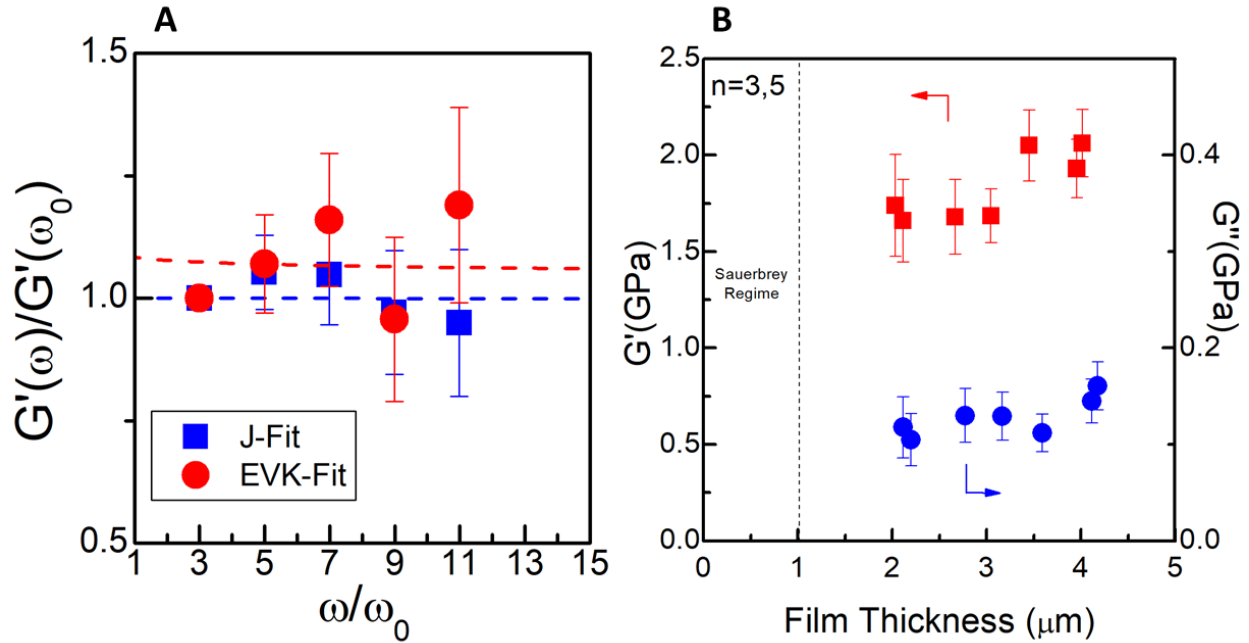


Figure S2: (A) shear modulus dependence on the overtone pair used for the data analysis versus the sensors resonant frequency ω compared to the reference frequency ω_0 ($\omega/\omega_0=n$). The point at $n=3$ is the 3rd/5th overtones, at $n=5$ is the 5th/7th overtones, etc.. The moduli are divided by the modulus extracted using the 3rd/5th overtone data (i.e., $G'/G'_0=1$). Results for the two different fit methods are shown. Each are individually fit to a power law of the form $\frac{G'(\omega)}{G'(\omega_0)} = \left(\frac{\omega}{\omega_0}\right)^\alpha$ to extract the dependence of the shear modulus on frequency. In both cases, $\alpha \approx 0$ indicating that the G' of PMA is relatively constant at such high frequencies. Similar results are found for the GNPs. (B). The thickness dependence of G' and G'' of PMA extracted using the 3rd/5th overtone data. A single sensor was spin-cast multiple times after data acquisition to create a successively thicker film. Films with thickness $< \approx 1\mu\text{m}$ are expected to only exhibit an inertial response (i.e., the QCM-D is insensitive to the viscoelastic properties of the film) and are in the Sauerbrey Regime.²⁷

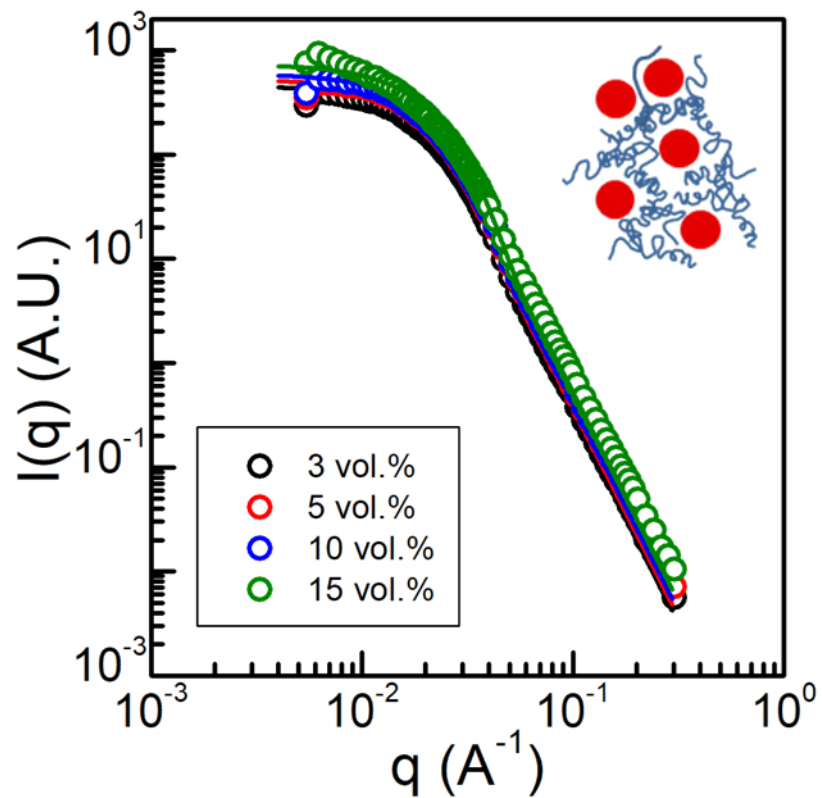


Figure S3: 1-D SAXS curves of ungrafted silica NPs in PMA ($M_n=132\text{kDa}$). The points are the experimental data, while the solid lines are fits. For clarity, only every 5th data point is shown. The fits to the data are for a polydisperse sphere form factor with parameters identical to those used to model the GNPs (average core radius of 6.8 nm, dispersity of .29).

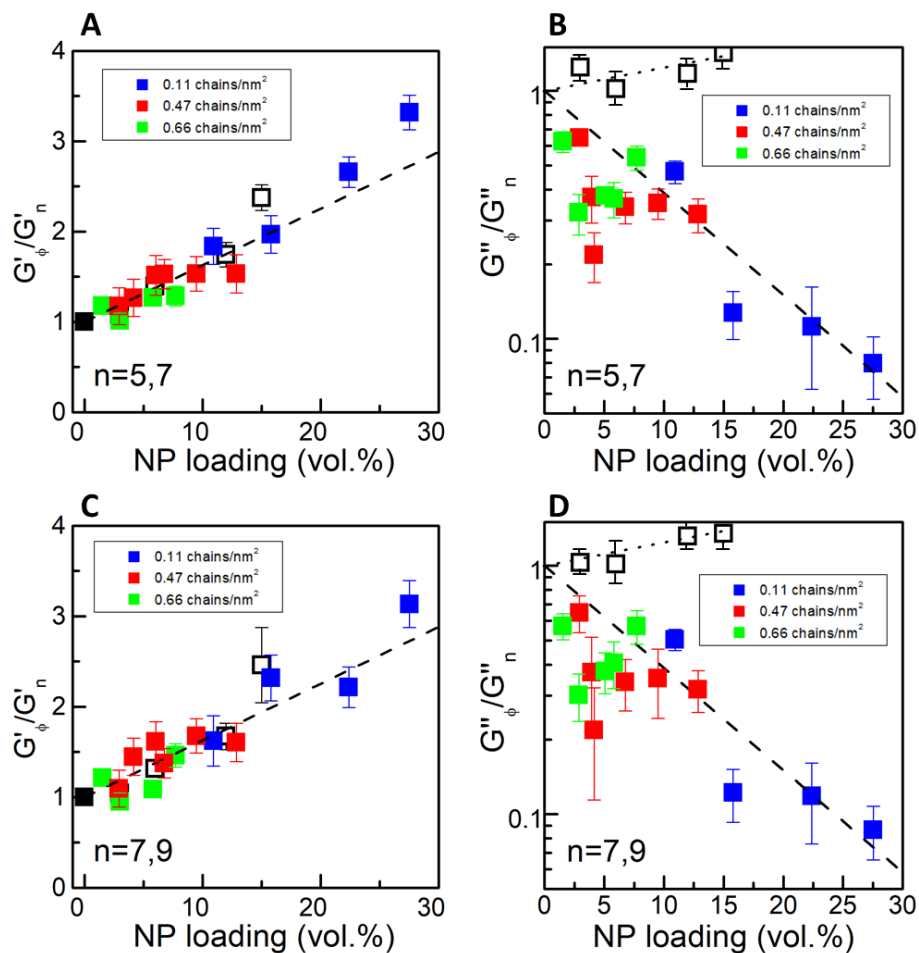


Figure S4: Shear Storage (A,C) and Shear Loss (B,D) Moduli of the GNPs relative to that of pure PMA where the data are fit using a different pair of overtones; data in (A) and (B) are for the 5th and 7th overtones, and data in (C) and (D) are for the 7th and 9th overtones. Other higher order overtone pairs are possible (e.g., 9th and 11th) however these overtones become overdamped for film with thicknesses $>\approx 3.5\mu\text{m}$ and are therefore difficult to provide for each GNP film. We report the highest-order pair for which we have data on all materials. The systematic increase in the size of the error bars is also a result of the higher-order overtones being close to overdamped. Data at both overtone pairs are qualitatively similar to that of the 3rd and 5th overtone pair discussed in the main text.

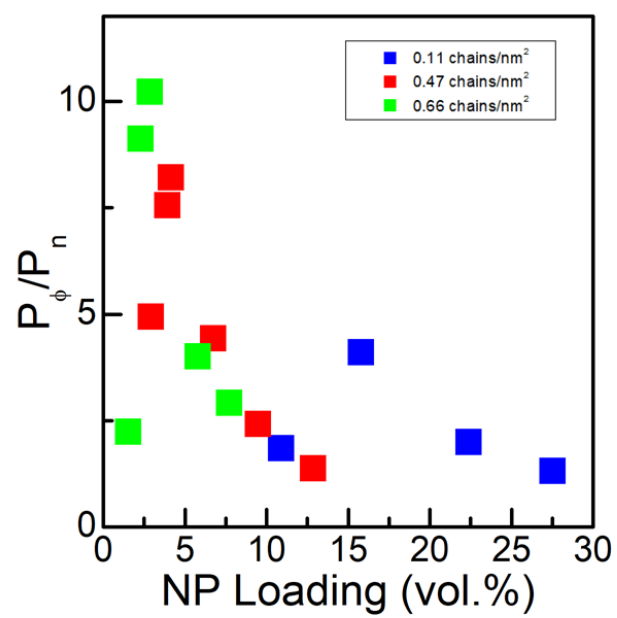


Figure S5: Enhancement of CO₂ permeability in the GNPs as a function of NP loading (in volume percent).

Table S1: Molecular weights (M_n), dispersity indices (DI), and NP loadings of the GNPs used in this work

$\sigma=0.11$ chains/nm ²		
Graft M_n (kDa)	DI	NP loading (vol. %)
41	1.20	27.6
54	1.19	22.4
83	1.16	15.8
127	1.18	10.8
$\sigma=0.47$ chains/nm ²		
Graft M_n (kDa)	DI	NP loading (vol. %)
30	1.14	13.8
53	1.15	10.4
80	1.16	7.7
92	1.13	5.2
100	1.22	4.9
132	1.22	3.9
$\sigma=0.66$ chains/nm ²		
Graft M_n (kDa)	DI	NP loading (vol. %)
31	1.11	7.8
64	1.15	5.3
82	1.11	2.9
108	1.24	2.3
127	1.32	1.5

References

(S1) Johannsmann, D. Viscoelastic, mechanical, and dielectric measurements on complex samples with the quartz crystal microbalance. *Physical Chemistry Chemical Physics*, 10(31), 4516–4534 (2008)