

Supplementary Information

Enhanced Glassy State Mechanical Properties of Polymer Nanocomposites via Supramolecular Interactions

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hydrogen bonding, reinforcement

I. Materials and Methods

Materials

N,N-Dimethylformamide DMF (99.8%) was purchased from Sigma Aldrich. 98400 g/mol (PDI=1.16) poly(methyl methacrylate) PMMA was synthesized by homemade ATRP. 193000 g/mol (PDI=1.17) and 387900 g/mol (PDI=1.07) PMMA were purchased from Polymer Source and Scientific Polymer, respectively. To avoid thermal degradation during annealing Irganox 1010, donated by BASF, was used. Bare silica nanoparticles (NPs), initially dispersed in isopropanol (IPA-ST) and transferred in DMF, were purchased from Nissan Chemical. UPy supramolecular polymers (named here **UPy 1** and **UPy 2**) were grafted on Grace Davison AS-40 colloidal silica ($d = 30$ nm) and dispersed in DMF. The synthesis of the grafted polymers and the NP functionalization are described in SI.

Nanocomposites (PNCs) preparation and sample transfer for characterization

PNCs solutions in DMF with a concentration of 35 mg/mL were prepared by mixing appropriate amounts of PMMA solution with the varying silica NPs solutions to get a final silica core concentration of 5%wt. Then the PNCs solutions were spun-coat on mica sheets (highest grade mica (V1) purchased from Ted Pella Inc. or SPI supplies) at 2000 rpm for 60s and 2 accelerations using a Spin Coater Model P6700 Series from Specialty Coating Systems INC. Prior to spin-coating, the treatment of mica included acetone wash followed by a DI water wash followed by air dry. After spin-coating the thin films sat for 24 hours. Then the films were cut into three sections for easier removal and were immersed in DI water for transfer through the wetting of the mica/PNCs interface to new surfaces: silicon ellipsometry wafer for thickness measurements (using a Woollam ellipsometer), TEM grid, or mechanical testing wafer (bulge window).

Transmission Electron Microscopy (TEM)

The PNCs samples were transferred onto a 400 mesh uncoated copper TEM grid (from Electron Microscopy Sciences). TEM images were obtained with a Jeol JEM-100 CX electron microscope.

Dynamic and Static Light Scattering (DLS and SLS)

The light scattering measurements (DLS and SLS) were performed at 25°C with a BI-200SM (Brookhaven Instruments) equipped with diode-pumped solid state (DPSS) laser operating at $\lambda = 532$ nm and a BI-9000 AT digital correlator. The DLS experiments were also performed using a Zetasizer NanoZS (Malvern Instruments) equipped with a 633 nm HeNe laser and operating at a scattering angle of 173° (backscattering setup); the CONTIN analysis (already defined in the instruments software) has been used to determine the apparent diffusion coefficient D_{app} . Its extrapolation to $q=0$ gives the mutual diffusion coefficient D_0 leading to the hydrodynamic diameter D_h through the Stokes-Einstein relation. We compared the D_h calculated from D_0 (using different scattering angles) with D_{app} obtained at one angle (173° using the Zetasizer NanoZS) and found similar tendency (see Figure S1 and Table 1 in the main text).

II. Dynamic and Static light scattering (DLS and SLS)

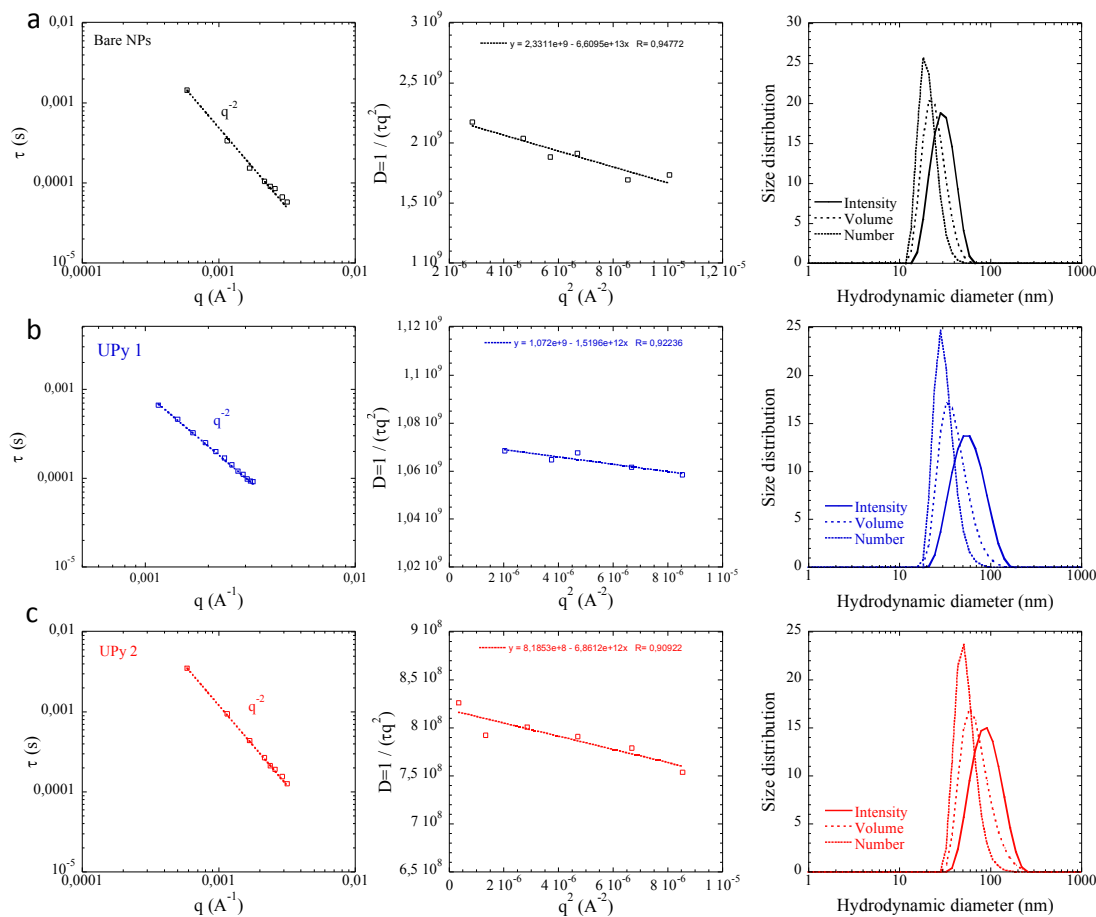


Figure S1. Left: Variation of the characteristic relaxation time τ as a function of scattering vector q . Middle: Diffusion coefficient $D=1/(\tau q^2)$ as the function of q^2 . Right: intensity (continuous line), volume (dash line) and number (point dash line) size distribution obtained by applying the CONTIN analysis at 173° (using Zetasizer NanoZS instrument) for (a) bare NPs (Nissan Chemicals), (b) **UPy 1** NPs and (c) **UPy 2** NPs in DMF. See also main text.

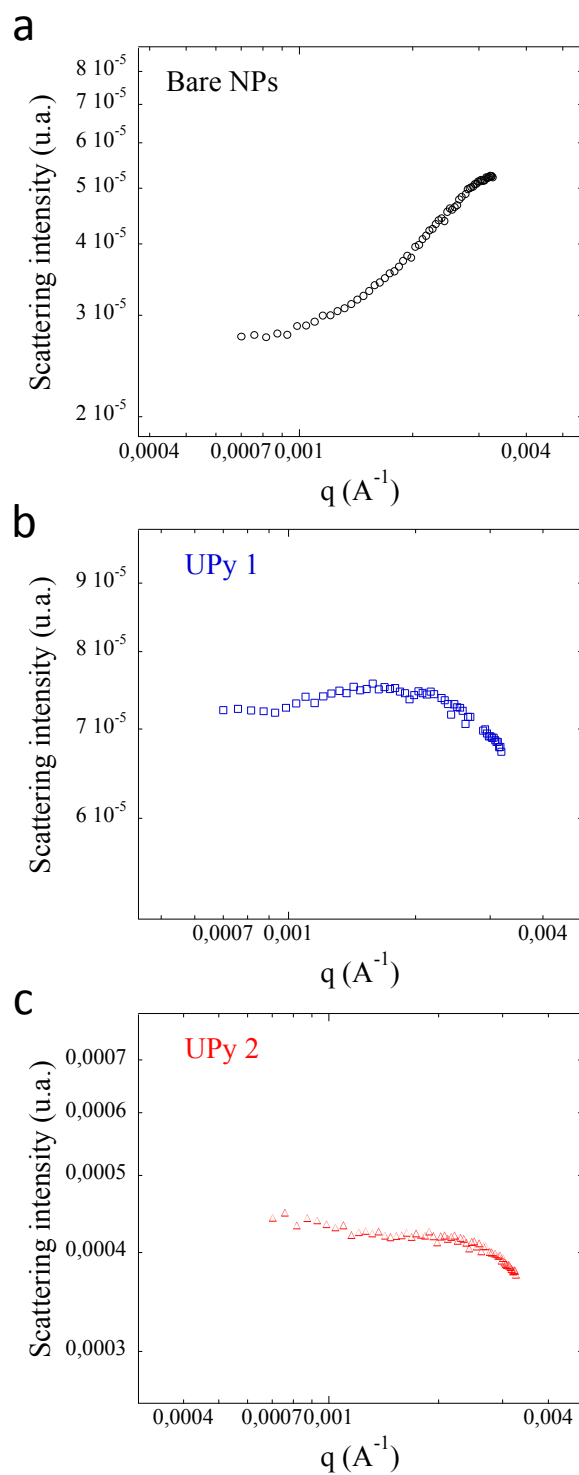


Figure S2. Scattering intensity as a function of scattering vector q obtained by SLS measurements for (a) bare NPs (Nissan Chemicals), (b) **UPy 1** and (c) **UPy 2** NPs in DMF.

III TEM images

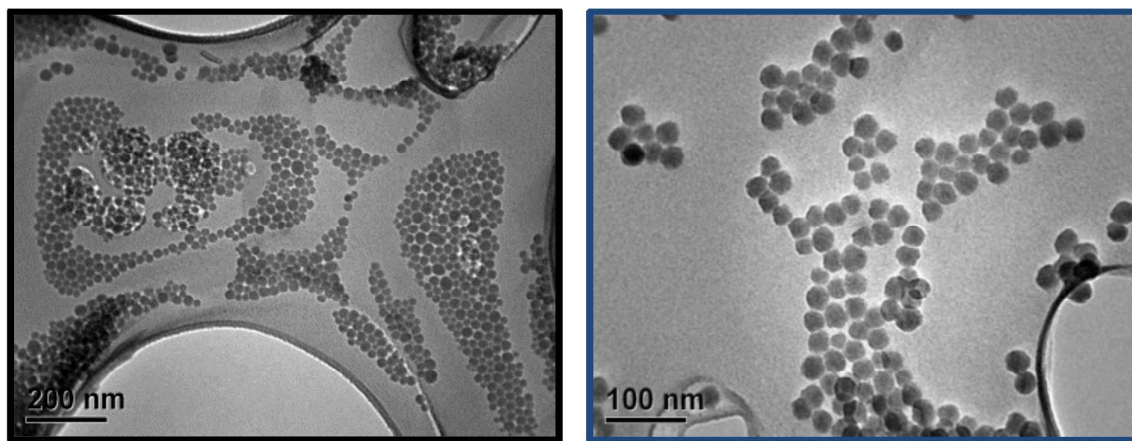


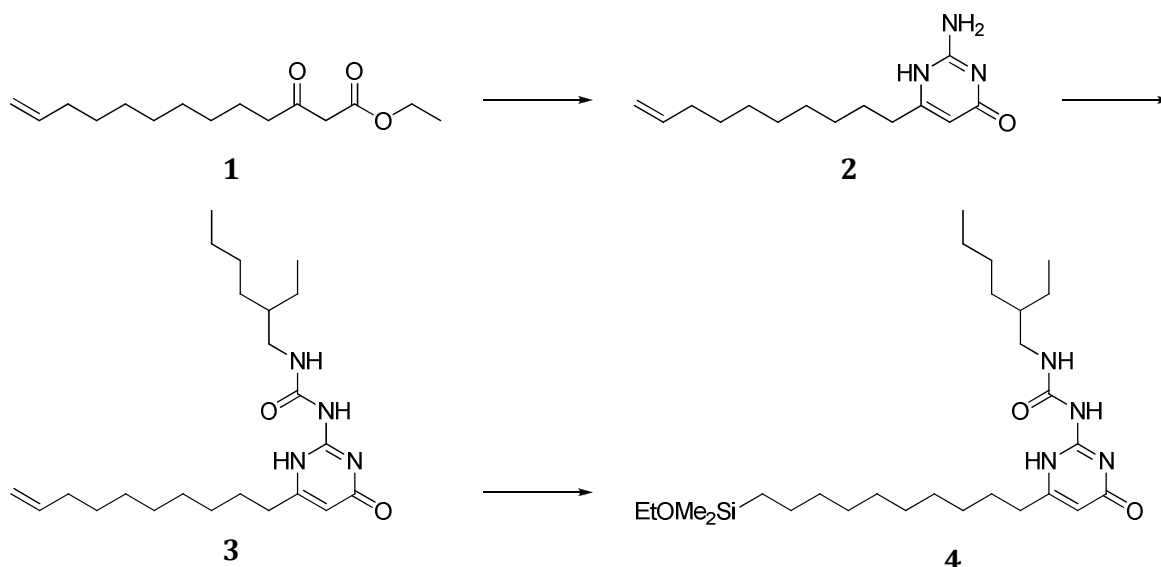
Figure S3. TEM images of bare silica Nissan-St (left) and UPy systems (right) drop-casted on TEM grid.

IV. Synthesis of grafted NPs

^1H NMR spectra were recorded at 500 and 600 MHz and ^{13}C NMR spectra were recorded at 125 MHz on Bruker instruments. ^1H NMR chemical shifts are reported as δ values in ppm relative to TMS or residual solvent: CDCl_3 (7.24 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constants in Hertz (Hz), and integration. Multiplets (m) and broad peaks (br) are reported over the range (ppm), which they appear at the indicated field strength. Carbon NMR spectra were recorded in ppm relative to TMS or the solvent signals: CDCl_3 (77.23 ppm). Mass spectral data was obtained on a Micromass LCT (ES-MS) spectrometer. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on Fisher silica gel 60 (230-400 mesh). Gel Permeation Chromatography (GPC) was carried out using an Agilent 1100 Series GPC-SEC Analysis System along with a mixed bed Plgel Mixed-C column from Polymer Labs. The eluent was DMF with 0.1% LiBr and a flow rate of 1.0 mL / min was used. The calibration was performed using poly(ethylene glycol) (PEG)-based molecular weight standards. Moisture sensitive reactions were carried out under nitrogen atmosphere using flame-dried glassware and standard air free techniques. All reactions were performed in HPLC grade solvents that were further purified by passing through an alumina column, and reagent grade solvents were used for aqueous workup and flash chromatography.

Preparation of Short Graft Length UPy Modified Nanoparticles: UPy 1

Ethylhexyl Dimethylethoxysilane UPy Synthesis



(2) 2-amino-6-(dec-9-enyl)pyrimidin-4(1H)-one. Ethyl 3-oxo-12-tridecenoate **1** (3.72 g, 14.6 mmol) was added to a 100 mL round bottom flask, followed by anhydrous ethanol (73 mL, 0.2 M). After completely dissolving by stirring, guanidine carbonate (2.68 g, 14.6 mmol) was added and the reaction mixture was heated at reflux for 24 h. The ethanol was evaporated down to approximately 10 mL and the product precipitated by the addition of water (50 mL). The product was washed with water (50 mL) and acetone (50 mL) to give isocytosine **2** as a white solid (2.70 g, 74%) without further purification.

(3) 1-(6-(dec-9-enyl)-4-oxo-1,4-dihydropyrimidin-2-yl)-3-(2-ethylhexyl)urea. Olefin isocytosine derivative **2** (2.70 g, 10.8 mmol) was added to a flame-dried 100 mL round bottom flask followed by anhydrous pyridine (54 mL, 0.2 M). While stirring, 2-ethylhexyl isocyanate (2.52 g, 16.2 mmol) was added. The reaction mixture was heated at reflux for 24 h, subsequently cooled to room temperature, and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (0:100 – 1:99 MeOH:DCM) to give compound

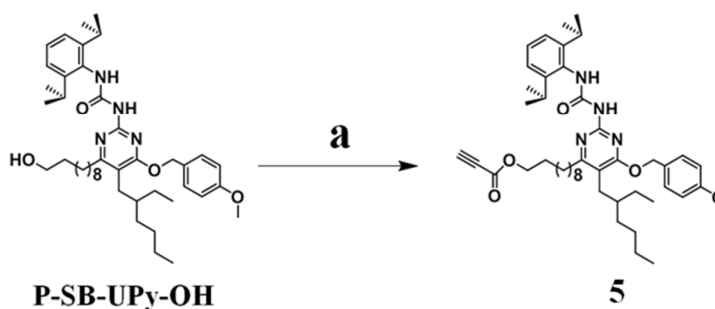
3 as a white solid (4.07 g, 93%). ^1H NMR (CDCl_3) δ : 13.16 (s, 1H), 11.92 (s, 1H), 10.05 (s, 1H), 5.81 (m, 2H), 4.99 (d, $J = 17.4$ Hz, 1H), 4.93 (d, $J = 10.6$ Hz, 1H), 3.17 (m, 2H), 2.45 (t, $J = 7.7$ Hz, 2H), 2.04 (q, $J = 10.4$ Hz, 2H), 1.69-1.53 (m, 5H), 1.48-1.18 (m, 16H), 0.94-0.84 (m, 6H); ^{13}C NMR (CDCl_3) δ : 173.1, 156.8, 154.8, 152.3, 139.2, 114.3, 105.9, 43.5, 39.9, 39.2, 33.8, 32.7, 30.7, 29.3, 29.2, 29.1, 29.0, 28.7, 27.0, 24.0, 23.2, 14.2 10.7 ; HRMS (DCM) m/z calcd for $\text{C}_{23}\text{H}_{40}\text{N}_4\text{O}_2$ ($\text{M} + \text{Na}$) $^+$ 427.3049, observed 427.3040.

(4) 1-(6-(10-(ethoxydimethylsilyl)decyl)-4-oxo-1,4-dihydropyrimidin-2-yl)-3-(2-ethylhexyl)urea. Olefin **3** (1.00 g, 2.5 mmol) was added to a flame-dried 5 mL round bottom flask followed by anhydrous toluene (2.0 mL, 1.25 M). After completely dissolving with stirring, platinum divinyltetramethyldisiloxane in xylene (200 μL) was added. While stirring, dimethylethoxysilane (3.40 mL, 25.0 mmol) was added dropwise. The reaction mixture was then heated at 50 $^\circ\text{C}$ until the reaction was complete by NMR (~ 5 h). The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The brown residue was diluted in dichloromethane and passed of a silica plug with 20% ethyl acetate/dichloromethane. The solvent was removed under reduced pressure to yield **4** as a yellow oil (1.02 g, 80%). ^1H NMR (CDCl_3) δ : 13.15 (s, 1H), 11.91 (s, 1H), 10.05 (s, 1H), 5.80 (s, 1H), 3.65 (q, $J = 7.0$ Hz, 2H), 3.17 (m, 2H), 2.46 (t, $J = 7.6$ Hz, 2H), 1.69-1.56 (m, 5H), 1.44-1.22 (m, 20H), 1.18 (t, $J = 7.0$ Hz, 3H), 0.92-0.84 (m, 6H), 0.58 (m, 2H), 0.08 (s, 6H); ^{13}C NMR (CDCl_3) δ : 173.2, 156.9, 154.9, 152.5, 106.0, 58.3, 43.6, 40.0, 39.3, 33.6, 32.9, 31.2, 30.8, 29.6, 29.4, 29.3, 29.0, 28.8, 27.2, 24.4, 24.1, 23.3, 23.3, 23.2, 18.7, 16.5, 14.3, 10.8, -1.9; HRMS (DCM) m/z calcd for $\text{C}_{27}\text{H}_{52}\text{N}_4\text{O}_3\text{Si}$ ($\text{M} + \text{Na}$) $^+$ 531.3707, observed 531.3716.

Procedure for the Functionalization of AS-40 Silica Nanoparticles with Dimethylethoxysilane Terminated UPy. Grace Davison AS-40 colloidal silica ($d = 30$ nm)

was received as an aqueous solution (pH = 9.1 to 9.7). The colloidal solution was first passed through an Amberlite IR-120 cation exchange column to adjust the pH to ~ 3.5. To a 1 L round-bottom flask was added **4** (1.5 g, 2.8 mmol) and 1-propanol (80 mL). This mixture was stirred while pH adjusted colloidal silica (8.0 mL silica solution, 2.60 g SiO₂) was added dropwise via an addition funnel. The mixture was then heated at reflux for 48 h. Water was subsequently removed by azeotropic distillation. The volume of the mixture was then reduced to ~ 25 mL and the functionalized silica was precipitated into stirring hexanes (500 mL). The supernatant was discarded and the precipitate was resuspended in THF (10 mL). This solution was added to hexanes (100 mL) and centrifuged at 4000 rpm for 5 min. The supernatant was discarded and the precipitate resuspended in THF (10 mL) followed by precipitation in hexanes and subsequent centrifugation. This process was repeated 5 times to remove any unreacted silane. Finally, the purified functionalized silica was dried under vacuum to yield a slightly yellow powder (2.15 g, 83%). The particles were then analyzed by TGA to determine a graft density of 0.34 units/nm².

Preparation of Long Graft Length UPy Modified Nanoparticles: UPy 2



Scheme S1. Synthesis of P-SB-UPy-Alkyne.

Conditions: a) propiolic acid, DCC, DMAP, DCM, rt, 18 h, 87%.

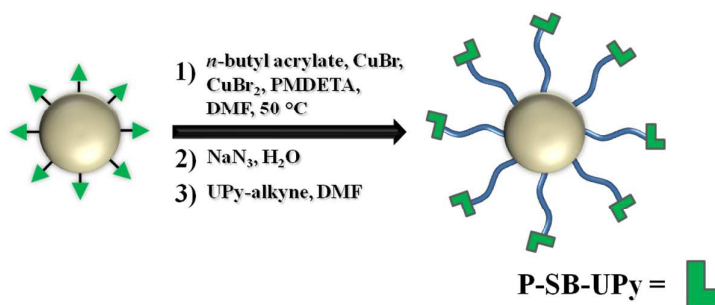
P-SB-UPy-OH. This UPy molecule was prepared following a previously reported synthesis¹.

(5) 10-(2-(3-(2,6-diisopropylphenyl)ureido)-5-(2-ethylhexyl)-6-(4-methoxybenzyloxy)pyrimidin-4-yl)decyl propiolate: Propiolic acid (0.175 mL, 2.85 mmol) was added to P-SB-UPy-OH (1.02 g, 1.45 mmol) in DCM (0.71 mL). The resulting solution was stirred at 0°C. Separately, 4-dimethylaminopyridine (0.035 g, 0.29 mmol) was added to N,N'-dicyclohexylcarbodiimide (0.588 g, 2.85 mmol) in DCM (1.4 mL). The DCC/DMAP solution was added dropwise over 1 hour at 0°C while stirring the reaction mixture. After addition was complete, the mixture was stirred 18 h, allowing the temperature to equilibrate to room temperature. Without workup, the product was purified by flash chromatography (0 – 8 % ethyl acetate: dichloromethane) to give **5** as a colorless oil (0.94 g, 87 %). ¹H NMR (CDCl₃) δ: 10.79 (br s, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.30 (t, *J* = 7.70 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.28 (apparent doublet, *J* = 6.9 Hz, 3H), 4.17 (t, *J* = 6.8 Hz, 2H), 3.82 (s, 3H), 3.24 (septet, *J* = 6.7 Hz, 2H), 2.87 (s, 1H), 2.60-2.55 (m, 2H), 1.68-1.43 (m, 5H), 1.35-1.10 (m, 35 H), 0.89-0.81 (m, 6H); ¹³C NMR (CDCl₃) δ: 171.3, 168.7, 167.8, 159.7, 155.0, 153.9, 153.0, 146.6, 131.6, 130.2, 128.5, 128.1, 114.0, 112.8, 74.9, 74.6, 68.3, 66.6, 60.5, 55.4, 39.9, 34.1, 32.9, 29.6, 29.5, 29.5, 29.4, 29.2, 29.1, 29.0, 28.4, 26.0, 25.9, 24.3, 23.2, 21.2, 14.3, 14.3, 11.2; HRMS (CHCl₃) *m/z* calcd for C₄₆H₆₆O₅N₄ (M + Na)⁺ 777.4931, observed 777.4932.

Preparation of ATRP Initiator Functionalized Silica Nanoparticles. Grace Davison AS-40 colloidal silica (d = 30 nm) was received as an aqueous solution (pH = 9.1 to 9.7). The colloidal solution was first passed through an Amberlite IR-120 cation exchange column to adjust the pH to ~3.5. To a 1 L round-bottom flask was added 3-(ethoxydimethylsilyl)propyl 2-bromo-2-methylpropanoate (8.00 g, 25.8 mmol) and 1-propanol (430 mL). This mixture

was stirred while pH adjusted colloidal silica (43.0 mL silica solution, 13.99 g SiO₂) was added dropwise via an addition funnel. The mixture was then heated at reflux for 48 h. Water was subsequently removed by azeotropic distillation. The volume of the mixture was then reduced to ~ 50 mL and the functionalized silica was precipitated into stirring hexanes (2 L). The supernatant was discarded and the precipitate was resuspended in THF (40 mL). This solution was divided equally among 2 x 250 mL centrifuge bottles containing hexanes (2 x 200 mL). The bottles were stirred vigorously and then centrifuged at 4000 rpm for 5 min. The supernatant was discarded and the precipitate resuspended in THF (2 x 20 mL) followed by precipitation in hexanes and subsequent centrifugation. This process was repeated 5 times to remove any unreacted silane. Finally, the purified functionalized silica was dried under vacuum to yield a slightly yellow powder (13.5 g, 96%). Elemental Analysis (Atlantic Microlabs): 1.5 wt% Bromine, 1.2 initiator/nm² for radius = 15 nm.

One Pot Synthesis of UPy Functionalized Polymer Grafted Nanoparticles.



Scheme S2. One Pot Polymerization, Azidation, and Cycloaddition on Silica Nanoparticles.

To a flame dried 25 mL round-bottom air-free flask was added ATRP silica (0.300 g, 0.057 mmol, 1 equiv), Cu(II)Br₂ (2.5 mg, 0.011 mmol, 0.2 equiv), PMDETA (34 µL, 0.171 mmol, 3 equiv), *n*-butyl acrylate (2.2 g, 17.1 mmol, 300 equiv), and DMF (7.1 mL, 0.008 M) (Scheme S2). The oxygen was removed through three freeze-pump-thaw cycles. While

frozen, Cu(I)Br (8.2 mg, 0.057 mmol, 1 equiv) was added to the reaction mixture. The flask was then evacuated and refilled with argon three times. The flask was thawed under vacuum, filled with argon, and then heated at 50 °C until the desired conversion was reached, as determined by NMR.

After reaching the desired conversion, a degassed aqueous solution of sodium azide (0.0074 g, 0.114 mmol, 2 equiv) in 1:1 DMF:H₂O (0.5 mL) was added to the polymerization mixture all at once. After addition, a noticeable color change was observed, from green to yellow. Several time points were monitored after the azide addition, and no increase in monomer conversion was observed, confirming that an azide group had displaced the bromide group. This was further confirmed via FT-IR with a peak corresponding to the azide observed at 2090 cm⁻¹ (Figure S4 B). A degassed solution of the UPy-alkyne **5** (0.0886 g, 0.114 mmol, 2 equiv) in DMF (0.5 mL) was then added to the reaction mixture causing a color change from yellow back to green. FT-IR showed the disappearance of the azide peak, and no alkyne peak (2090 cm⁻¹), confirming the completion of the click reaction (Figure S4 C).

The mixture was stirred for 12 h at 50 °C and then exposed to air. The reaction mixture was evaporated to dryness, dissolved in toluene and washed with saturated ammonium chloride, saturated EDTA, and saturated NaCl solutions to remove the copper and DMF. The organic layer was dried with sodium sulfate, filtered, and then concentrated. The nanoparticles were then precipitated into methanol two times, collected, and dried to yield P-SB-UPy functionalized polymer grafted nanoparticles.

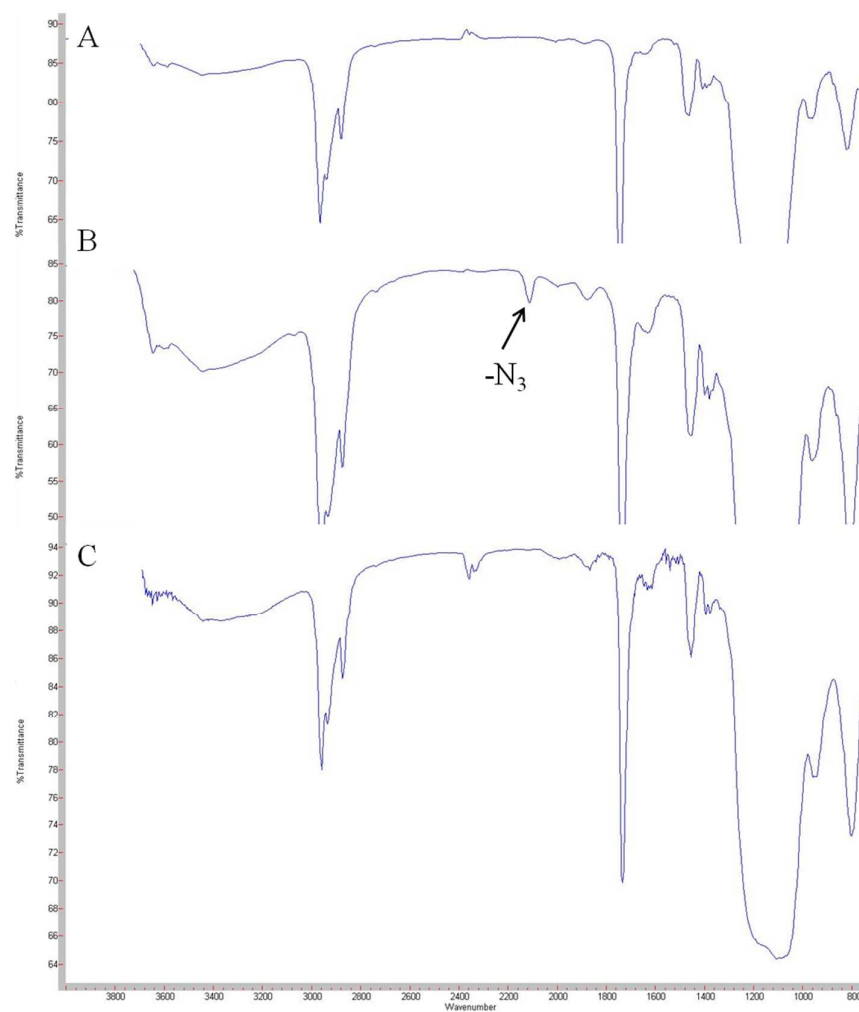
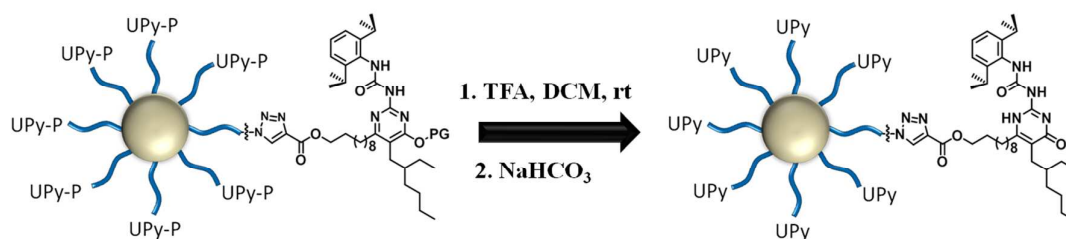


Figure S4: FT-IR of one-pot polymerization, azidation, click reaction with UPy 2. A) IR spectrum after polymerization, B) IR spectrum after azidation of polymer chain end, C) IR spectrum after click reaction showing the disappearance of the azide peak.

Deprotection of UPy Polymer Nanoparticles.



Scheme S3. Deprotection of UPy NPs.

P-SB-UPy functionalized nanoparticles (0.500 g, 0.095 mmol) were dissolved in DCM (2 mL). While the mixture was stirring, a solution of 20 % TFA in DCM (1.0 mL, 2.6 mmol TFA) was added dropwise. The mixture was stirred for 12 h at which point it was washed with saturated sodium bicarbonate (3 x 10 mL) and brine (1 x 10 mL). The organic layer was dried, filtered, and concentrated. The concentrated solution was precipitated into hexanes three times, collected, and dispersed in DMF to use for further studies.

The UPy NPs were analyzed by ¹H NMR before and after deprotection to monitor the hydrogen bonding region (10.0-13.5 ppm) (see Figure S5). Prior to deprotection there is one peak corresponding to the intramolecular hydrogen bond between the proton of the urea and the nitrogen of the pyrimidinone ring. After deprotection, three peaks were observed corresponding to the intramolecular hydrogen bond between the carbonyl of the urea and the N-H of the pyrimidinone, and the two intermolecular hydrogen bond between the N-H of the ureas and the carbonyl and nitrogen of the pyrimidinone (Figure S5). This confirmed that UPy units were present on polymer chain ends.

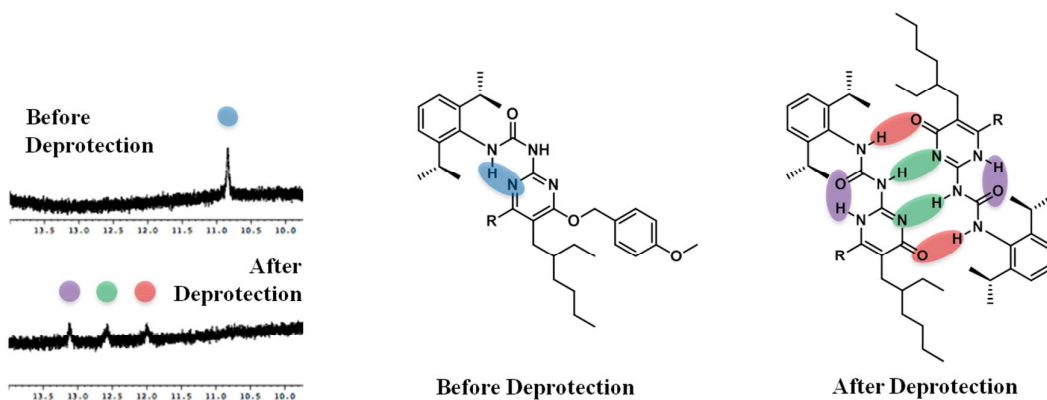


Figure S5: ^1H NMR spectra revealing the change in hydrogen bonds before and after deprotection. The hydrogen bonds are color coded to match their corresponding peak.

V. Thin film thicknesses by ellipsometry

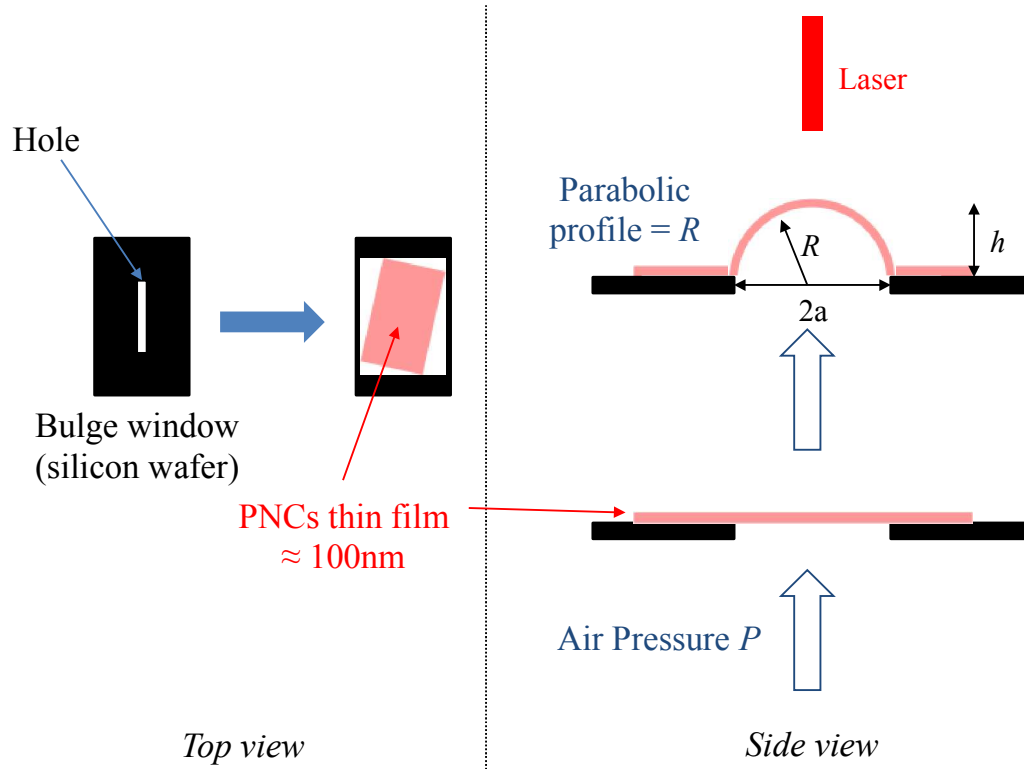
PMMA M_w (kg.mol⁻¹ or K)	NPs	Thickness (nm)
97	-	110
97	UPy 2 (6.3%)	101.4
97	UPy 2 (6.3%)	87.8

PMMA M_w (kg.mol⁻¹ or K)	NPs	Thickness (nm)
193	-	125.5
193	Bare NPs (5%)	138.4
193	UPy 1 (5%)	150
193	UPy 1 (5%)	107.5
193	UPy 2 (6.3%)	121.3
193	UPy 2 (6.3%)	118.6

PMMA M_w (kg.mol⁻¹ or K)	NPs	Thickness (nm)
387.9	-	107.6
387.9	UPy 2 (6.3%)	65.1

Table S1.

VI. Mechanical properties in the glassy state: the bulge test



Scheme S4: Schematic representation of bulge window (top and side view).

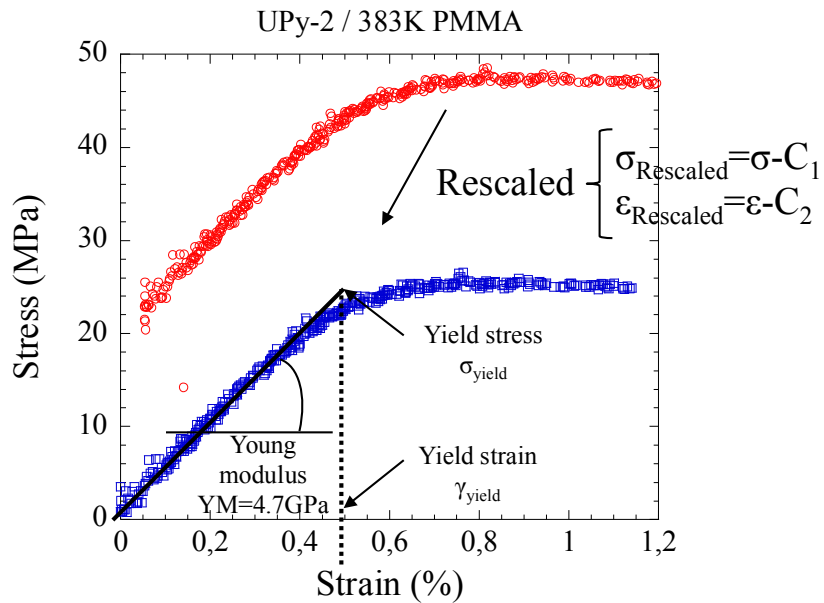


Figure S6: Stress versus strain curves for **UPy 2** / 387.9 K PMMA. In red circle: raw data, in blue squares: rescaled data after applying a vertical and horizontal offset to get zero stress at zero strain.

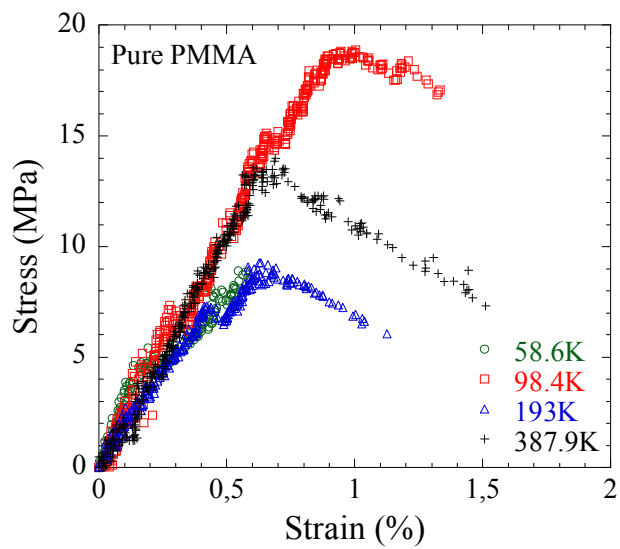


Figure S7: Stress versus strain for different pure PMMA M_w s.

VII. Annealing effect

Since the PMMA PNCs remain stuck on the mica surface after annealing, it is difficult to float off the thin PNCs films from mica to transfer it on the bulge window (note that direct annealing on bulge window is not possible, the thin film can flow in the hole). Annealed samples required two steps for spin coating by using an intermediate base layer (polyvinyl alcohol PVA or polystyrene sulfonate PSS) on top of which the PNCs will be deposited. Silicon wafers were cleansed utilizing piranha solution. Next, the base layers were deposited on the silicon wafer (2500 rpm for 60 seconds at a concentration of 10 mg/ml). The thickness for PVA obtained was approximately 20nm. Substrate with base layer let sit for 24 hours. Before spin-coating the PNCs layer, the substrate underwent ultraviolet ozone for 30 minutes to remove impurities. PNCs solutions utilized for PVA base coat annealing were dissolved in 25% DMF and 75% tetrahydrofuran (THF) due to base layer solubility issues. PNCs solutions utilized for PSS were dissolved in pure DMF solvent. Due to increased surface roughness from the base layer on top of the silicon wafer, annealed samples presented greater thicknesses than un-annealed samples at standard 35 mg/ml; to combat this effect, sample concentration was reduced to 20mg/ml leading to a thickness of approximately 110 nm (samples were spun at 2000 rpm for 60 seconds and 2 accelerations). Finally, PSS samples were annealed for 3 days in vacuum at 150 °C. PVA samples were annealed for 2 days in vacuum at 125 °C. To show that the existence of the base layer doesn't perturb the NPs dispersion under the conditions described above, TEM was conducted on PVA based PMMA (Figure S8).

After annealing, the base layer is dissolved in water and the annealed thin PNCs film can be transferred onto the bulge window. This delicate operation was done for two samples: 177K and 387K PMMA filled with 6.2%wt UPy **2** using PSS as a base layer (see Figure S9) and similar YM was found before and after annealing.

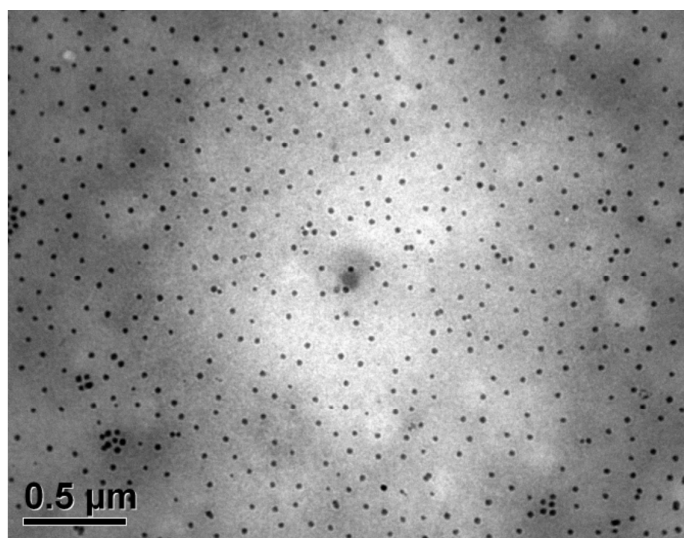


Figure S8: TEM image of UPy 2 / 387.9 K PMMA prepared by using a PVA base layer (see text for details).

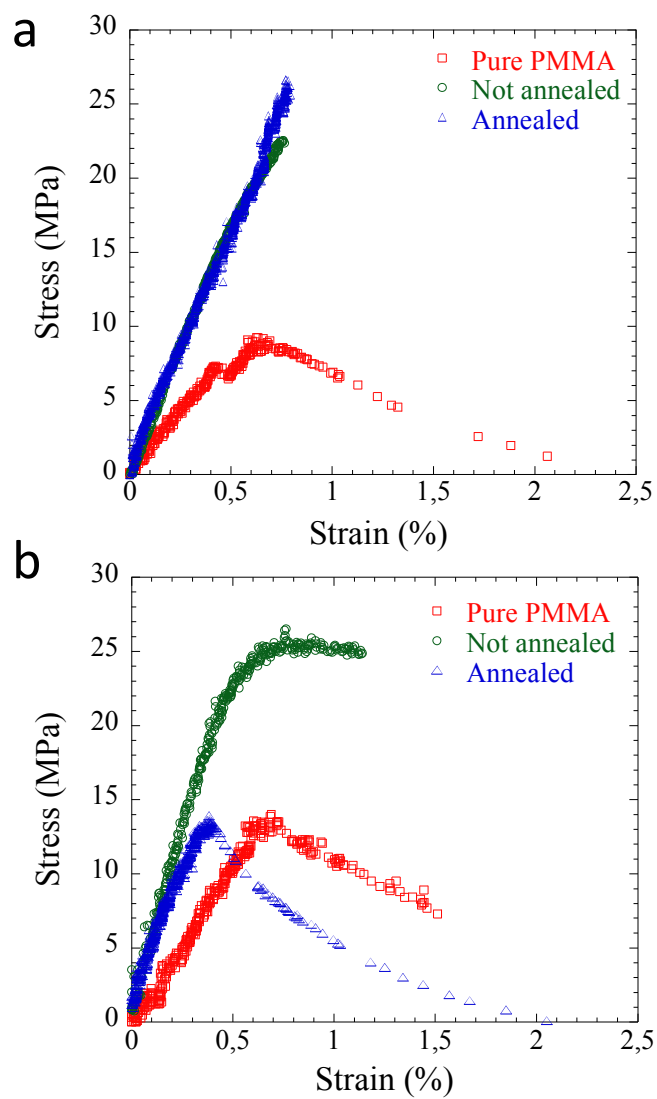


Figure S9: Effect of annealing (3 days at 150°C) on **UPy 2** / PMMA PNCs, (a) 193 K and (b) 387.9 K. The base layer is PSS.

References

- 1 Hentschel, J., Kushner, A. M., Ziller, J. & Guan, Z. B. Self-healing supramolecular block copolymers. *Angew. Chem.* **51**, 10561-10565 (2012).