Process-Dependent Hypersonic Phonon Dispersion of Brush Particle Metamaterials

Qiqi Li,[a d] Iyad Ramdane,[b] Jirameth Tarnsangpradit,[c] Pascal Rembert,[b] Rebecca Sainidou,[b] Yu Cang,[d] Krzysztof Matyjaszewski,[e f] Michael R Bockstaller,[c] Bartłomiej Graczykowski,[f] and George Fytas [*a g h]

a. Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany.
b. Laboratoire Ondes et Milieux Complexes UMR CNRS 6294, UNIHAVRE Normandie University, 75 rue Bellot, Le Havre F-76600, France.
c. Department of Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, Pennsylvania 15213, United States.
d. School of Aerospace Engineering and Applied Mechanics Tongji University Zhangwu Road 100, Shanghai 200092, China.
e. Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave., Pittsburgh, Pennsylvania 15213, United States.
f. Department of Molecular Physics, Faculty of Chemistry, Lodz University of Technology, Żeromskiego 116,90-924, Łódź, Poland
g. Faculty of Physics, Adam Mickiewicz University Uniwersytetu Poznanskiego 2, Poznan 61-614, Poland.
h. Institute of Electronic Structure and Laser, 71110 Heraklion, Greece.

Supporting Information

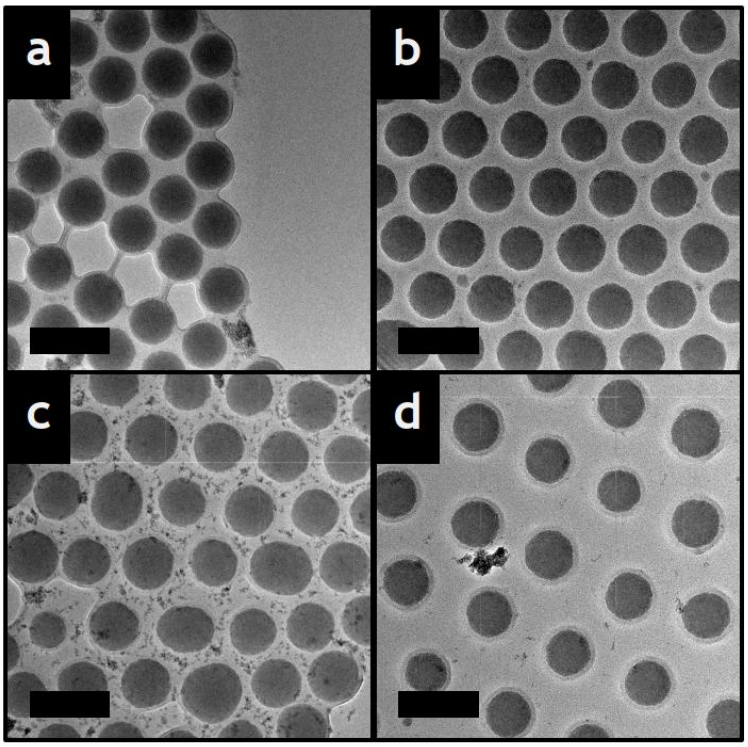

Fig. S1. Transmission electron microscope (TEM) images of two of the SiO_2-PMMA samples (N=553 and N=1244) in **(c)** and **(d)**; the other two are for **(a)** N=254 and **(b)** N=337. Scale bars are 200 nm. TEM was utilized to estimate the spacing *d* and polymer thickness *h* in 4th and 6th column of Table 1, respectively.

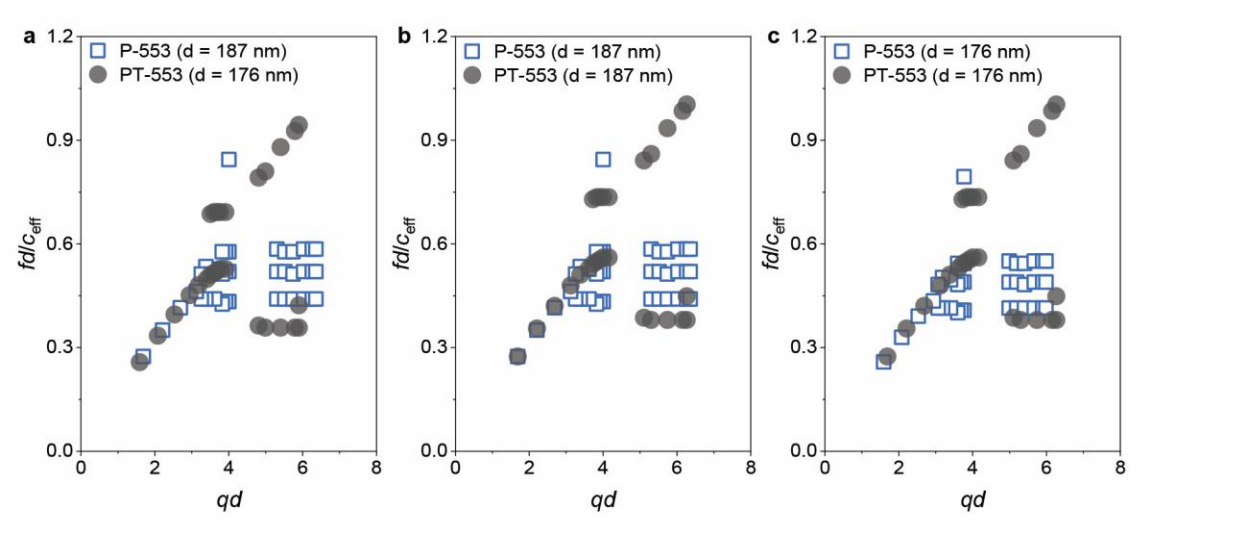

Fig. S2: Reduced band diagram fd/c_{eff} vs qd for P-553 (open squares) and PT-553 (solid symbols) using c_{eff} =2590 m/s and 3000 m/s, respectively. (**a**) d = 187 nm for the P-553 and d =176 nm for PT-533. **(b**) d = 187 nm and (**c**) d = 176 nm for both systems. A good superposition of the acoustic branch is obtained in all cases, indicating that the long-wavelength regime is insensitive to the choice of diameter and mainly determined by the experimental c_{eff}. For PT-553, a band gap appears at fd/c_{eff}≈0.65 and qd ≈ 3.8. In contrast, superposition of the flat modes is achieved only when the TLM diameter d=176 nm is assumed for both films, highlighting the sensitivity of the short-wavelength regime to particle size and local structural differences related to metastability. Due to the later, it is conceivable that the sound velocity in the cluster of PGN's is lower than c_{eff} rendering the superposition of the band diagram incomplete.

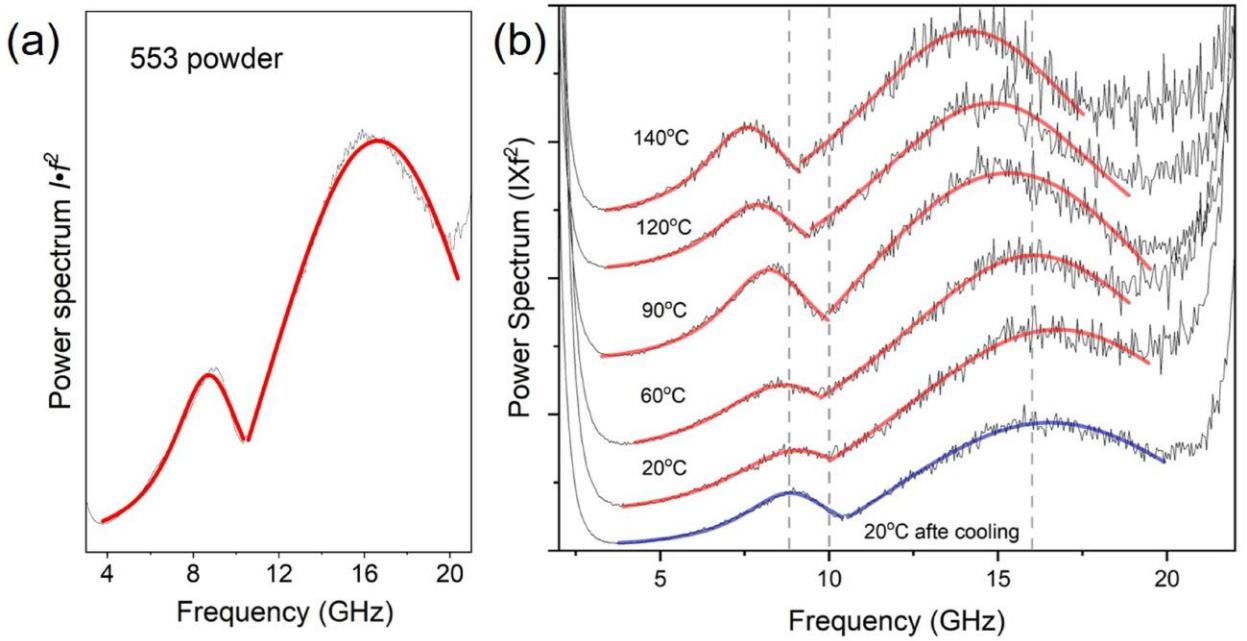

Fig. S3. Power vibration spectrum for P533 powder at **(a)** 20 °C and **(b)** different temperatures below and above T_g (~110 °C) of PMMA. The low-frequency modes in Figure 2b yielding to a broad peak at ~8.7 GHz in the power spectrum in **(a)** are attributed to inter-PGN interactions. The spectra of solvent-cast films in **(b)** remain essentially unchanged upon annealing up to 140 °C (above T_g) and after cooling, indicating robust and reversible PGN interactions associated with trapped, metastable configurations.

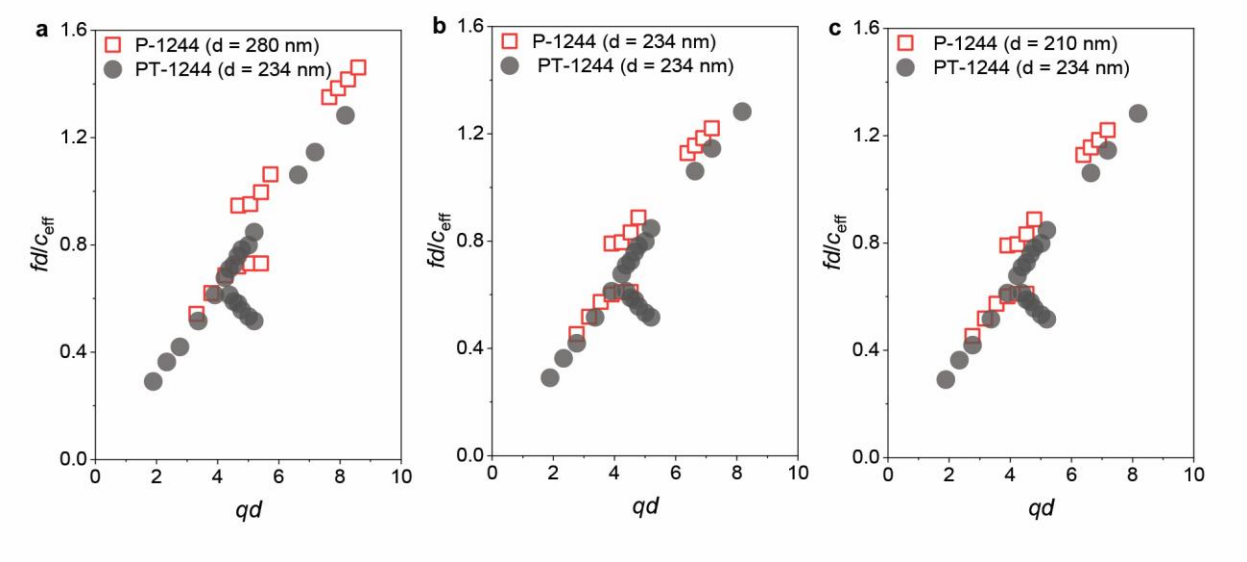

Fig. S4. Reduced band diagram fd/c_{eff} vs qd for SiO_2-PMMA-1244 drop casted from THF (P-1244) and toluene (PT-1244) solutions. (**a**) For PT-1244, d= 234 nm and for P-1244, d=280 nm (Table 1). (**b**) For both PT-1244 and P-1244, d=234 nm. (**c**) For PT-1244, d=234 nm and for P-1244, d=210 nm. Using d=280 or 234 nm for P-1244 fails to reproduce the narrow Bragg gap of PT-1244 at $fd/c_{eff}\approx0.65$, $qd\approx4$ and the gap is shifted to higher reduced frequency values. A satisfactory superposition is obtained only when a smaller effective local diameter ($d_{loc}\approx210$ nm) is assumed for P-1244, consistent with the TLM prediction.

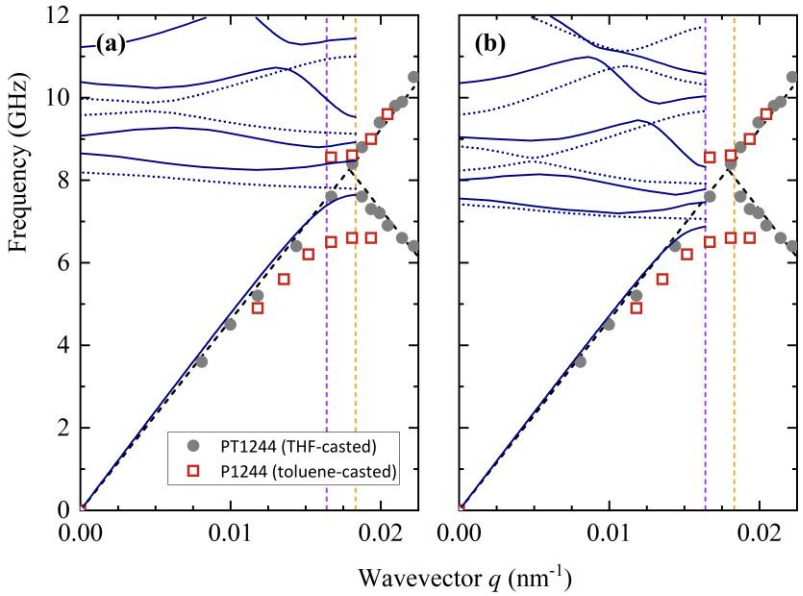

Fig. S5. Calculated band structure assuming core-to-core (first-neighbour) distance (**a**) d=210 nm (TLM value) and (**b**) d=234 nm (TEM value), along [111] direction of *fcc* lattice, assuming PBC for silica particles embedded in PMMA host, compared to the experimental data for both PT-1244 and P-1244 films. Coloured (orange and violet) vertical dashed lines indicate the corresponding BZ edges. Blue solid/dotted lines: longitudinal/deaf (inactive) modes.