

# Supporting Information

## Using Unentangled Oligomers to Toughen Materials

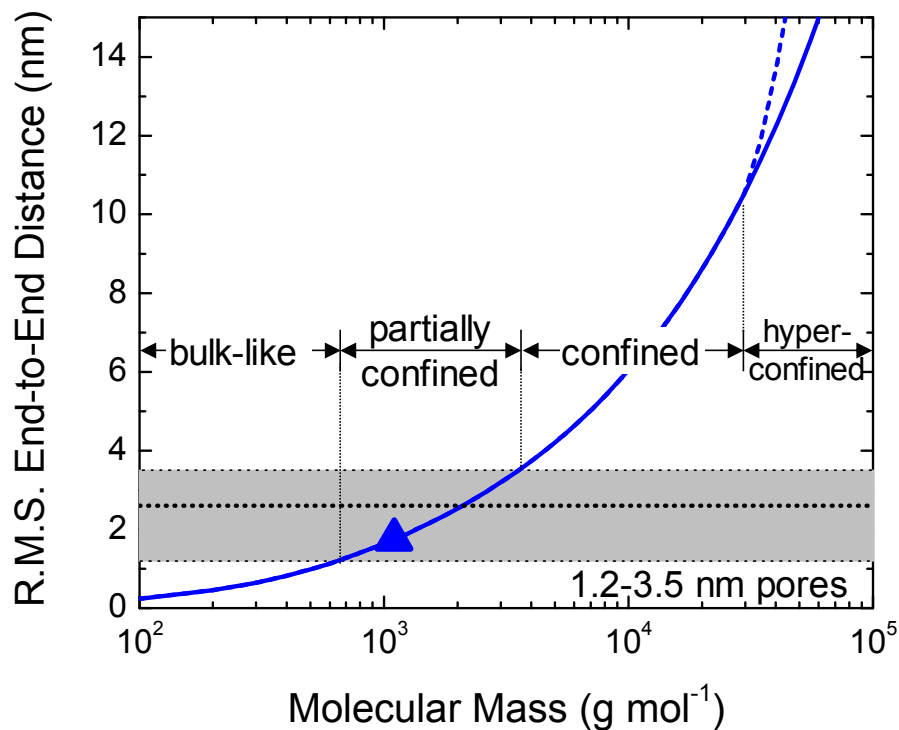
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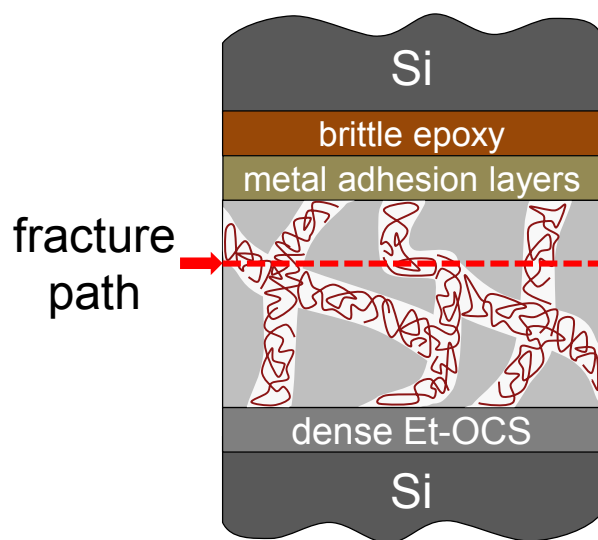
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**Figure S1.** PMMA with  $M_w = 1100 \text{ g mol}^{-1}$  has an r.m.s. end-to-end distance  $R_{ee}$  of 1.7 nm, meaning that only some chains meet the confinement condition of  $R_{ee} > d_{\text{pore}}$ . For a nanoporous matrix with a pore diameters between  $d_{\text{pore,min}} = 1.2 \text{ nm}$  and  $d_{\text{pore,max}} = 3.5 \text{ nm}$ , PMMA chains with  $M_w \leq 700 \text{ g mol}^{-1}$  are bulk-like in character (root mean square end-to-end distance  $R_{ee} \leq d_{\text{pore,min}}$ ). PMMA molecules with  $700 \text{ g mol}^{-1} < M_w < 3700 \text{ g mol}^{-1}$  are partially confined, possessing molecular sizes that are larger than some of the pores ( $d_{\text{pore,min}} < R_{ee} < d_{\text{pore,max}}$ ). Chains with  $M_w \geq 3700 \text{ g mol}^{-1}$  are subjected to full confinement within the pore structure ( $R_{ee} > d_{\text{pore,max}}$ ). Remarkably, even under confinement, PMMA chains in 2.6 nm pores retain their bulk end-to-end distances up to a molecular mass of approximately  $32000 \text{ g mol}^{-1}$  (confined size of 11 nm) and only adopt more extended conformations at higher molecular masses (hyper-confined regime).



**Figure S2.** Schematic cross-section of the double-cantilever beam specimens used to measure the cohesive fracture energy of the hybrid nanocomposite films. The fracture path was determined to be cohesive within the nanocomposite layer through x-ray photoelectron spectroscopy measurements.

## **Supplementary Methods:**

**Fabrication of double cantilever beam fracture mechanics specimens.** After infiltrating the oligomer within the nanoporous matrix, a 200 mm silicon wafer substrate was cleaved into 50 mm square coupons. Bonding layers were added to the top of the film by sputtering 25 nm of titanium and evaporating 125 nm of aluminum onto the film surface. The resulting film stack was bonded to a blank silicon wafer with a brittle epoxy adhesive and held at 125 °C for one hour to cure the epoxy. The resulting sandwich structure was then diced with a high-speed wafer saw to create double cantilever beam (DCB) fracture mechanics samples that were 5 mm wide, 1.46 mm in total thickness, and 50 mm in length. The cohesive fracture energy,  $G_c$ , of the hybrid nanocomposite films was then measured by DCB fracture mechanics-based testing with a high-resolution micromechanical test system (DTS, Menlo Park, CA).