# Supporting Information

*for*

**Controlling the Thermomechanical Behavior of Nanoparticle/Polymer Films**

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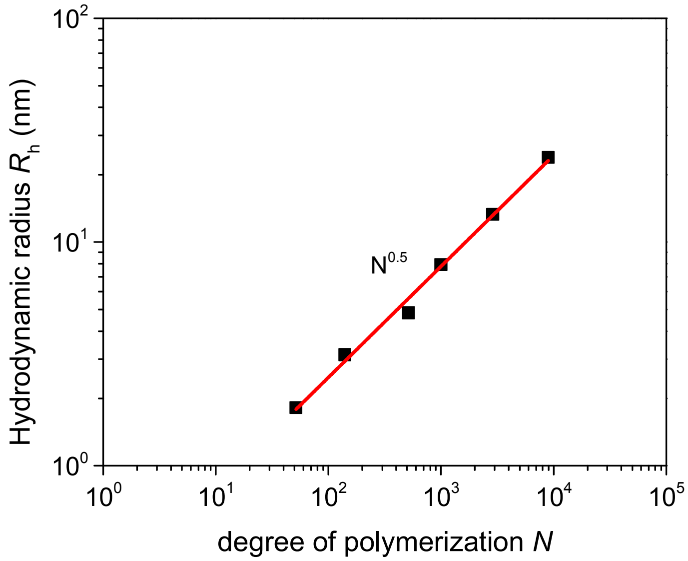


**Figure S1.** Variation of hydrodynamic radius ($R_h$) with the degree of polymerization ($N$) for a dilute P2VP solution in MEK. The scaling of $R_h$ vs. $N$ implies MEK is a θ-like solvent for P2VP.

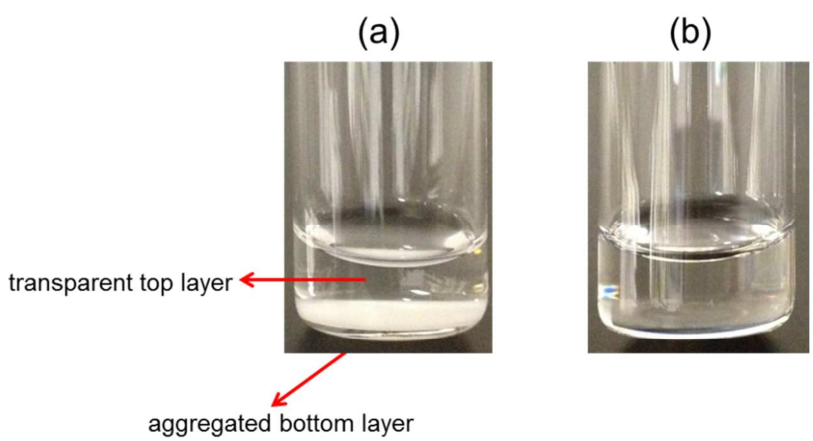


**Figure S2.** Long-term phase behavior in composite solutions in (a) MEK or (b) PYR. In MEK, there is a silica aggregate layer (as indicated by the arrow) on the bottom of the glass vial after several weeks while the solution in PYR is still stable and transparent after several months.

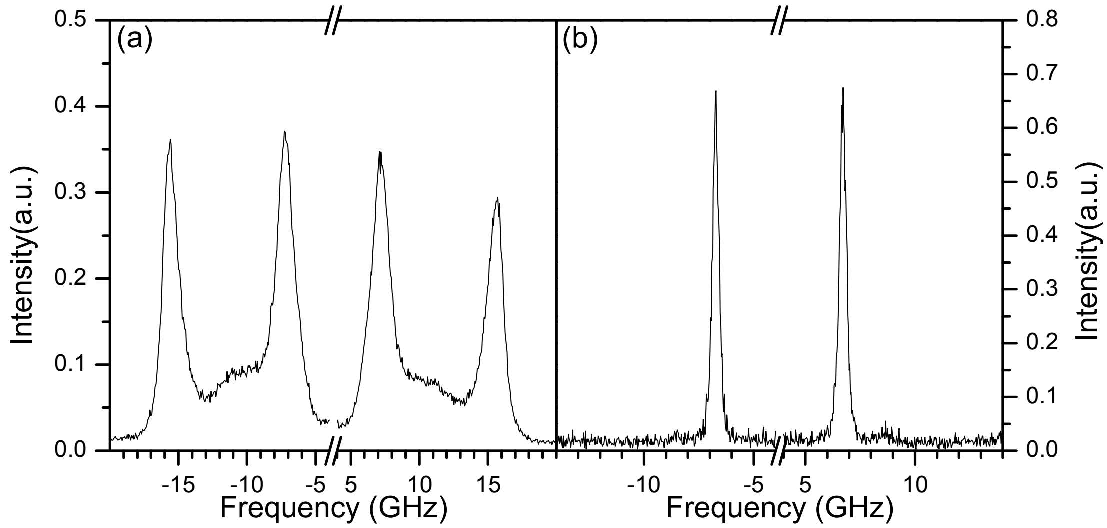


**Figure S3.** VV-polarized BLS spectra of MEK-10%-AA for the in-plane phonon propagation at a scattering vector of $q$ = 0.0167nm$^{-1}$ with a (a) rough surface, directly cast from a regular petri dish and (b) flat surface, when the sample is re-molded in between two flat glass slides.

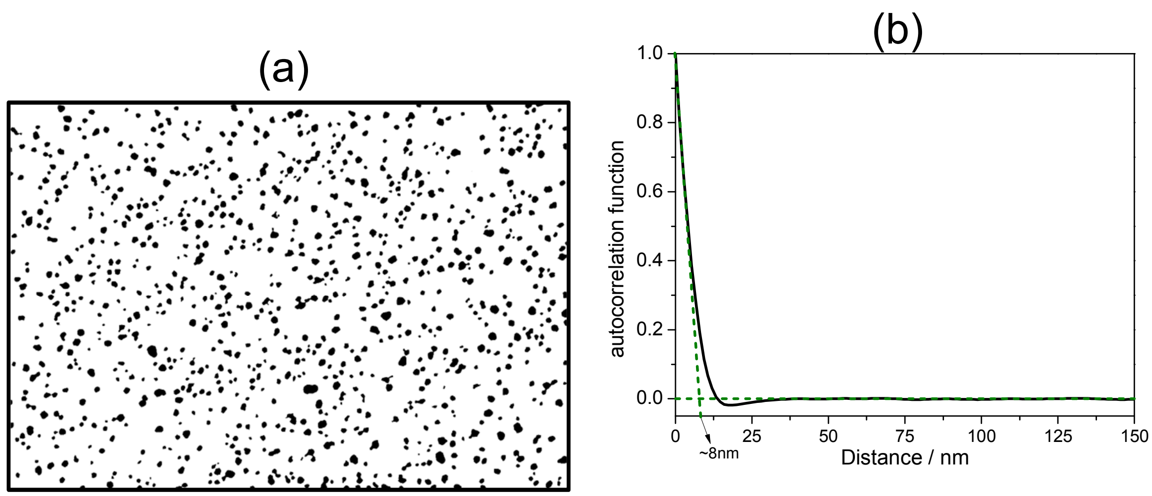


**Figure S4.** (a) A binary image for MEK-10%-As cast, where the black dots represent silica NPs while the white background is occupied by the P2VP matrix. (b) Autocorrelation function (C(r)) with respect to distance obtained from ImageJ analysis for the sample of MEK-10%-As cast. In order to examine the particle dispersion and particle-particle correlation from the TEM images, we first convert the micrograph into a binary format (shown in (a)), which comprises of only black (NP particles) and white (polymer matrix) pixels. Based on that, (i) we estimate the size of these "2-D" particles (obtained in TEM from a 2-D projection of the real 3-D particles) based on their areas and then get an average diameter of ~12.4nm; (ii) we calculate the autocorrelation of the black pixels in the image as a function of distance. The negative correlation can indicate a particle-particle repulsion within that range of distance.

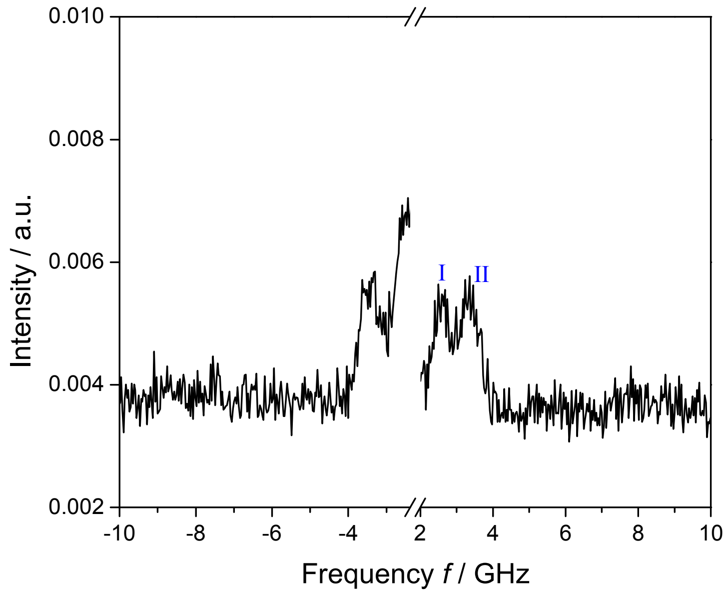


**Figure S5.** VH-polarized BLS spectra of MEK-45%-As cast for the in-plane phonon propagation at a scattering vector of $q = 0.0118\ nm^{-1}$.

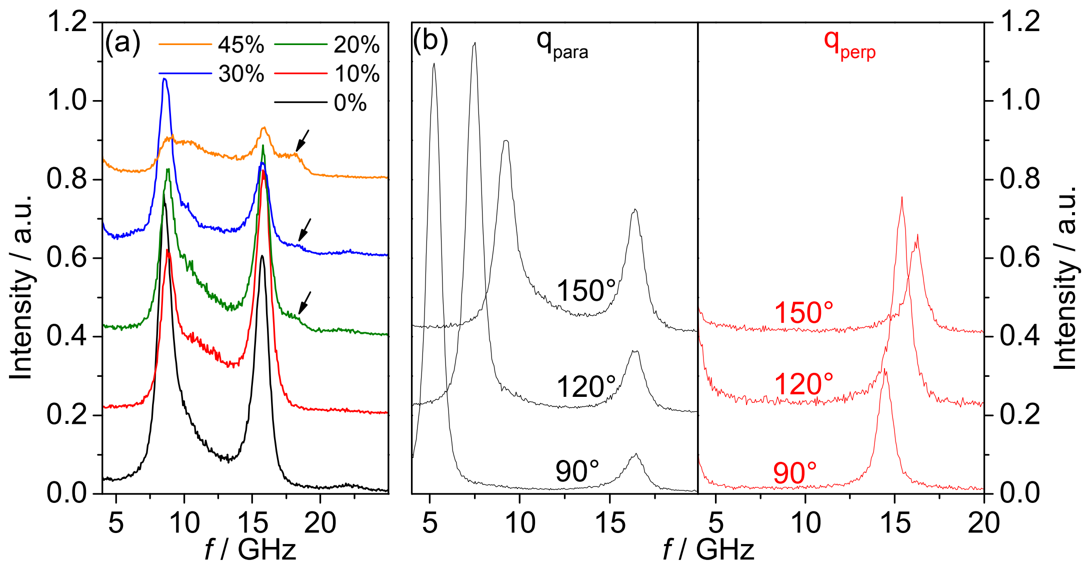


**Figure S6.** (a) VV-polarized BLS spectra of MEK-As cast samples with different particle loadings for the in-plane phonon propagation at a scattering vector of $q = 0.0205\ nm^{-1}$. The black arrows indicate the appearance of the back-scattering peaks originating from the newly-found acoustic phonon. (b) VV-polarized BLS spectra of PYR-45%-As cast for both in-plane (black, left panel) and out-of-plane (red, right panel) phonon propagation at three different scattering vectors as indicated inside the plot.

**Table S1.** Surface-to-surface inter-particle distance as a function of silica loading.

| | | | | |
|---|---|---|---|---|
| silica wt% | 0.1 | 0.2 | 0.3 | 0.45 |
| silica vol.% | 0.053 | 0.111 | 0.176 | 0.290 |
| Inter-particle distance (nm)[a] | 18.16 | 11.07 | 7.49 | 4.20 |

[a] The inter-particle separation is given by $d_{NP}\left([\phi_{max}/\phi]^{1/3} - 1\right)$, where $\phi_{max} = 0.638$, is the maximum fraction of spheres for random dense packing, $\phi$ is the NP volume fraction and $d_{NP}$ is the diameter of the nanofiller.