Supporting Information

One-Pot Synthesis of Sequence-Controlled Mesoporous Heterostructures

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Experimental

Materials

All materials were used as received unless specified otherwise. Methanol (99.8%, Fisher), diethyl (hydroxymethyl)-phosphonate (≥97.0%, TCI), methacrylic acid (>99% Alfa Aesar), *N'N*-dicyclohexylcarbodiimide (DCC, ≥99%, BeanTown Chemical), 4-cyano-4-(phenylcarbonthioylthio)pentoic acid (4CPDB, 97% Strem Chemicals), sodium hydroxide (≥97%, Sigma), tetrahydrofuran (Fisher), methylene chloride (Fisher), 4-dimethylaminopyridine (DMAP, >99%, TCI), acetonitrile (≥99.9%, Sigma), titanium(IV) isopropoxide (TTIP, ≥98%, Acros Organics), poly(ethylene glycol) methyl ether (PEO-OH, M_n= 5000 g/mol, Aldrich), concentrated hydrochloric acid (HCl, 37% w/w, ACS grade, VWR), ethanol (200 proof, 100%, Fisher) 2-bromopropionic acid (>99%, Aldrich), niobium(V) ethoxide (NbEtOH, 99.9%, Fisher), copper(I) bromide (99.99%, Aldrich), *N,N,N',N'',N''*-pentamethlydiethylenetriamine (PMDETA) (99%,

Sigma), copper(II) bromide (99, Aldrich), zirconium(IV) butoxide (≥80% w/w in 1-butanol, BeanTown Chemical). Cyclohexyl methacrylate (≥98.0%, TCI), styrene monomer (99%, Acros), poly(ethylene glycol) methyl ether methacrylate (PEOMA, M_n = 500 g/mol, contains 100 ppm MEHQ, 200 ppm BHT, Sigma-Aldrich) were run over a basic alumina column prior to use. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 97%, Sigma) was recrystallized from methanol. Bromotrimethylsilane (TMSBr, 97%, Chem Impex Intl Inc MS) was stored in the glovebox. Dry methanol and ethanol was dried at room temperature by storage over 30% w/v of molecular sieves (3Å, 8-12 mesh, Acros Organics) for one week.

Poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) Synthesis

PS-*b*-PEO was synthesized by a two-step synthesis. A Steglich esterification of poly(ethylene glycol)methyl ether was used to form a macroinitiator (PEO-Br), followed by atom transfer radical polymerization to grow the PS block. A detailed procedure has been reported elsewhere.[1] The PS-*b*-PEO diblock was prepared by dissolving PEO-Br (5 g, 1 mmol) in 7 mL of DMF followed by the addition of styrene monomer (23 mL, 200 mmol) in a Schlenk flask and the solution was subjected to three cycles of freeze-pump-thaw to remove oxygen and brought into an argon glovebox. In the glovebox, Cu(I)Br (161.3 mg, 1.125 mmol) and PMDETA (235μL, 1.125 mmol) were added to the polymer solution. The mixture was then added to a preheated oil bath at 100°C for 6 hrs. The flask was placed in the freezer for 1 hr before exposure to air and diluted with THF and passed over a basic alumina column to remove copper complexes. The eluent was then precipitated in cold (-78°C) methanol and the final polymer was collected by vacuum filtration.

Methacryloyloxymethyl diethylphosphonate Synthesis (DEPMMA)

DEPMMA was synthesized via a procedure described previously.[2] Diethyl(hydroxymethyl)phosphonate (5 g, 4.27 mL, 29.73 mmol), methacrylic acid (2.56 g, 29.73 mmol), and 15 mL of chloroform were mixed in a round bottom flask. The solution was cooled to 0 °C and sparged with nitrogen for 30 min. A solution of N′N-dicyclohexylcarbodiimide (DCC) (6.75 g, 32.70 mmol), 4-dimethylaminopyridine (DMAP) (0.40 g, 3.27 mmol), and 5 mL of chloroform was then added in a dropwise manner. The suspension was left to vigorously stir at room temperature for 2 hrs. The suspension was then filtered and the chloroform was removed using reduced pressure. The crude product was then purified via vacuum distillation at 175 °C. The final product (diethoxyphosphoryl)methyl methacrylate (DEPEMA) was verified using ^{1}H-NMR and ^{31}P-NMR (Figures S6 and S7).

Macro-Initiator: Poly(cyclohexyl methacrylate) Synthesis (PCHMA)

Two separate PCHMA macro-initiators (40k & 17k) were synthesized, one for diblock synthesis and one for the triblock synthesis. The ratios of AIBN:4CPDB:CHMA for the diblock are outlined below. The triblock ratios were 0.1:1:101 and the same experimental procedures were as follows. Cyclohexyl methacrylate (CHMA) (7.50 mL, 42.95 mmol), 2,2′-azobis(2-methylpropionitrile) (AIBN) (8.80 mg, 0.027 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (4CPDB) (100 mg, 0.18mmol), and 4.50 mL of tetrahydrofuran (THF) were combined in a Schlenk flask and were subjected to three cycles of freeze–pump–thaw. The reaction flask was then brought into an argon-filled glovebox to backfill the flask with argon. The polymerization was then carried out in a preheated oil bath at 70 °C for 18 hrs. Once the polymerization was complete, the reaction was cooled in a freezer before venting and dilution with THF to fully dissolve the viscous product.

PCHMA was then precipitated using cold methanol, filtered, and then dried in a vacuum oven overnight. The molar mass of PCHMA was calculated based on the ratio of reversible addition-fragmentation chain-transfer (RAFT) agent to cyclohexyl methacrylate assuming 100% conversion. The molar mass and conversion were quantified using ^{1}H NMR in $CDCl_3$ (Figure S8, S8). The molar-mass dispersity (Đ) was verified by gel permeation chromatography (GPC) (Figure S10, S11).

Poly(cyclohexyl methacrylate-*b*-methacryloyloxymethyl diethylphosphonate) (PCHMA-*b*-PDEPMMA) Synthesis

PCHMA-4CPDB (~40k g/mol) macroinitiator (3.0 g, 0.07 mmol), 2,2′-azobis(2-methylpropionitrile) (AIBN) (3.66 mg, 0.023 mmol), DEPMMA (4.04 g, 4.29 mL, 17.09 mmol), and 10 mL of THF were mixed in a Schlenk flask and were subjected to three cycles of freeze–pump–thaw. The reaction flask was then brought into an argon-filled glovebox to backfill the flask with argon. The polymerization was then carried out in a preheated oil bath at 70 °C for 18.25 hrs. The reaction was then cooled in a freezer before venting and dilution with THF to fully dissolve the viscous product. PCHMA-*b*-PDEPMMA was then precipitated out using cold hexane, filtered, and then dried in a vacuum oven overnight. The molar mass and conversion were quantified using ^{1}H NMR in CDCl3 (Figure S12). The molar-mass dispersity (Đ) was verified by GPC (Figure S10).

Poly((cyclohexyl methacrylate)-*b*-(methacrylic acid)) (PCHMA-*b*-PMAA) Synthesis

PCHMA-4CPDB (~17k g/mol) macroinitiator (2.5 g, 0.15 mmol), 2,2′-azobis(2-methylpropionitrile) (AIBN) (3.62 mg, 0.023 mmol), methacrylic acid (0.84 g, 0.83 mL, 9.86

mmol) previously passed over a basic alumina column, and 8.53 mL of THF were mixed in a Schlenk flask and were subjected to three cycles of freeze–pump–thaw. The reaction flask was then brought into an argon-filled glovebox to backfill the flask with argon. The polymerization was then carried out in a preheated oil bath at 70 °C for 18.25 hrs. The reaction was then cooled in a freezer before venting and dilution with THF to fully dissolve the viscous product. PCHMA-*b*-PMAA was then precipitated out using cold hexane, filtered, and then dried in a vacuum oven overnight. The molar mass and conversion were quantified using ^{1}H NMR in $CDCl_3$.

Poly(cyclohexyl methacrylate-*b*-methacrylic acid-*b*-poly(ethylene glycol)methacrylate) (PCHMA-*b*-PMAA-*b*-PPEGMA) Synthesis

PCHMA-*b*-PMAA (~23k g/mol) macroinitiator (2.5 g, 0.11 mmol), AIBN (2.7 mg, 0.016 mmol), PEGMA (1.43g, 1.48 mL, 2.86 mmol), and 15 mL of THF were mixed in a Schlenk flask and were subjected to three cycles of freeze–pump–thaw. The reaction flask was then brought into an argon-filled glovebox to backfill the flask with argon. The polymerization was then carried out in a preheated oil bath at 70 °C for 22 hrs. The reaction was then cooled in a freezer before venting and dilution with THF to fully dissolve the viscous product. PCHMA-*b*-PMAA-PPEGMA was then precipitated out using cold hexane, filtered, and then dried in a vacuum oven overnight. The molar mass and conversion were quantified using ^{1}H NMR in $CDCl_3$.

Poly(cyclohexyl methacrylate-*b*-methacryloyloxymethyl diethylphosphonate-*b*-poly(ethylene oxide)methacrylate) (PCHMA-*b*-PDEPMMA-*b*-PPEGMA) Synthesis

PCHMA-*b*-PMAA-*b*-PPEGMA (~33k g/mol) (3g, 0.09 mmol) and diethyl(hydroxymethyl)phosphonate (2 g, 11.90 mmol) were dispersed in 20 mL of THF. A

separate solution of DCC (2.7 g, 13.08 mmol) and DMAP (160 mg, 1.31 mmol) were dispersed in 10 mL of THF. The DCC/DMAP suspension was added dropwise to the polymer solution and stirred at room temperature overnight. The final product was separated via dialysis against THF and the solvent was removed by evaporation. The conversion of all methacrylic acid groups to the phosphonated ester was confirmed via ^{1}H-NMR and ^{31}P-NMR (Figures S14a).

Hydrolysis of Phosphonated Ester to Phosphonic acid

The phosphonated ester functionality of both the PCHMA-*b*-PDEPMMA and PCHMA-*b*-PDEPMMA-*b*-PPEGMA polymers were converted to phosphonic acid via the Mckenna reaction. Complete removal of the esters is feasible as previously demonstrated.[2] In general the polymer was dispersed in a 50/50 (v/v) solution of THF/acetonitrile at a concentration of 100 mg/mL and TMSBr was added dropwise to the solution. A ratio of 6:1 of TMSBr(mol):Phosphonates(mol) was used where the degree of polymerization and two esters per repeat unit must be considered. The solution was then allowed to stir at 50°C overnight. The intermediate product was isolated by the removal of the solvent via evaporation and the polymer was dispersed in a 50/50 (v/v) solution of methylene chloride/methanol at 100 mg/mL. The final product was then isolated by the removal of the solvent via evaporation and conversion of the ester to the acid was tracked via ^{1}H-NMR and ^{31}P-NMR (Figures S13-S14).

PS-*b*-PEO Micelle Formation

PS-*b*-PEO based micelles were carried out following previous work.[1] The final concentration was adjusted to 1 mg/mL of polymer to be comparable to PIM based micelles.

PS-*b*-PEO Oxide Templating for Induced Precipitation

PS-*b*-PEO (10mg) was dispersed in 10 mL of methanol prepared as described above. To the solution 0.266 mL of the TiO_2 stock was added. The solution pH was then brought to 7.0 with the addition of NaOH in methanol (10 mg/mL). The resulting suspension was filtered and checked via ^{1}H-HNMR.

TiO_2 Nanoparticle (NP) Stock Solution Synthesis

Concentrated HCl (0.36 mL) was added to 2mL of methanol. While stirring at 300 rpm TTIP (1.2 mL 4.05 mmol) was added rapidly. The solution was then diluted with 11 mL of dry methanol. The final concentration of TiO_2 was calculated to be 22.53 mg/mL.

Nb_2O_5 NP Stock Solution Synthesis

Concentrated HCl (0.113 mL) was dispersed in 3 mL of dry methanol. While stirring at 300 rpm NbEtOH (0.3 mL, 1.19 mmol) was added rapidly. The final concentration of Nb_2O_5 was calculated to be 91.63 mg/mL.

ZrO_2 NP Stock Solution Synthesis

Concentrated HCl (3 mL) was dispersed in 10 mL methanol. While stirring at 300 rpm 1.4 mL of zirconium(IV) butoxide (≥80% w/w in 1-butanol) was added rapidly. The final concentration of ZrO_2 was calculated to be 25.65 mg/mL.

PS-*b*-PEO Oxide Templating

PS-*b*-PEO (10mg) was dispersed in 10 mL of methanol prepared as described above. To the solution 0.109 mL of the Nb_2O_5 stock was added while stirring. After 5 minutes of stirring 0.889 mL of TiO_2 stock was added. An aliquot (1 mL) was taken from the solution and diluted with the addition of 2 mL of methanol. TEM grids were prepared by submerging carbon only (CF300-CU-50 from Electron Microscopy Sciences) in a solution and wicking the solvent away with a torn kimwipe.

Mesoporous Powder Synthesis

A generalized procedure for mesoporous materials is as follows. The solvent of the oxide/polymer solutions were removed by evaporation at atmosphere. The samples were then aged at 80°C for 12 hours followed by calcination at 350°C for 6 hours.

Transmission Electron Microscopy (TEM)

TEM images were acquired using a JEOL 1400 Plus TEM operated in bright field mode with an accelerating voltage of 120 keV.

Scanning Transmission Electron Microscopy (STEM)

STEM measurements were collected on a Thermo Fisher Scientific Talos F200X, Titan G2 at North Carolina State University, and JOEL NEOARM at Oak Ridge National Laboratory. Talos Images were collected at either 80kv or 200kv. Simultaneous HAADF and BF STEM images were collected using a camera length of ~130 mm and using a convergence semi-angle of ~10 mrad at 200kv and ~8 mrad at 80kv. EDS maps were collected using similar STEM optical conditions as

above using beam current of around 500 pA. The X-rat signals were collected by a Super-X quad EDS detector setup with a solid angle of 0.9 sr. EDS maps were processed to subtract the background signal and deconvolute any overlapping X-ray lines. All signal processing was performed using standard routines within the Thermo Fisher Velox software package.

Titan images were collected at either 80kv or 200kv. The convergence semi-angle was set to ~19 mrad, probe current to 500 pA, and camera length to ~100 mm. Elemental maps were acquired and processed using the standard background subtraction and peak deconvolution methods built into the Velox software package. EELS spectrum images were acquired at 200kV in EFSTEM mode, with a convergence semi-angle of ~19 mrad and a collection angle of ~60 mrad. Beam currents were reduced to 250pA for EELS acquisition. The ZLP position was monitored using the DualEELS functionality and the spectrometer dispersion was adjusted to enable the fitting of the Ti L and Nb M edges. NEOARM images were collected at 80kv equipped with 100 mm^2 windowless solid state device (SDD) spectrometers. EDS maps were gathered using the JOEL Analysis Station software.

Scanning Electron Microscopy (SEM)

Top-view images of calcined films were acquired with a Zeiss Ultraplus thermal field emission SEM using an accelerating voltage of 5 kev an in-lens secondary electron detector.

Small-Angle X-ray Scattering

SAXS measurements were conducted using a SAXSLab Ganesha at the South Carolina SAXS Collaborative. A Xenocs GeniX3D microfocus source was used with a Cu target to generate a monochromic beam with a 0.154 nm wavelength. National Institute of Standards and Technology

(NIST) reference material 640c silicon powder was used for instrument calibration with the peak position at $2\theta = 28.44°$ where 2θ is the total scattering angle. Two-dimensional scattering patterns were collected on a Pilatus 300 K detector (Dectris).

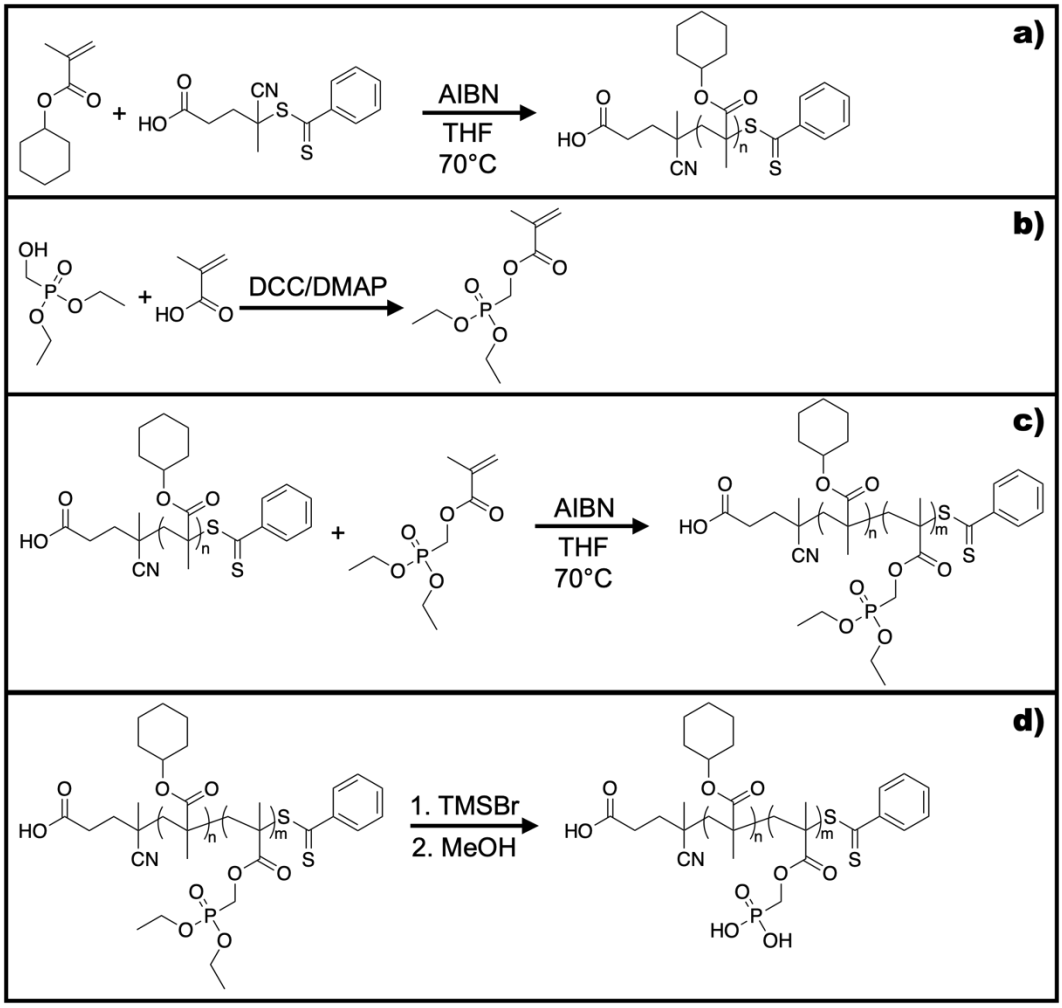

Figure S1. Schematic for the synthesis of PCHMA-*b*-PMMPA. First, PCHMA macro-initiator was synthesized via RAFT (a). DEPMMA monomer was synthesized through the esterification of diethyl(hydroxymethyl)phosphonate and methacrylic acid (b). A diblock polymer was then synthesized via RAFT with the PCHMA macro-initiator and DEPMMA (c). Finally, PCHMA-*b*-PMMPA was synthesized through the hydrolysis of PDEPMMA via the Mckenna reaction (d).

Table S1. Polymer properties for PCHMA-*b*-PDEPMMA.

Block	Composition	Mn (g/mol)	DP	Molar-Mass Dispersity
1	PCHMA	40,375	240	1.06
2	PDEPMMA	41,725	177	1.18*

*Dispersity of the total diblock polymer.

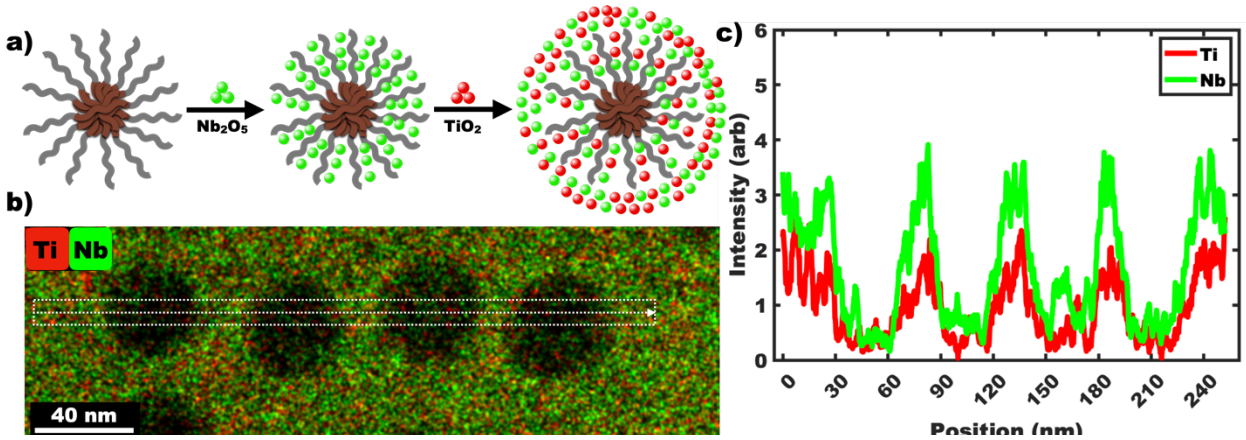

Figure S2. The schematic for D-Nb_2O_5-TiO_2 (a) (PS-*b*-PEO) with the resulting STEM-EDS image (b) and line-scan (c) showing a mixture of oxides due to lack of persistent interactions between NPs and the SDA.

Table S2. Polymer properties for PCHMA-*b*-PMAA-*b*-PPEGMA. Here M_n and DP were determined via ^{1}H-NMR conversion.

Block	Composition	Mn (g/mol)	DP	Molar-Mass Dispersity
1	PCHMA	16,991	101	1.05
2	PMAA	5,593	67	N/A
3	PPEGMA	10,010	20	N/A

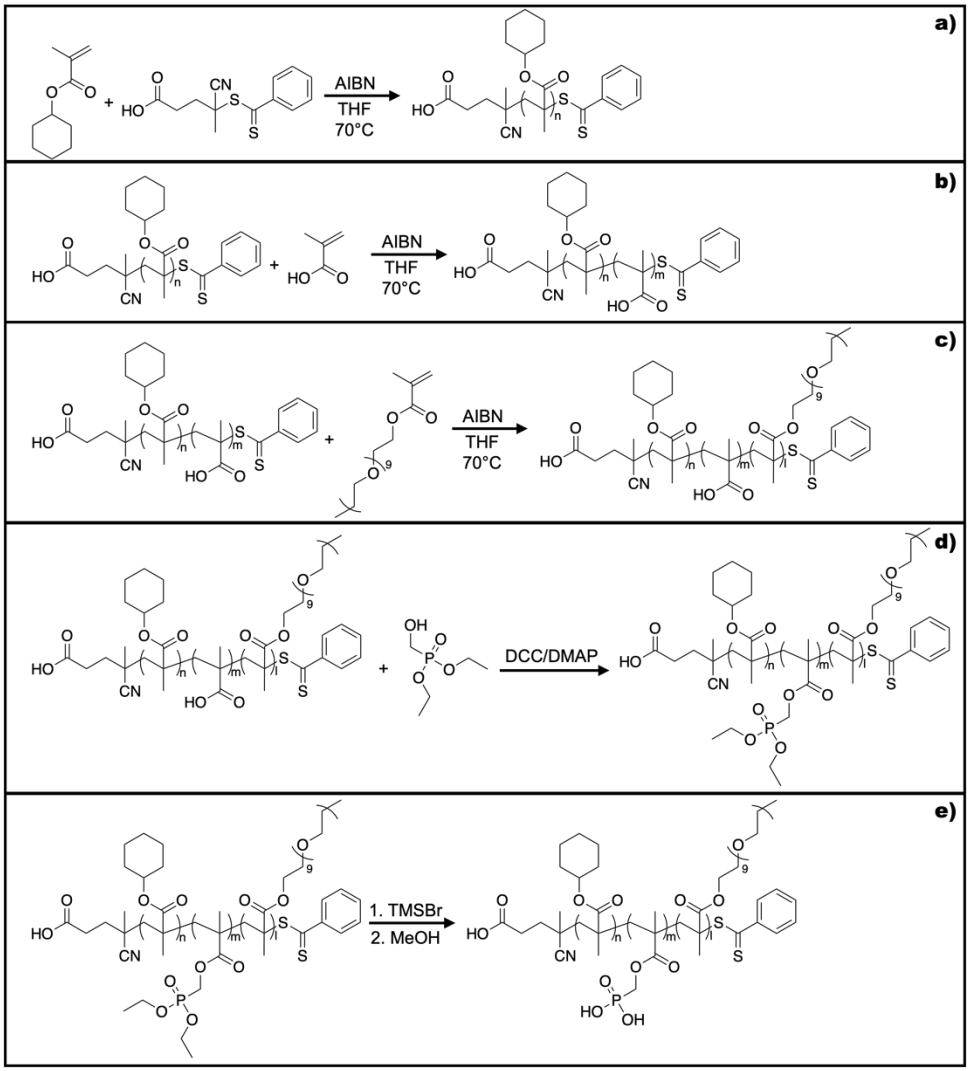

Figure S3. Schematic for the synthesis of PCHMA-*b*-PMMPA-*b*-PPEGMA. Here PCHMA was first synthesized via RAFT (a). Then PCHMA-*b*-PMAA was synthesized with the PCHMA macroinitiator and MAA (b). Then PCHMA-*b*-PMAA-*b*-PPEGMA was synthesized from the PCHMA-*b*-PMAA macroinitiator with PEGMA (c). PCHMA-*b*-PMAA-*b*-PPEGMA was subsequently esterified with diethyl(hydroxymethyl)phosphonate (d). Finally, PCHMA-*b*-PMMPA-*b*-PPEGMA was synthesized via the hydrolysis of the phosphonated ester via the Mckenna reaction (e).

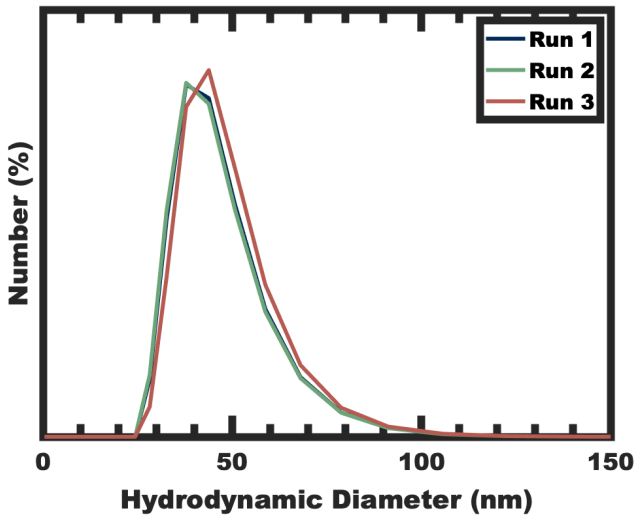

Figure S4. DLS measurements for PCHMA-*b*-PMMPA dispersed in MeOH (10 mg/mL) to verify micelle formation.

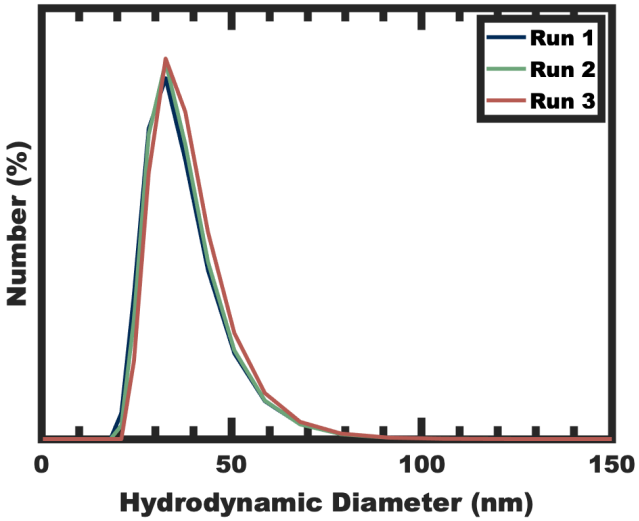

Figure S5. DLS measurements for PCHMA-*b*-PMMPA-*b*-PPEGMA dispersed in MeOH (10 mg/mL) to verify micelle formation.

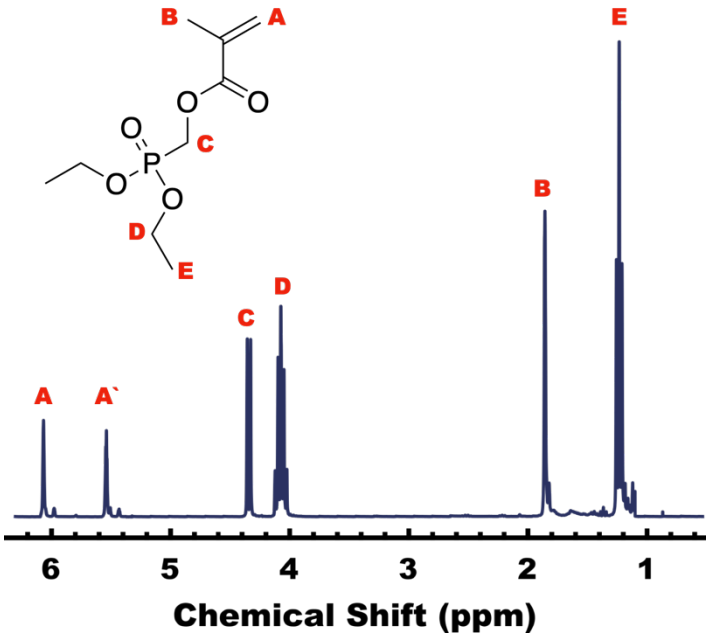

Figure S6. ^{1}H-NMR for DEPMMA in $CDCl_3$.

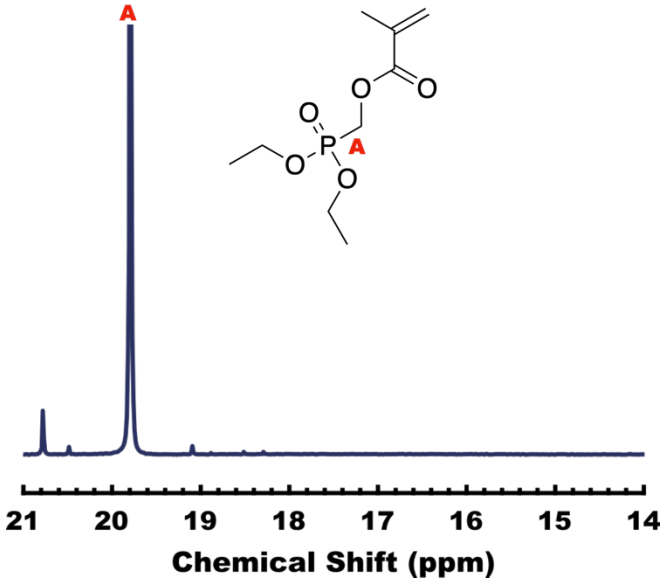

Figure S7. ^{31}P-NMR for DEPMMA in $CDCl_3$.

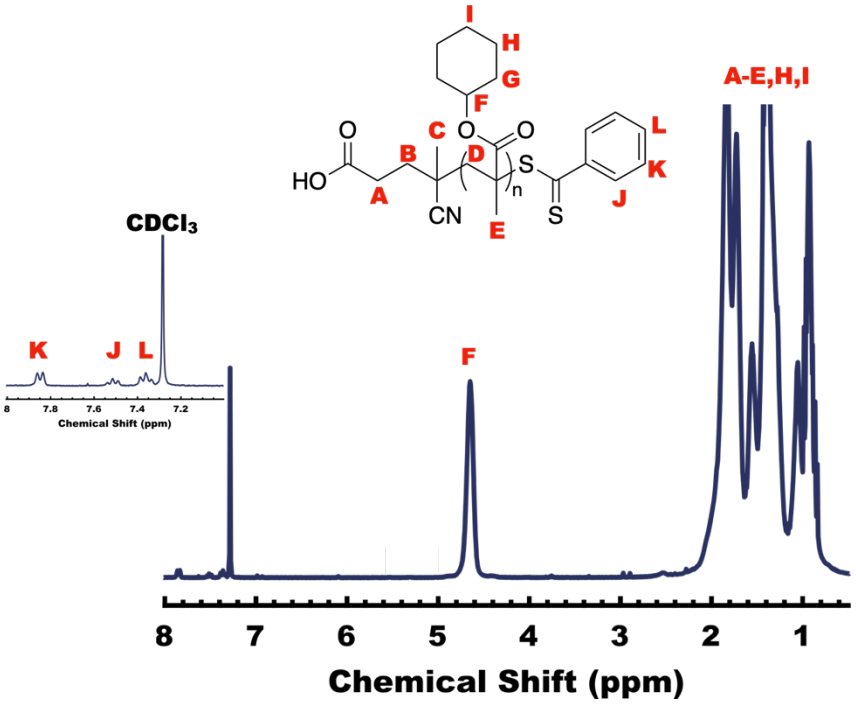

Figure S8. ^{1}H-NMR of PCHMA used for the synthesis of the triblock dispersed in $CDCl_3$.

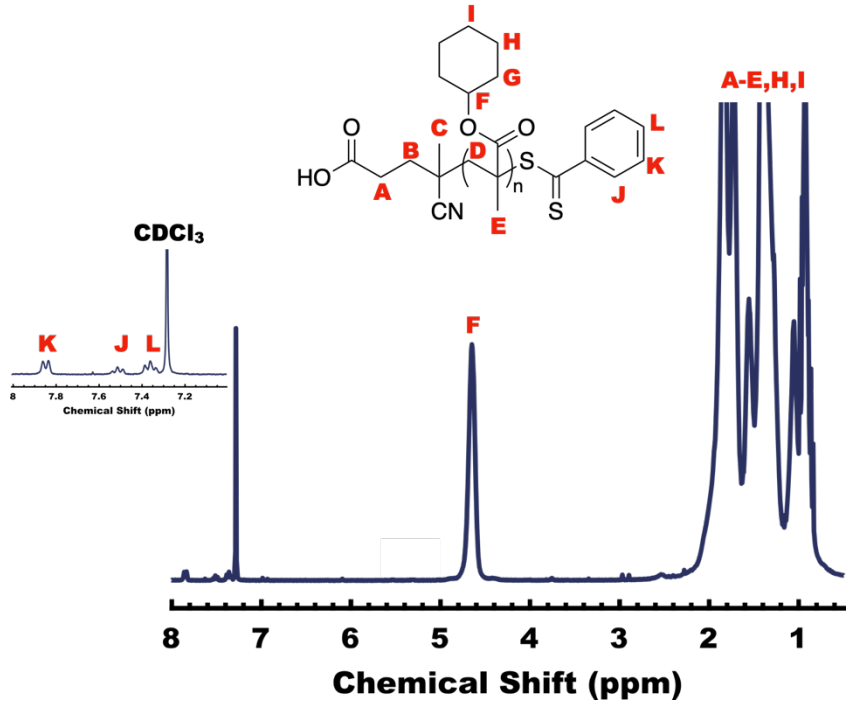

Figure S9. ^{1}H-NMR of PCHMA used for the synthesis of the diblock dispersed in $CDCl_3$.

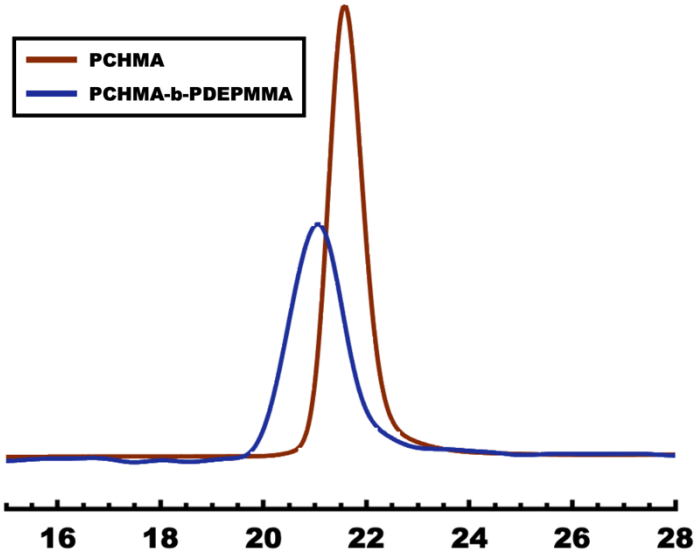

Figure S10. GPC trace overlays for PCHMA used for the synthesis of the diblock and PCHMA-*b*-PDEPMMA.

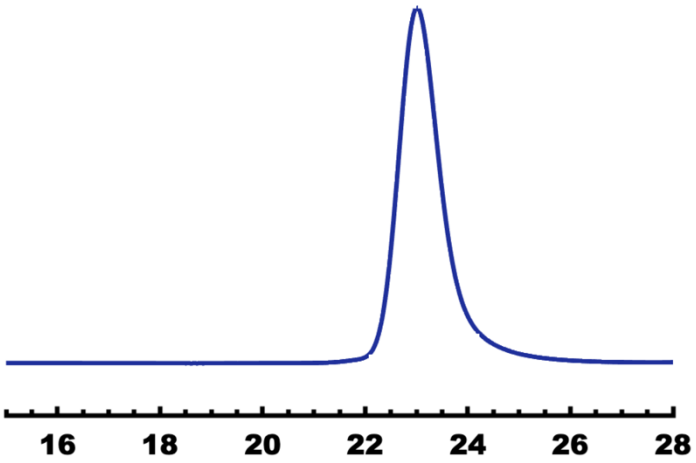

Figure S11. GPC trace for PCHMA used in the synthesis of the triblock.

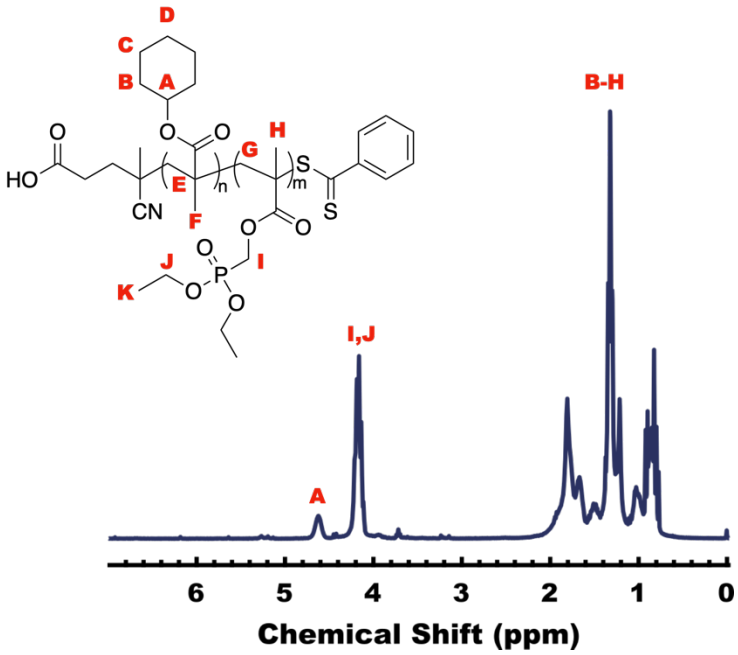

Figure S12. ^{1}H-NMR for PCHMA-*b*-PDEPMMA in $CDCl_3$. Conversion of PDEPMMA was based on the ratio of proton "A" to protons "I" and "J".

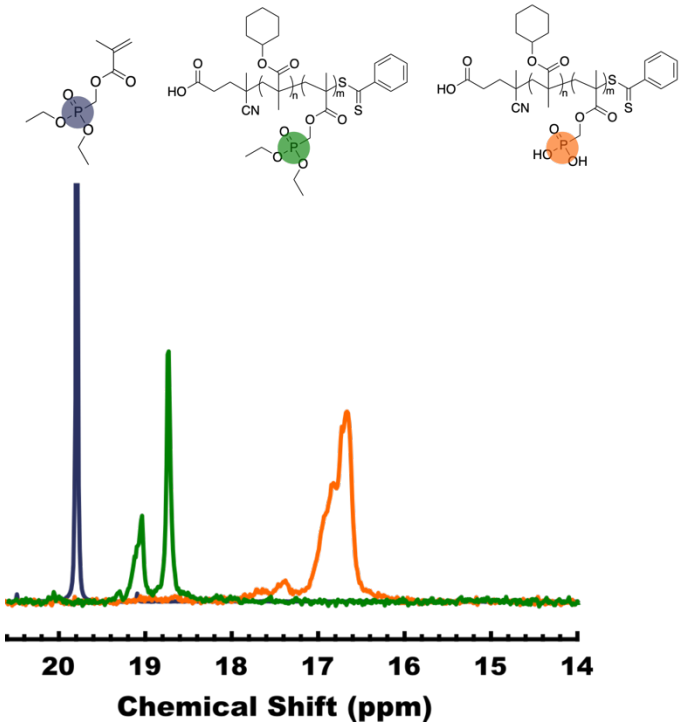

Figure S13. ^{31}P-NMR results for DEPMMA (~20 ppm), PCHMA-*b*-PDEPMMA (~19 ppm), and PCHMA-*b*-PMMPA (17 ppm) showing the chemical shifts associated with the polymerization and resulting hydrolysis of DEPMMA.

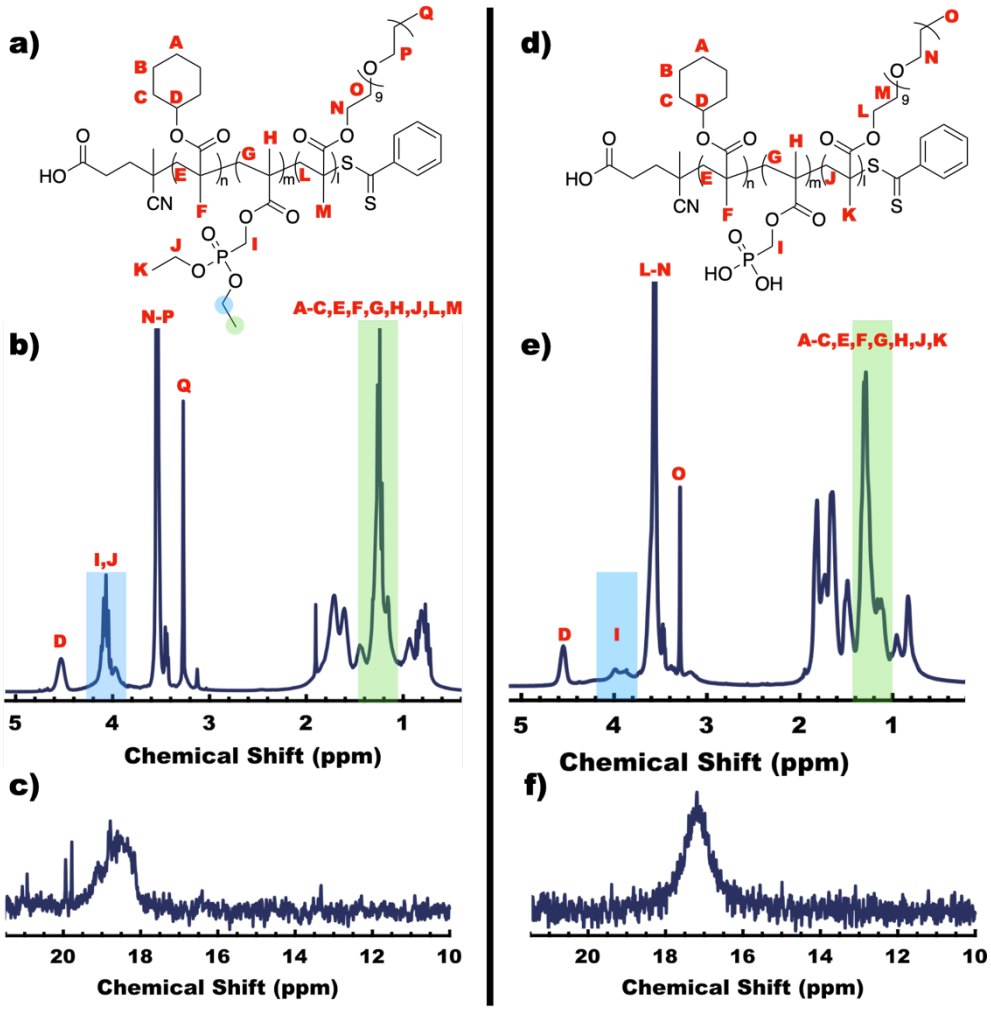

Figure S14. ^{1}H-NMR (b) and ^{31}P-NMR (c) for PCHMA-*b*-PDEPMMA-*b*-PPEGMA (a) compared to the ^{1}H-NMR (e) and ^{31}P-NMR (f) for PCHMA-*b*-PMMPA-*b*-PPEGMA (d) tracking the hydrolysis of the phosphonated ester.

Table S3. NP:polymer mass ratios for samples prepared.

Figure	Sample Name	NP_1:Polymer Mass Ratio	NP_2:Polymer Mass Ratio
3a	P-ZrO_2-TiO_2	1.8	4.0
3d	P-Nb_2O_5-TiO_2	1.0	4.0
3e	P-ZrO_2-Nb_2O_5	1.8	4.0
3f	P-TiO_2-Nb_2O_5	0.6	4.0
3g	P-Nb_2O_5-ZrO_2	1.0	4.0
4a	P-TiO_2-Nb_2O_5	0.6	1.1
4b	N/A	0.6	0.5
5	PD-TiO_2-Nb_2O_5	0.1	1.0

Supplementary Discussion

NP Incorporation Experiments

Preliminary STEM-EDS results of as-made (Figure S15a) and calcined (Figure S15b) materials from PCHMA-*b*-PMMPA-*b*-PPEGMA with NP_1=TiO_2 and NP_2=Nb_2O_5 indicated random mixtures of the two oxides. This suggested that insufficient time was allotted to allow for permeation of NP_1 through the PPEGMA corona to reach PMMPA for persistent attachment.

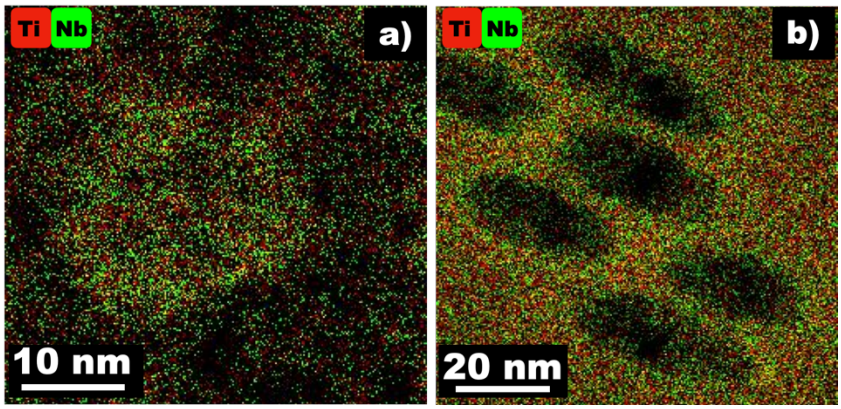

Figure S15. STEM-EDS images for PCHMA-*b*-PMMPA-*b*-PPEGMA micelles combined with NP_1=TiO_2 and NP_2=Nb_2O_5 as-made (a) and calcined (b) indicating a random mixture of the two oxides.

Bright-field TEM experiments revealed this NP penetration process. For this set of experiments PCHMA-*b*-PMMPA-*b*-PPEGMA was first dispersed as micelles followed by the addition of NP_1=TiO_2. A TEM sample was prepared promptly and another after 40 hrs of shaking. The gradual incorporation of NP_1 is apparent by the reduced size of the region containing oxide (dark, Figure S16), consistent with NP_1 passing through PPEGMA and reacting with PMMPA.

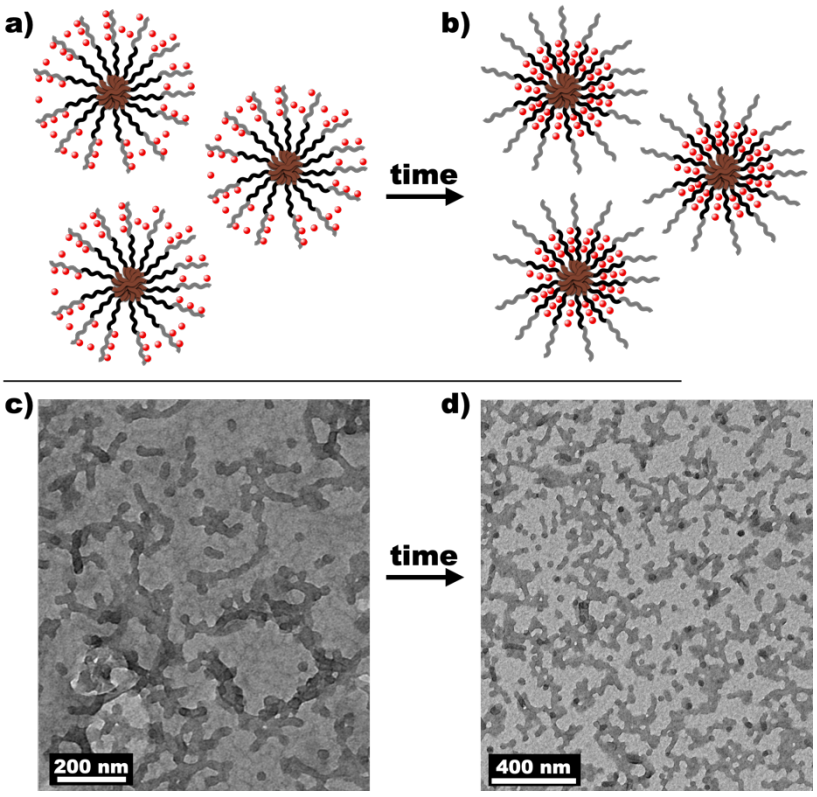

Figure S16. Schematic showing the NP integration process (a-b) and the corresponding TEM images of PCHMA-*b*-PDEPMMA-*b*-PPEGMA micelles combined with NP_1=TiO_2 either prepared promptly (c) or after 40hrs of shaking (d).

Further confirmation of this NP-diffusion process was observed by comparing powdered samples prepared by casting the solutions either promptly or after 40 hrs of agitation (Figure S17a,b). Despite both samples having the same overall NP:polymer mass ratio and having the same calcination conditions, the resulting SEM pore sizes were different. The promptly cast sample had larger 17.11±1.8 nm diameter pores whereas the 40 hr of agitation sample had 13.99±1.6 nm diameter pores, indicating NP diffusion farther towards the micelle core. This pore size trend was also evidenced by BJH analysis of physisorption data (Figure S17c). Lastly, SAXS measurements also supported this trend where the pore-to-pore distance (d-spacing) for the prompt sample was larger than that for the 40 hr of agitation sample, 27.4 nm vs 20.6 nm. Here, the incorporation of

NPs closer to the micelle core is expected to decrease the micelle-to-micelle spacing and thus the final pore-to-pore spacing.

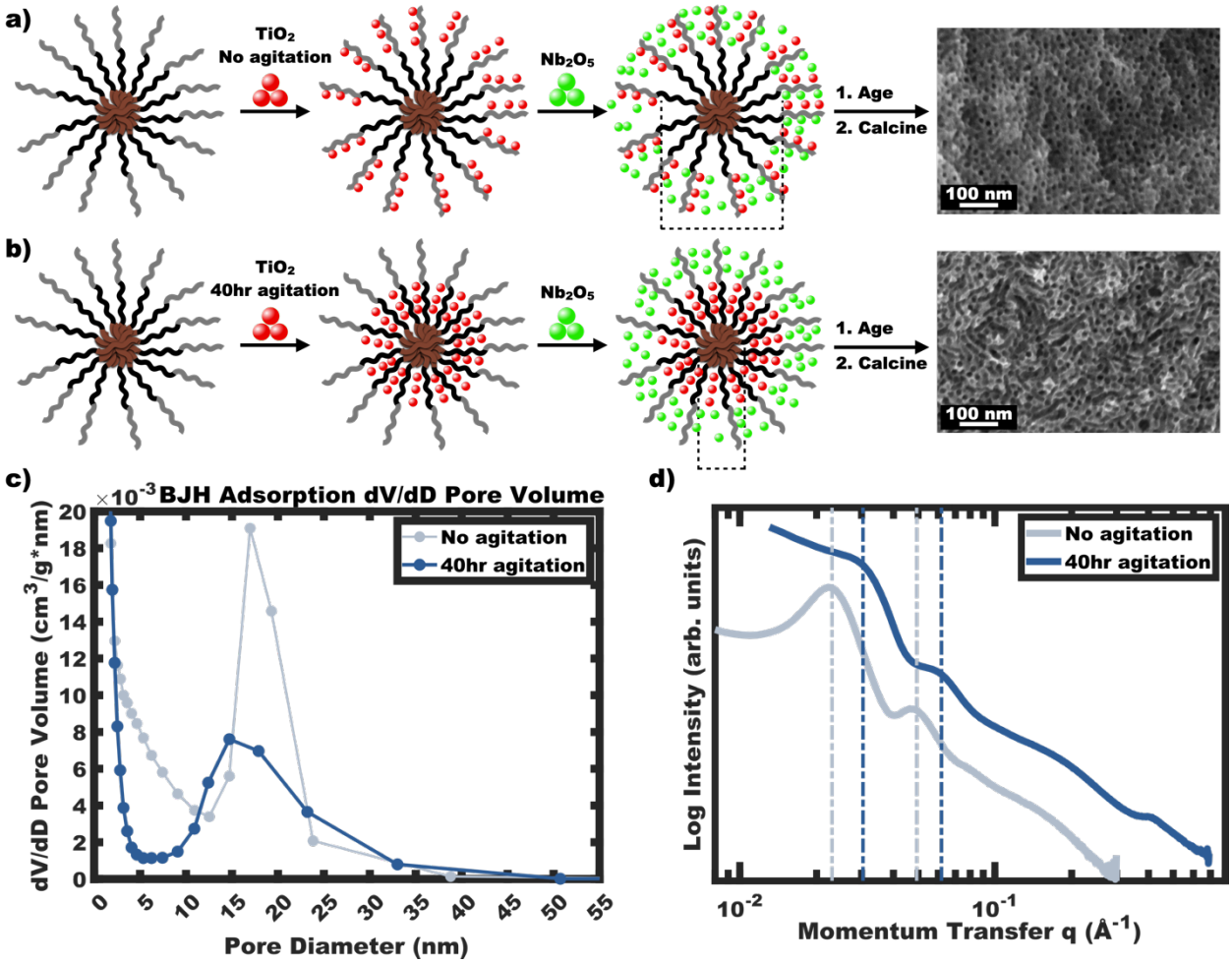

Figure S17. Schematic and resulting SEM images for PCHMA-*b*-PMMPA-*b*-PPEGMA materials prepared with no agitation of micelles and NP_1 (a) and with a 40 hr agitation of micelles and NP_1 (b). The respective materials were then compared via BET (c) and SAXS (d).

References

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