Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Nanonetwork Photogrowth Expansion: Tailoring Nanoparticle Networks' Chemical Structure and Local Topology

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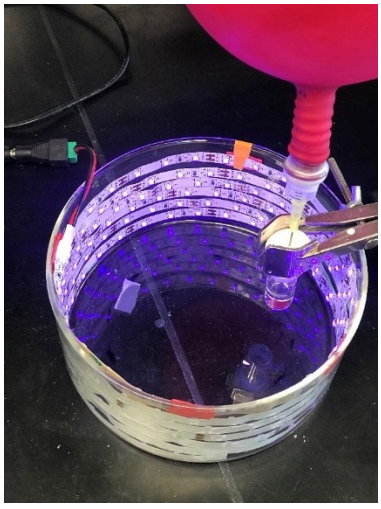
EXPERIMENTAL SECTION

Materials. All reagents and solvents were purchased from Sigma Aldrich and used as received unless otherwise stated. Methyl acrylate (MA, 99%), t-butyl acrylate (tBA, 98%), 2,2,2-trifluoroethyl acrylate (TFEA, 99%) were purified immediately before use by passing through a short column of inhibitor removers purchased from Sigma Aldrich. N-isopropylacrylamide (NIPAAM, 97%) was recrystallized from hexanes. 2-Hydroxyethyl acrylate (HEA, 96%) was purified by first dissolving the monomer in water (25% by volume). The solution was extracted with hexanes six times to remove diacrylate and with ether six times to remove acrylic acid. $MgSO_4$ drying agent was used to remove traces of water in the ether phase before evaporation. The monomer was then passed through short column of inhibitor removers immediately before use. The monomer was then dried under high vacuum for 20 minutes before use. 10-phenylphenothiazine (PTH)[1] was prepared according to literature. TTC **1a** and PGNNs were synthesized as previously reported [2]. All photogrowth polymerizations were performed in a circular glass dish lined with a 400 nm LED strip (390 nm - 405 nm, 24W/5m) and cooled by compressed air (showed below).



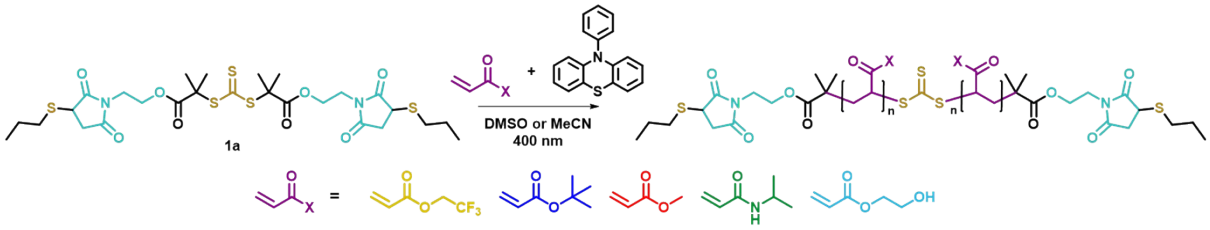
Material Characterization. All ^{1}H and ^{13}C spectra were obtained using a JEOL ECA 400 (400 MHz), JEOL ECA 500 (500 MHz), or ECA-600 (600 MHz) spectrometer. Chemical shifts were

measured relative to residual solvent peaks as an internal standard. TEM imaging was performed using either a JEOL 2000 FX or JEOL 2010 F Transmission Electron Microscope at 200 kV with formvar coated or holey carbon coated copper grids. Gel permeation chromatography (GPC) was performed using a Tosoh high performance GPC system HLC-8320 equipped with an auto injector, a dual differential refractive index detector and TSKgel G series columns connected in series (7.8×300 mm TSKgel G5000Hxl, TSKgel G4000Hxl, TSKgel G3000Hxl). GPC analysis was carried out in HPLC grade tetrahydrofuran (THF) with a flow rate of 1.0 mL/min at 40 °C or N,N-dimethylformamide (DMF) with a flow rate of 1.0 mL/min at 60 °C. Molecular weights (Mn and Mw) and molecular weight distributions were calculated from polymethyl methacrylate (PMMA) standards with molecular weights of 800 to 2.2×106 g mol-1 provided by Polymer Standard Service (PSS). Dynamic light scattering (DLS) was measured on a Malvern Zetasizer Nano ZS in THF, methanol, or water at 25°C with an angle of 173° and at appropriate sample concentrations.

Synthesis. All model polymerizations conducted used TTC:monomer ratio of 1:500. Model Polymerizations. TTC **1a** (4.0 mg, 0.0059 mmol) was dissolved in 2M monomer solution in DMSO or MeCN with PTH (0.02-0.1 mol%) in a 1-dram vial. The reaction vessel was sealed and sparged with nitrogen for 20 minutes. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes. The polymers were precipitated in cold diethyl ether, unless otherwise stated, and then analyzed by GPC.

Polymerization of ABA and ABABA block copolymers were conducted following the same procedure with macroinitiator and PTH (0.02-0.1 mol%) in 1M monomer solution in DMSO or MeCN.

(NOTE: MeCN was chosen as the solvent for tBA and NIPAAM, as PtBA is insoluble in DMSO and polymerizations of NIPAAM in DMSO yielded increased dispersites. TFEA can be polymerized in either DMSO or MeCN but produced lower dispersities in MeCN. PHEA has poor solubility in MeCN and was polymerized in DMSO. Solvents for the statistical copolymerizations were chosen to accommodate monomers with poor solubility. Copolymers of MA/tBA were performed in MeCN due to PtBA's poor solubility in DMSO. Copolymers of MA/HEA were performed in DMSO due to PHEA's poor solubility in MeCN. Copolymers of MA/TFEA were performed in DMSO as TFEA can be polymerized in both solvents and MA displayed lower dispersity when polymerized in DMSO. Solvents for the preparation of block copolymers were again chosen based off the solubilities of the previous block and the block that is to be added, or in the case of TFEA solvent was chosen based off conditions that produced the lowest dispersity.)



Scheme S1. Model polymerization of various monomers.

Procedure for results documented in Table S1.

Synthesis of PMA: TTC **1a** (4.0 mg, 0.0059 mmol) was dissolved in DMSO or MeCN (1.47 mL) and MA (264 µL, 2.94 mmol) with PTH (0.02 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes (MeCN solution in an ice bath). The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PtBA: TTC **1a** (4.0 mg, 0.0059 mmol) was dissolved in MeCN (1.47 mL) and MA (430 μL, 2.94 mmol) with PTH (0.1 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes in an ice bath. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes. The polymer was precipitated in cold hexanes.

Synthesis of PNIPAAM: TTC **1a** (4.0 mg, 0.0059 mmol) was dissolved in MeCN (1.47 mL) and MA (332 mg, 2.94 mmol) with PTH (0.05 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes (MCN solution in an ice bath). The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PHEA: TTC **1a** (4.0 mg, 0.0059 mmol) was dissolved in DMSO (1.47 mL) and HEA (337 μL, 2.94 mmol) with PTH (0.02 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PTFEA: TTC **1a** (4.0 mg, 0.0059 mmol) was dissolved in DMSO or MeCN (1.47 mL) and TFEA (372 μL, 2.94 mmol) with PTH (0.02 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes (MeCN solution in an ice bath). The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes. The polymer was precipitated in cold 1:1 mixture of hexanes:diethyl ether.

Procedure for results documented in Table S2.

Synthesis of PMA-*co*-PtBA(80/20): TTC **1a** (4.0 mg, 0.0059 mmol) was dissolved in MeCN (1.47 mL) and MA (211 μL, 2.35 mmol) and tBA (86 μL, 0.59 mmol) with PTH (0.1 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes in an ice bath. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PMA-*co*-PHEA(80/20): TTC **1a** (4.0 mg, 0.0059 mmol) was dissolved in DMSO (1.47 mL) and MA (211 μL, 2.35 mmol) and HEA (67 μL, 0.59 mmol) with PTH (0.02 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes (MeCN solution in an ice bath). The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PMA-*co*-PTFEA (80/20): TTC **1a** (4.0 mg, 0.0059 mmol) was dissolved in DMSO (1.47 mL) and MA (211 μL, 2.35 mmol) and TFEA (74 μL, 0.59 mmol) with PTH (0.02 – 0.1 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Procedure for results documented in Table S3.

Synthesis of PMA macroinitiator: TTC **1a** (36.0 mg, 0.0531 mmol) was dissolved in MeCN (13.23 mL) and MA (2.38 mL, 26.46 mmol) with PTH (0.1 mol%). The reaction vessel was sealed and sparged with nitrogen for 30 minutes in an ice bath. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PMA-*b*-PtBA-*b*-PMA: PMA macroinitiator (40.0 mg, 0.0036 mmol) was dissolved in MeCN (1.80 mL) and tBA (263 μL, 1.80 mmol) with PTH (0.02 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes in an ice bath. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PMA-*b*-PHEA-*b*-PMA: PMA macroinitiator (40.0 mg, 0.0036 mmol) was dissolved in DMSO (1.80 mL) and HEA (206 μL, 1.80 mmol) with PTH (0.02 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PMA-*b*-PTFEA-*b*-PMA: PMA macroinitiator (20.0 mg, 0.0027 mmol) was dissolved in MeCN (1.35 mL) and TFEA (171 μL, 1.35 mmol) with PTH (0.02 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes in an ice bath. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PMA-*b*-PNIPAAM-*b*-PMA: PMA macroinitiator (20.0 mg, 0.0023 mmol) was dissolved in MeCN (1.58 mL) and NIPAAM (130 mg, 1.15 mmol) with PTH (0.005 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes in an ice bath. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PMA-*b*-PtBA-*b*-PMA-*b*-PtBA-*b*-PMA: PMA-*b*-PtBA-*b*-PMA macroinitiator (40.0 mg, 0.0021 mmol) was dissolved in MeCN (1.04 mL) with PTH (0.1 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes in an ice bath. Degassed monomer MA (93

μL, 1.04 mmol) was added to the vessel. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

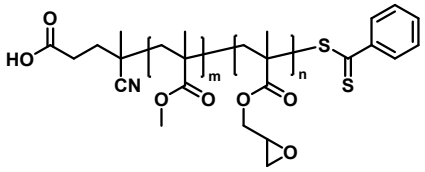
Synthesis of PMA-*b*-PHEA-*b*-PMA-*b*-PHEA-*b*-PMA: PMA-*b*-PHEA-*b*-PMA macroinitiator (80.0 mg, 0.0013 mmol) was dissolved in DMSO (0.64 mL) with PTH (0.02 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes. Degassed monomer MA (58 μL, 0.64 mmol) was added to the vessel. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PMA-*b*-PTFEA-*b*-PMA-*b*-PTFEA-*b*-PMA: PMA-*b*-PHEA-*b*-PMA macroinitiator (21.0 mg, 0.0019 mmol) was dissolved in DMSO (0.94 mL) with PTH (0.02 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes. Degassed monomer MA (84 μL, 0.94 mmol) was added to the vessel. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

Synthesis of PMA-*b*-PNIPAAM-*b*-PMA-*b*-PNIPAAM-*b*-PMA: PMA-*b*-PNIPAAM-*b*-PMA macroinitiator (40.0 mg, 0.0021 mmol) was dissolved in MeCN (1.04 mL) with PTH (0.1 mol%). The reaction vessel was sealed and sparged with nitrogen for 20 minutes in an ice bath. Degassed monomer MA (93 μL, 1.04 mmol) was added to the vessel. The reaction was then placed 2 cm from a 400 nm led light source and irradiated for 30 minutes.

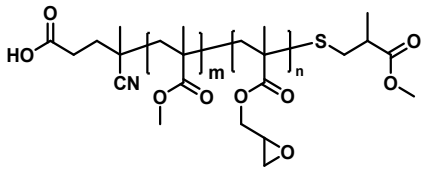
General Procedure for the Photogrowable Nanonetworks (PGNNs)

General procedure for the preparation of PMMA-co-GMA (2)



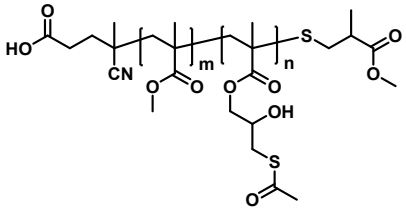
Reactions were prepared using the ratio (MMA/GMA/CPADB/EY/Et_3N) (80/20/1/0.02/1) in a 1:1 monomer:DMSO ratio. Reactions were irradiated with a 3.5 W blue light for the desired amount of time and then precipitated twice in diethyl ether. (Mn=6.20 kDa, PDI=1.09, MMA=81%, GMA=19%)

General aminolysis procedure of PMMA-co-GMA (3)



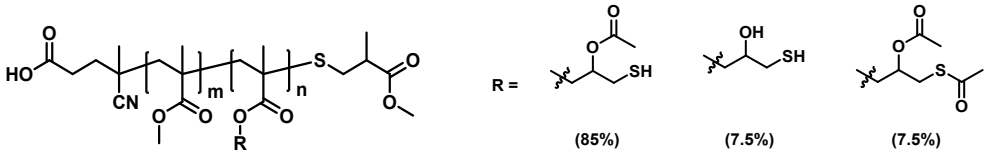
To a sealed 6 dram vial **2** (1.5 g) was added and covered with a nitrogen atmosphere, and then dissolved in degassed THF (15 mL). MMA (500 μL) and piperidine (250 μL) were added under nitrogen. After 6 hours the reaction was precipitated into diethyl ether. The product was dissolved in THF (10 mL) and treated with dithiothreitol (DTT) for 3 hours under nitrogen. MMA (500 μL) and triethylamine (50 μL) were added to the solution and the reaction stirred for 3 hours under nitrogen. The reaction was precipitated into diethyl ether twice and dried under vacuum to give 1.44 g of a colorless product.

General thiolation procedure of aminolyzed PMMA-co-GMA (4)



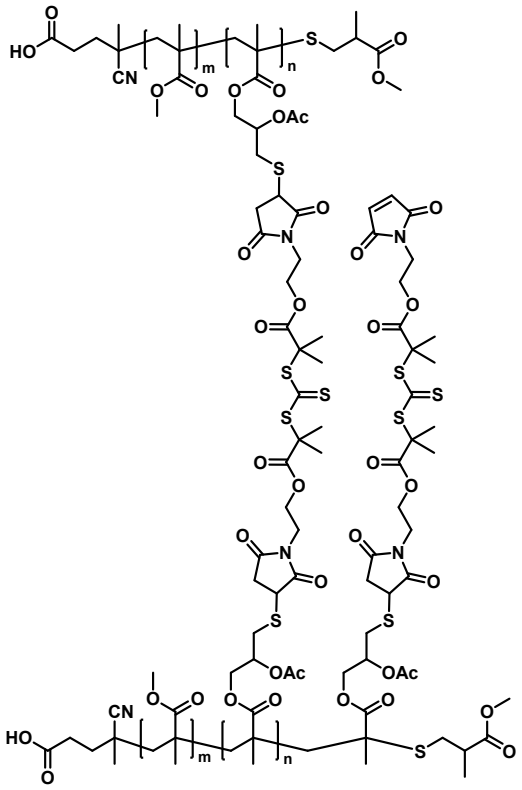
Thioacetic acid (207 μL, 2.9 mmol) and *i*-Pr_2NEt (84 μL, 0.48 mmol) were added to a solution of **3** (1.44 g, 2.42 mmol epoxide) in $CDCl_3$ (5 mL). The reaction stirred for 18 hours. The product was then precipitated twice in diethyl ether and dried under vacuum to give 1.39 g of the protected thiolated product.

General acetyl migration procedure of thiolated PMMA-co-GMA (5)



Triethylamine (Et_3N) (10 mL) was added dropwise to a vigorously stirring solution of **4** (1.39 g) in $CHCl_3$ (50 mL) under nitrogen. After 18 hours the reaction was concentrated and precipitated twice in diethyl ether to give 1.35 g of the deprotected product.

General procedure for thiol-maleimide nano-network formation



A solution of **5** in THF and stirred with DTT for 3 hours to reduce any disulfide bonds. The polymer was purified with Sephadex LH-20. The polymer (250 mg) was dried and then dissolved in $CHCl_3$ (50 mL) under a nitrogen atmosphere. Maleimide crosslinker **1** (327 mg, 2 equivalents to thiols) and Et_3N (73 uL, 0.2 equivalents to thiols) in $CHCl_3$ (12 mL) were added dropwise to the vigorously stirring solution of **5** under nitrogen. After 18 hours the reaction was diluted with CH_2Cl_2 and dialyzed for two days in 10 kDa MWCO snakeskin tubing against a 1:1 mixture of ACN:THF.

General Procedure for the Photogrowth of the PNN's

Nano-networks (4 mg) were sealed in a vial, covered with a nitrogen atmosphere, and dissolved in a solution of degassed monomer (MA, tBA, HEA, TFEA, NIPAAM) (3 mmol) in the appropriate solvent (MeCN or DMSO) (3 mL) with PTH (0.005 to 0.1 mol%). The reaction was then placed 2 cm from a 400 nm light source and irradiated for the desired amount of time. The crude product was diluted with CH_2Cl_2 or methanol and dialyzed in 10 kDa MWCO snakeskin tubing against a 1:1:1 mixture of CH_2Cl_2:MeCN:THF or a 1:1 mixture of methanol:MeCN for 2 days.

General procedure for controlled photo-growth of block copolymer nano-networks

PMA ENN macroinitiator (24 mg) was sealed in a vial and dissolved in a solution of degassed monomer (tBA, HEA, TFEA, NIPAAM) (3 mmol) in the appropriate solvent (MeCN or DMSO) (3 mL) with PTH (0.005 to 0.1 mol%). The reaction was then placed 2 cm from a 400 nm light source and irradiated for 30 minutes. The crude product was diluted with CH_2Cl_2 or methanol and dialyzed in 10 kDa MWCO snakeskin tubing against a 1:1:1 mixture of CH_2Cl_2:MeCN:THF or a 1:1 mixture of methanol:MeCN for 2 days.

PMA-*b*-X-*b*-PMA triblock ENN macroinitiator (50% of the total mg produced) was sealed in a vial and dissolved in a solution of degassed monomer (MA) (1.5 mmol) in the appropriate solvent (MeCN or DMSO) (1.5 mL) with PTH (0.005 to 0.1 mol%). The reaction was then placed 2 cm from a 400 nm light source and irradiated for 30 minutes. The crude product was diluted with CH_2Cl_2 or methanol and dialyzed in 10 kDa MWCO snakeskin tubing against a 1:1:1 mixture of CH_2Cl_2:MeCN:THF or a 1:1 mixture of methanol:MeCN for 2 days.

Procedure for the controlled photo-growth of nano-networks into microparticles

Nano-networks (4 mg) were sealed in a vial, covered with a nitrogen atmosphere, and dissolved in a solution of degassed MA (1.2 mL) in MeCN (13 mL) with PTH (0.1 mol%). The reaction was then placed 2 cm from a 400 nm light source and irradiated for the desired amount of time. The crude product was diluted with CH_2Cl_2 and dialyzed in 10 kDa MWCO snakeskin tubing against a 1:1 mixture of MeCN:THF for 2 days.

General procedure for the aminolysis of expanded nano-networks

Piperidine (10 uL) was added to a solution of expanded nano-networks (10 mg) in DMF (0.5 mL). The reaction was stirred for 18 hours and then treated with DTT for 3 hours before dialysis in 10 kDa MWCO snakeskin tubing against 1:1 MeCN:THF for 24 hours. The purified product was concentrated, dissolved in HPLC grade DMF, filtered and analyzed by GPC.

General procedure for NIPAAM ENN thermoresponse graph

NIPAAM and HEA ENN solutions were prepared in appropriate concentrations in water. Diameter measurements were taken in triplicate every 2°C while heating from 25°C to 45°C. Samples were equilibrated to the new temperature for 5 minutes in between measurements.

GPC Analysis of Optimized Model Polymerizations

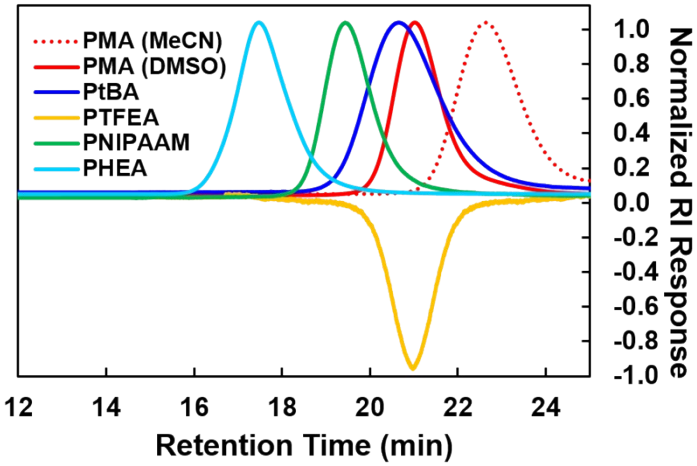


Figure S1. GPC traces of model homopolymerizations.

Table S1. Model homopolymerizations with TTC 1a

#	monomer	PTH (mol %)	solvent	M_n[a]	Đ[a]
1	MA	0.02	MeCN	6,400	1.06
2	MA	0.02	DMSO	11,100	1.09
3	tBA	0.10	MeCN	12,700	1.14
4	NIPAAM	0.005	MeCN	23,300	1.11
5	TFEA	0.02	MeCN	14,800	1.11
6	HEA	0.02	DMSO	75,600	1.31

[a] Molecular weight and polydispersity were determined by GPC analysis (DMF as eluent).

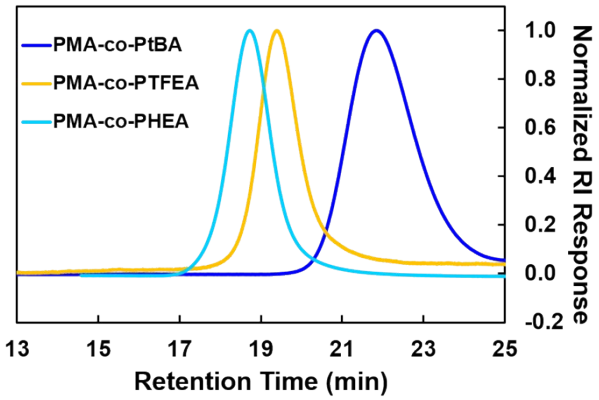


Figure S2. GPC traces of model statistical copolymerizations.

Table S2. Model statistical copolymerizations with TTC 1a

#	sample	monomers	monomer feed (MA/X)	PTH (mol %)	solvent	M_n[a]	Đ[a]	monomer incorporation (MA/X)
1	PMA-co-tBA	MA/tBA	80/20	0.10	MeCN	12,800	1.10	78/22
2	PMA-co-PTFEA	MA/TFEA	80/20	0.02	DMSO	24,200	1.12	76/24
3	PMA-co-PHEA	MA/HEA	80/20	0.02	DMSO	35,900	1.17	81/19

[a] Molecular weight and polydispersity were determined by GPC analysis (DMF as eluent).

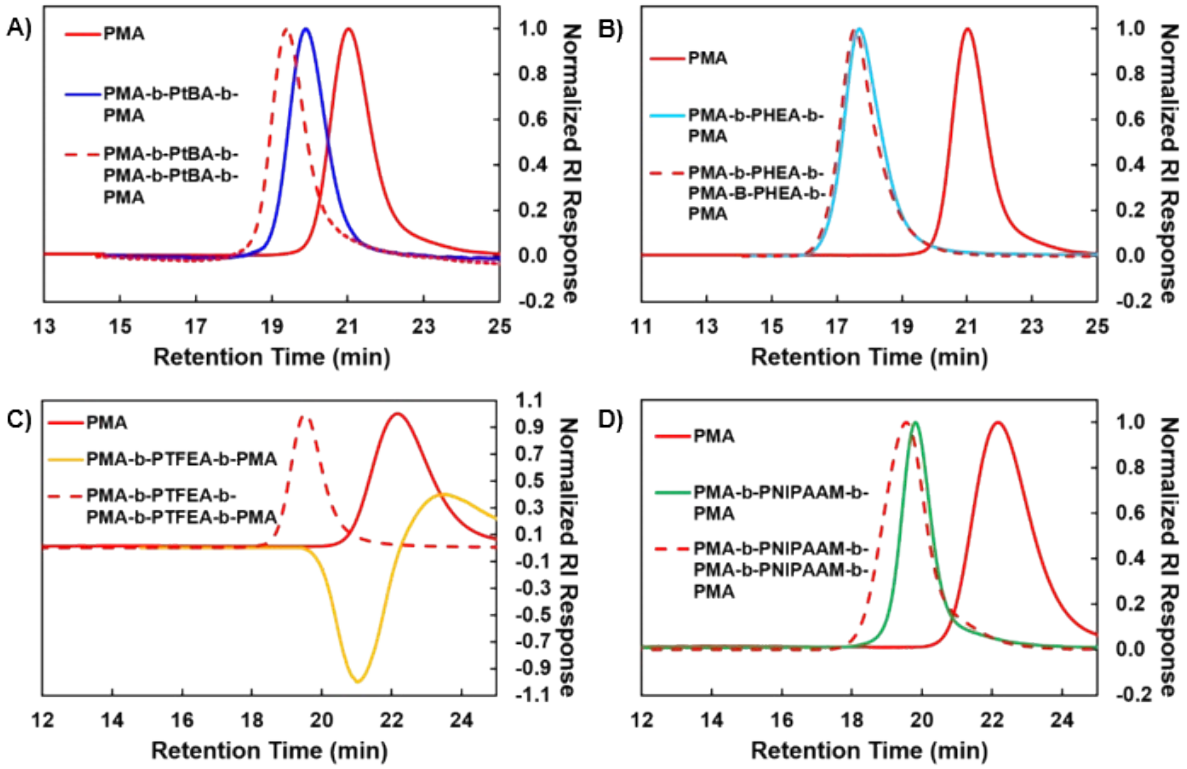


Figure S3. GPC traces of model block copolymerizations with MA and A) tBA, B) HEA, C) TFEA, D) PNIPAAM.

Table S3. Model block copolymerizations with TTC 1a

#	sample	Macroinitiator (MI)	MI M_n[a] (g/mol)	MI Đ[a]	monomer	PTH (mol%)	solvent	M_n[a] (g/mol)	Đ[a]
1	PMA-*b*-PtBA-*b*-PMA	PMA	11,100	1.09	tBA	0.10	MeCN	19,500	1.07
2	PMA-*b*-PHEA-*b*-PMA	PMA	11,100	1.09	HEA	0.02	DMSO	62,100	1.28
3	PMA-*b*-PTFEA-*b*-PMA	PMA	8,700	1.10	TFEA	0.02	MeCN	-	-
4	PMA-*b*-NIPAAM-*b*-PMA	PMA	8,700	1.10	NIPAAM	0.005	MeCN	24,900	1.14
5	PMA-*b*-PtBA-*b*-PMA- *b*-PtBA-*b*-PMA	PMA-*b*-PtBA-*b*-PMA	19,500	1.07	MA	0.10	MeCN	23,600	1.11
6	PMA-*b*-PHEA-*b*-PMA- *b*-PHEA-*b*-PMA	PMA-*b*-PHEA-*b*-PMA	62,100	1.28	MA	0.02	DMSO	65,500	1.33
7	PMA-*b*-PTFEA-*b*-PMA-*b*-PTFEA-*b*-PMA	PMA-*b*-PTFEA-*b*-PMA	-	-	MA	0.02	DMSO	29,000	1.14
8	PMA-*b*-NIPAAM-*b*-PMA-*b*-NIPAAM-*b*-PMA	PMA-*b*-PNiPAAm-*b*-PMA	24,900	1.14	MA	0.10	MeCN	28,400	1.24

[a] Molecular weight and polydispersity were determined by GPC analysis (DMF as eluent).

Selected NMR Spectra

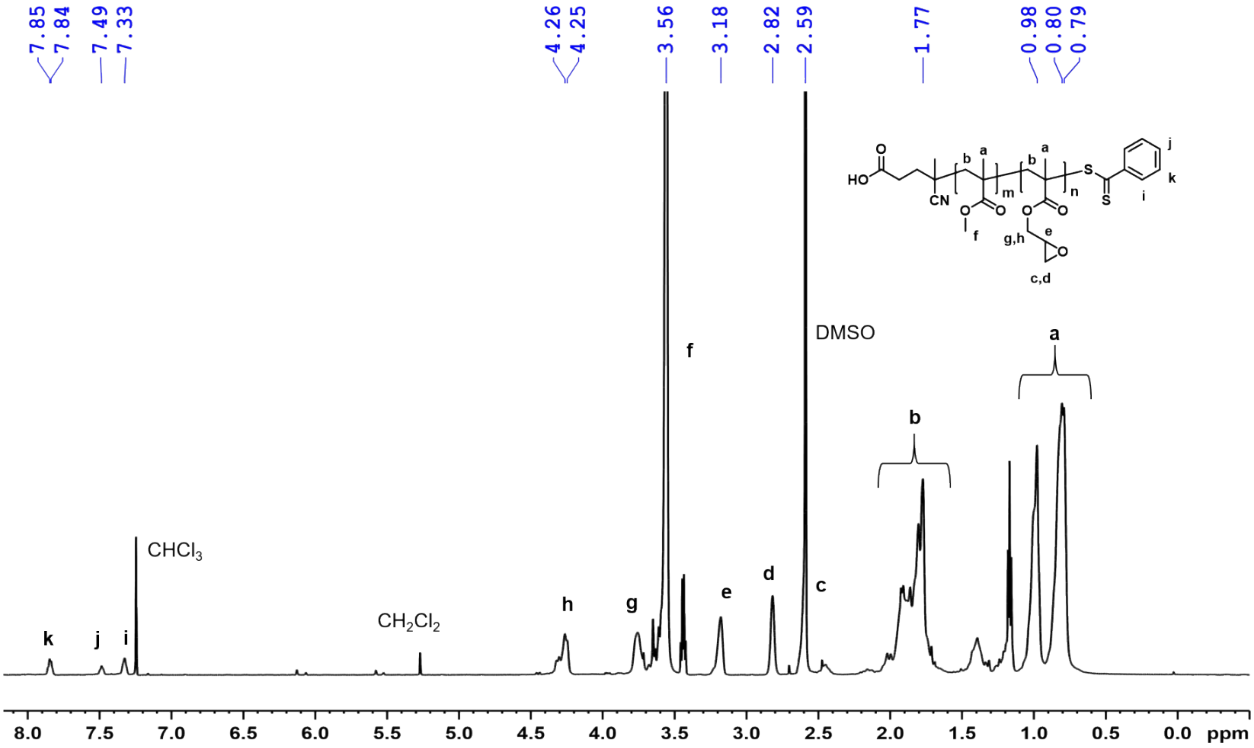


Figure S4. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of polymer 2.

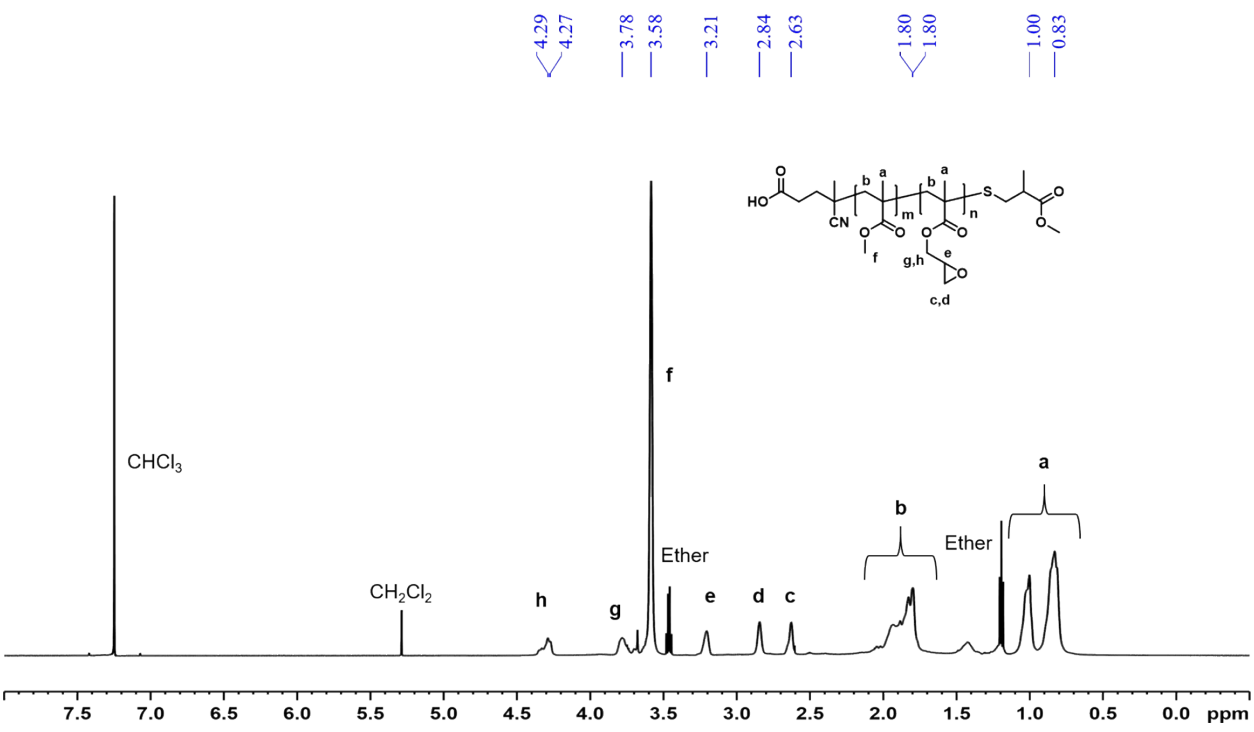


Figure S5. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of polymer 3.

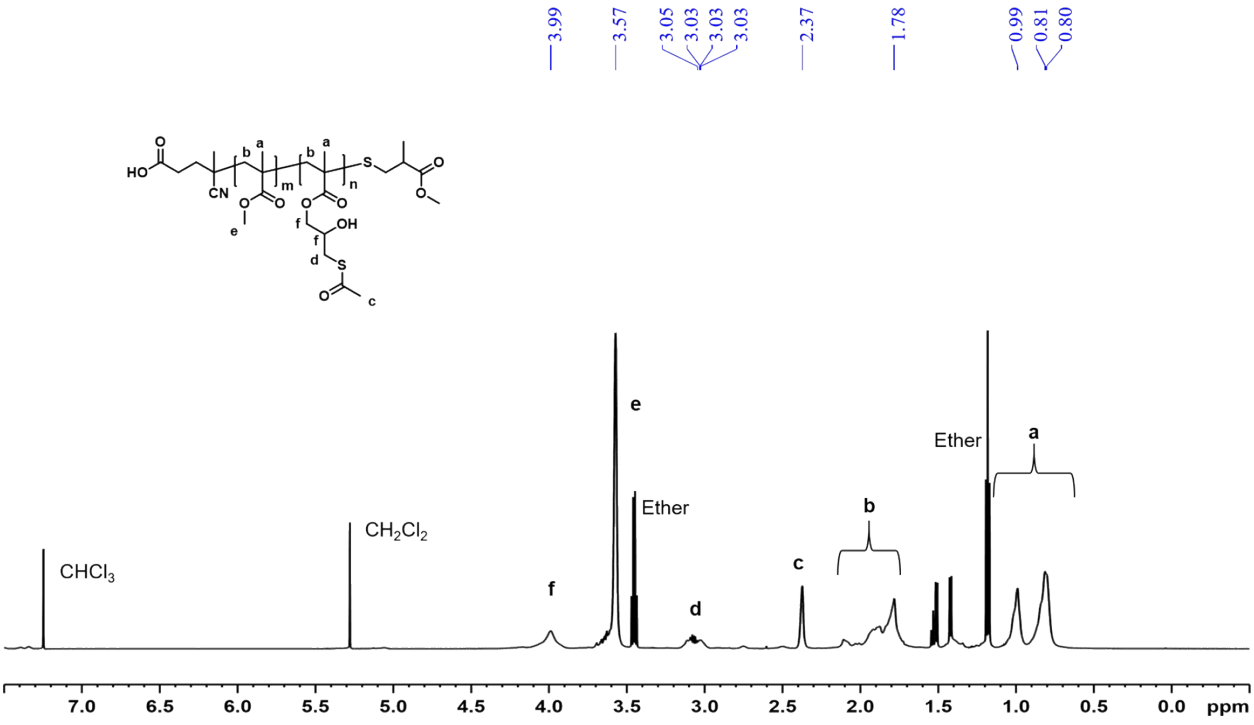


Figure S6. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of polymer 4.

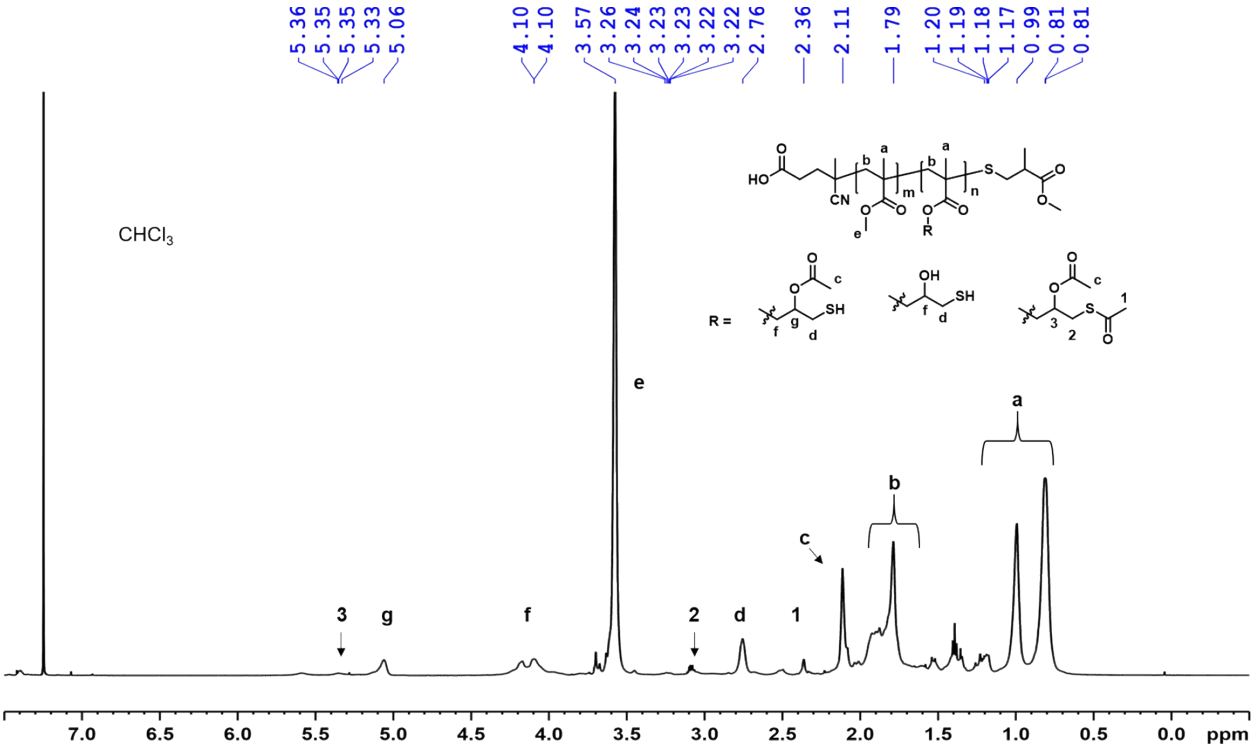


Figure S7. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of polymer 5.

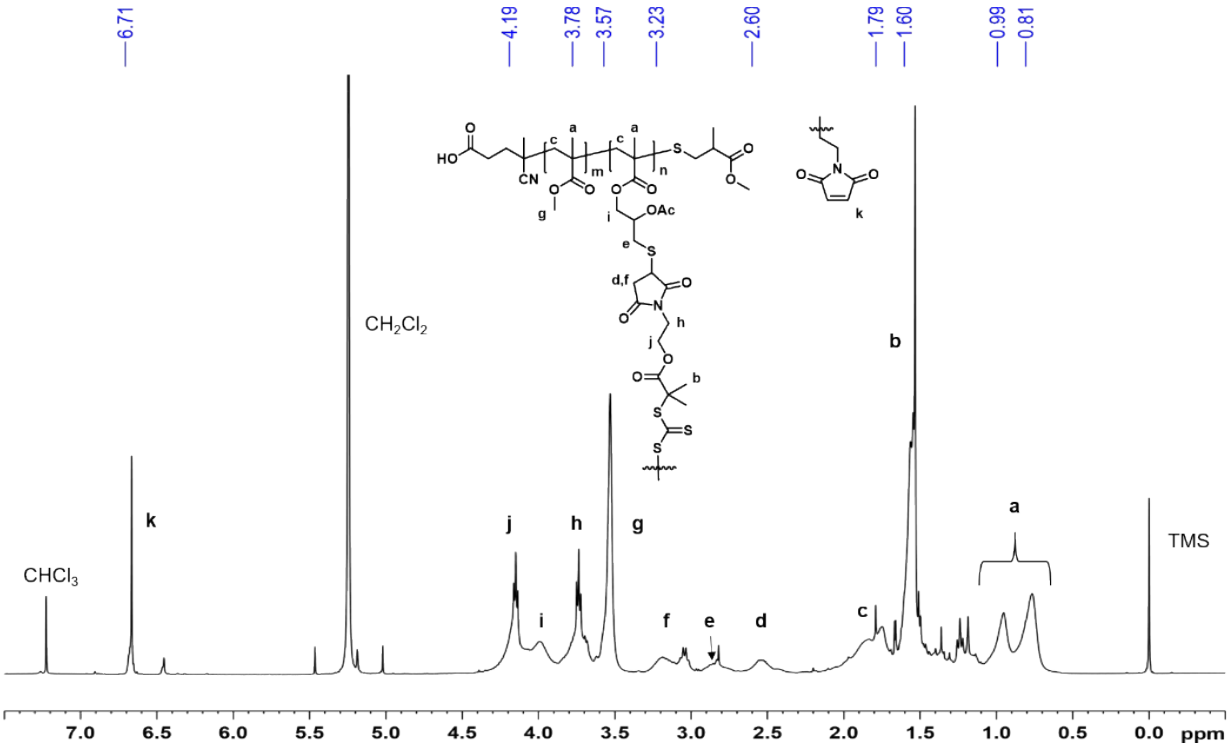


Figure S8. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of photo-growable nano-network.

Parent PGNN Spectra

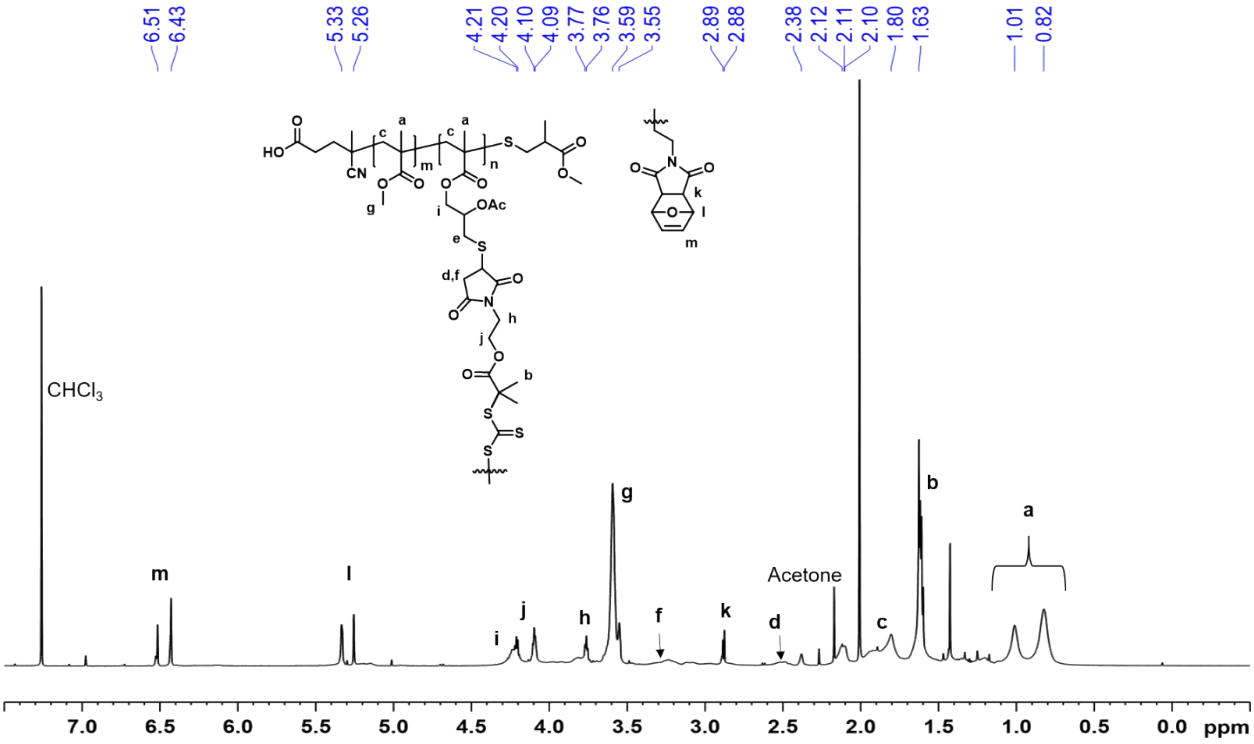


Figure S9. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of parent photogrowable nanonetwork.

Homopolymer ENN Spectra

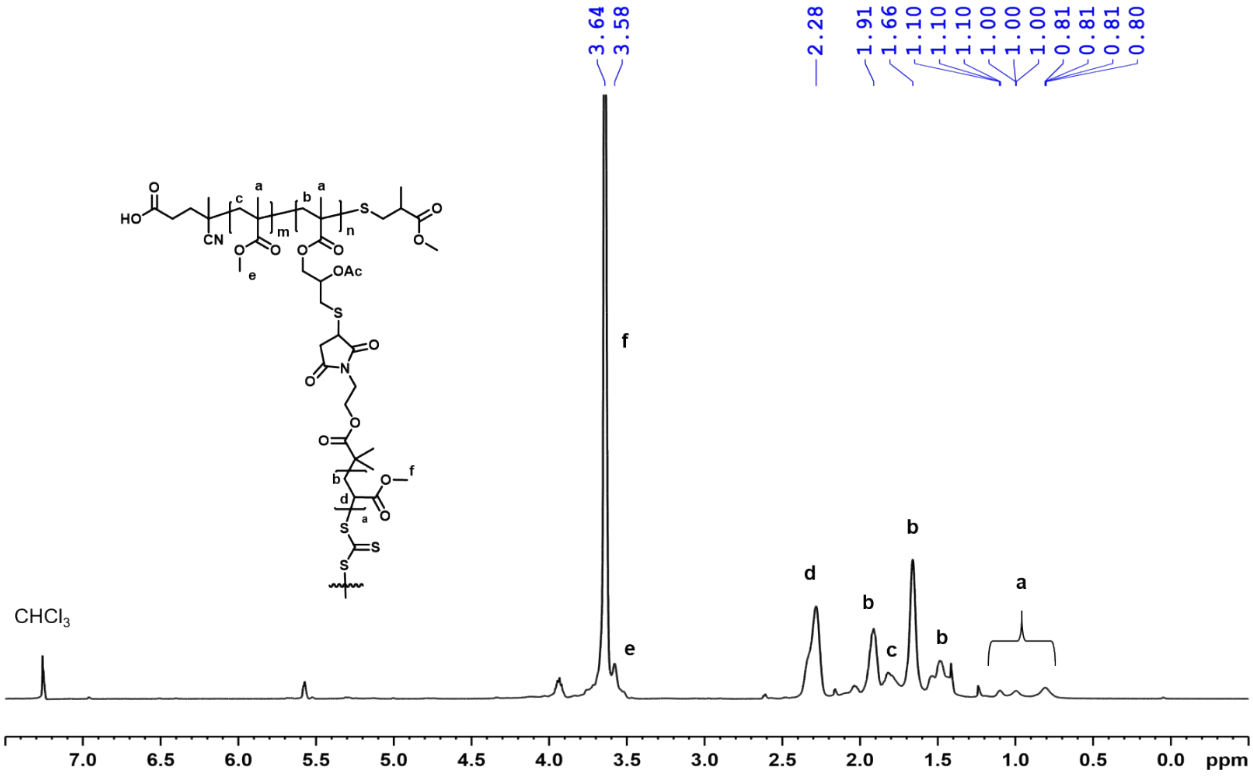


Figure S10. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of expanded nano-network with MA after 30 minutes of irradiation.

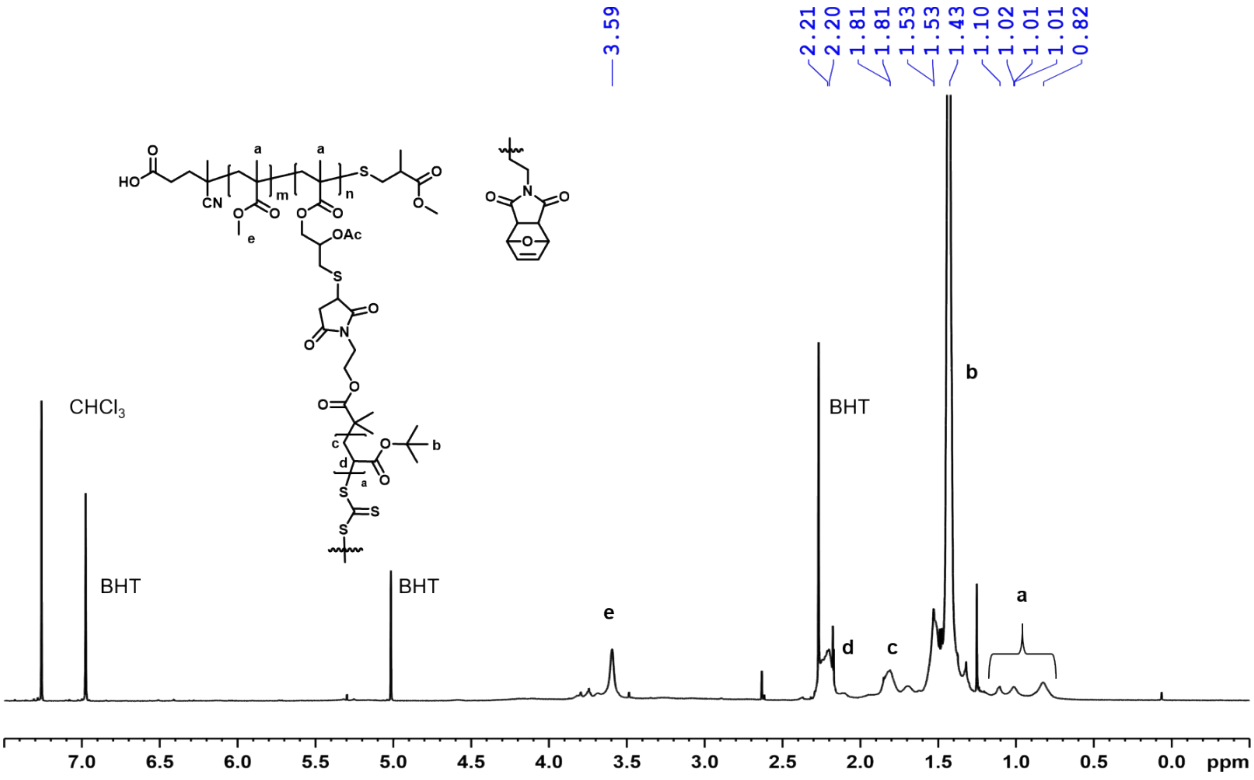


Figure S11. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of expanded nano-network with tBA after 30 minutes of irradiation.

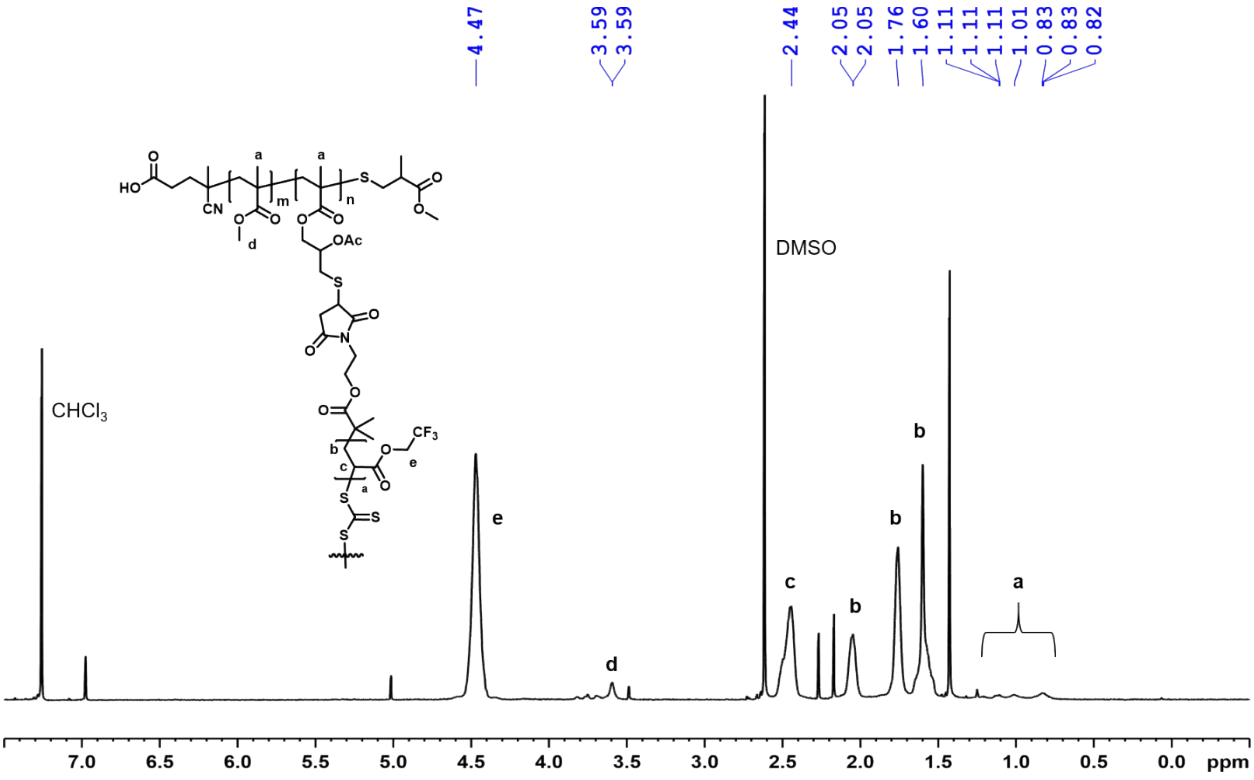


Figure S12. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of expanded nano-network with TFEA after 30 minutes of irradiation.

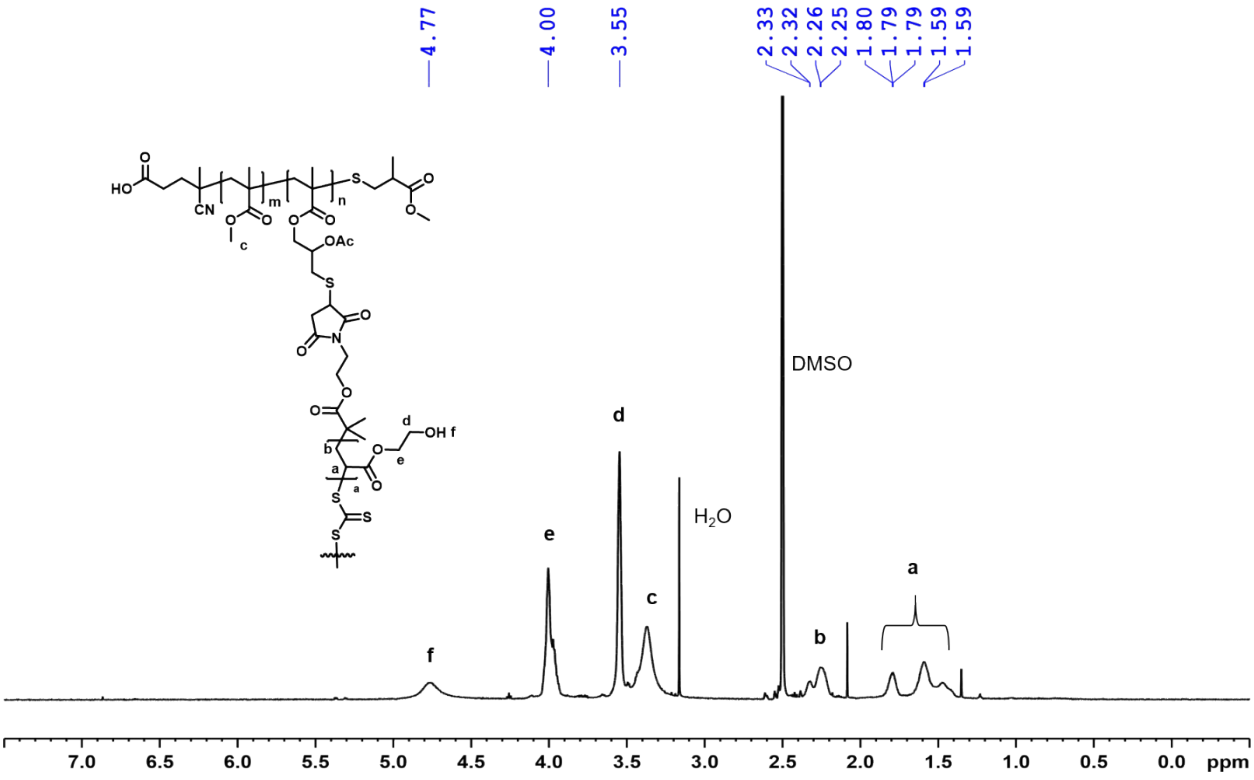


Figure S13. ^{1}H NMR (DMSO-d_6, 600 MHz) spectrum of expanded nano-network with HEA after 30 minutes of irradiation.

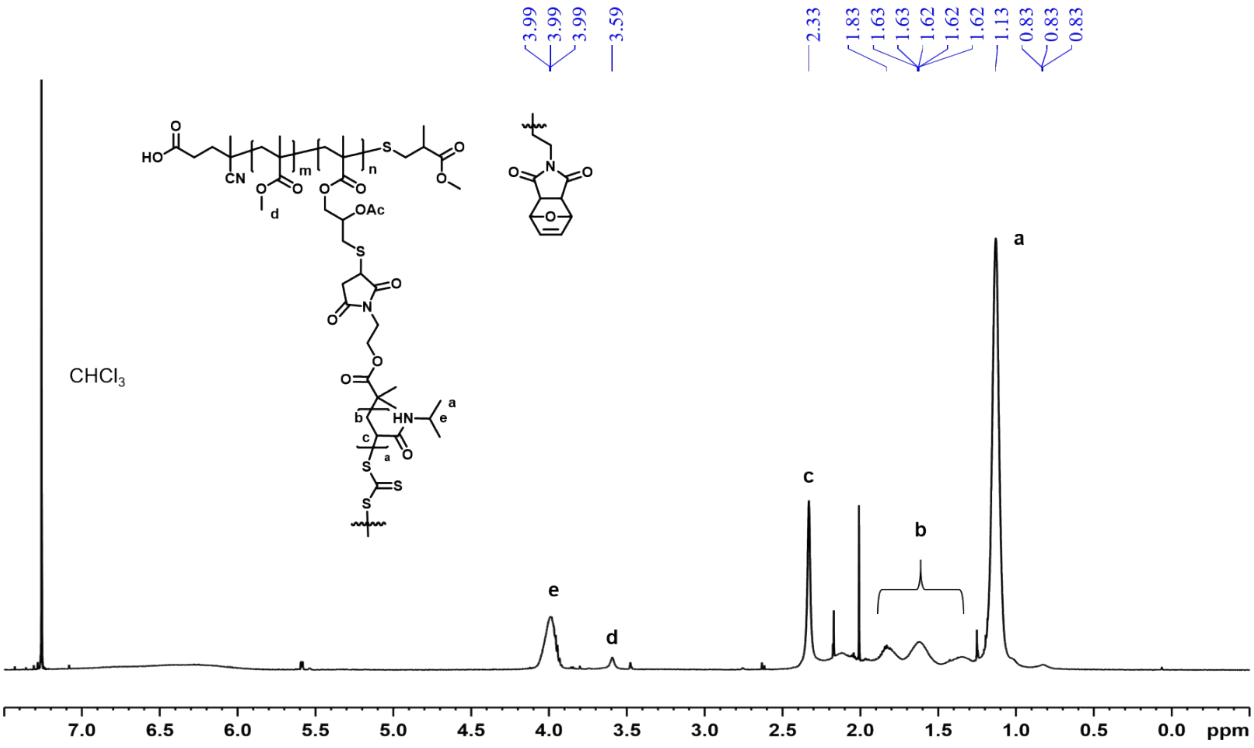


Figure S14. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of expanded nano-network with NIPAAM after 30 minutes of irradiation.

Statistical Copolymer ENN Spectra:

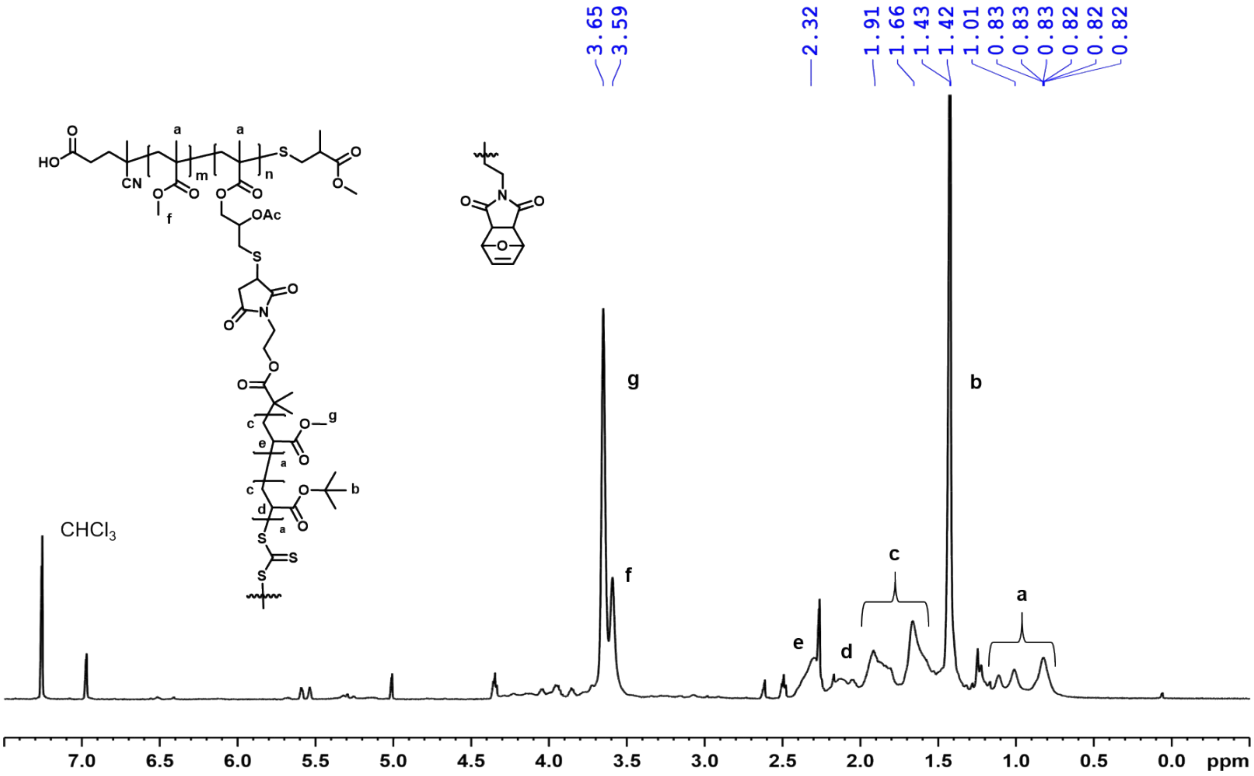


Figure S15. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of statistical copolymer expanded nanonetwork with MA and tBA after 30 minutes of irradiation.

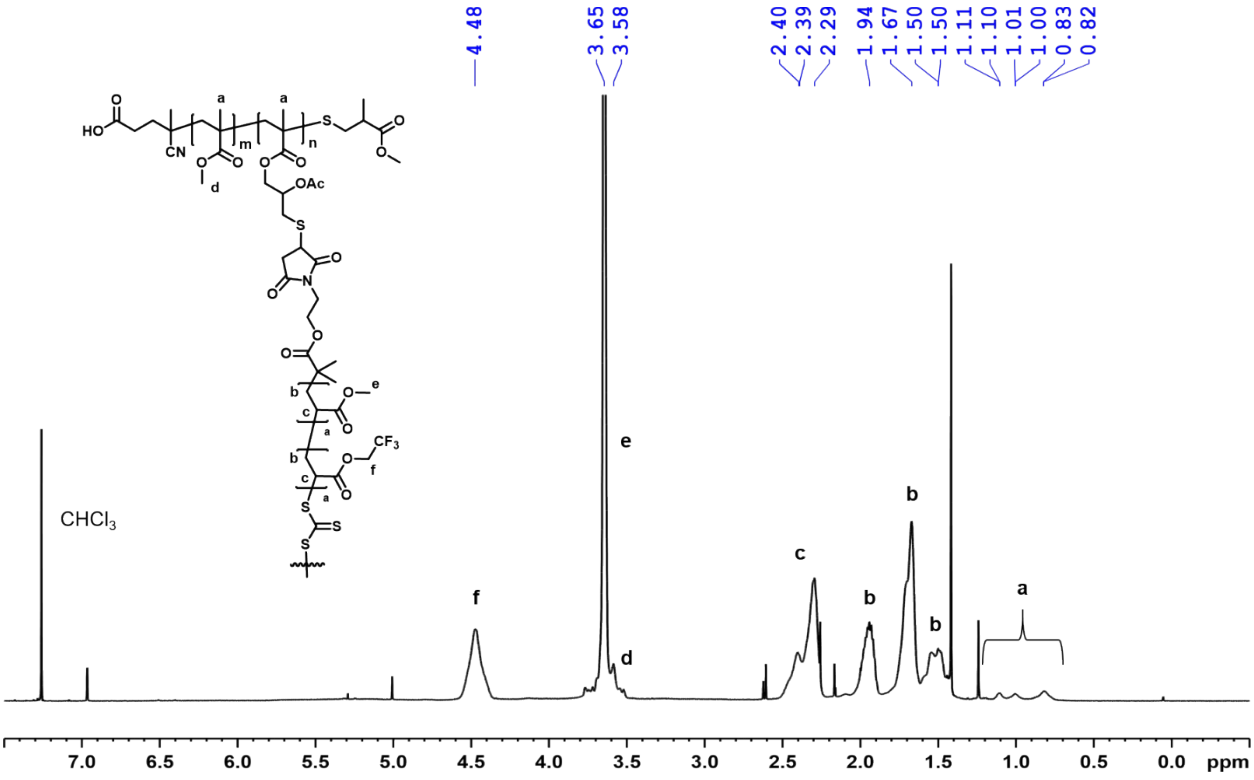


Figure S16. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of statistical copolymer expanded nanonetwork with MA and TFEA after 30 minutes of irradiation.

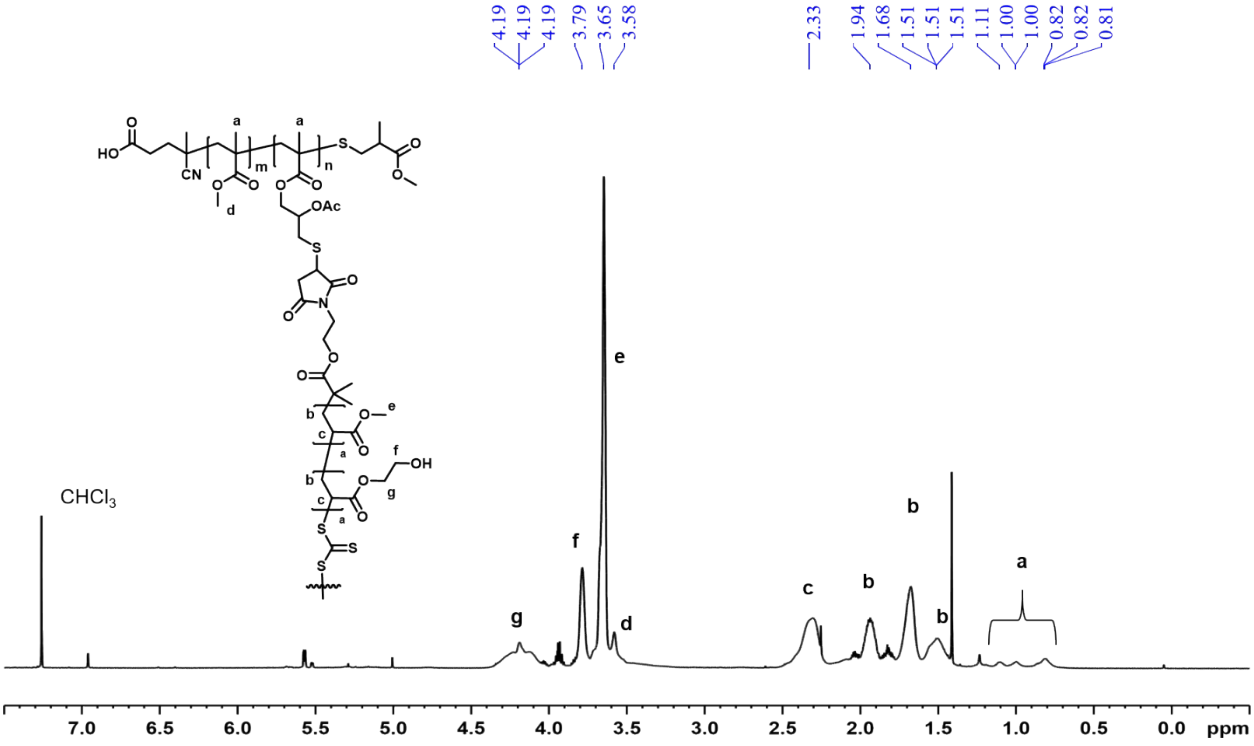


Figure S17. ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of statistical copolymer expanded nanonetwork with MA and HEA after 30 minutes of irradiation.

Block ENN Spectra:

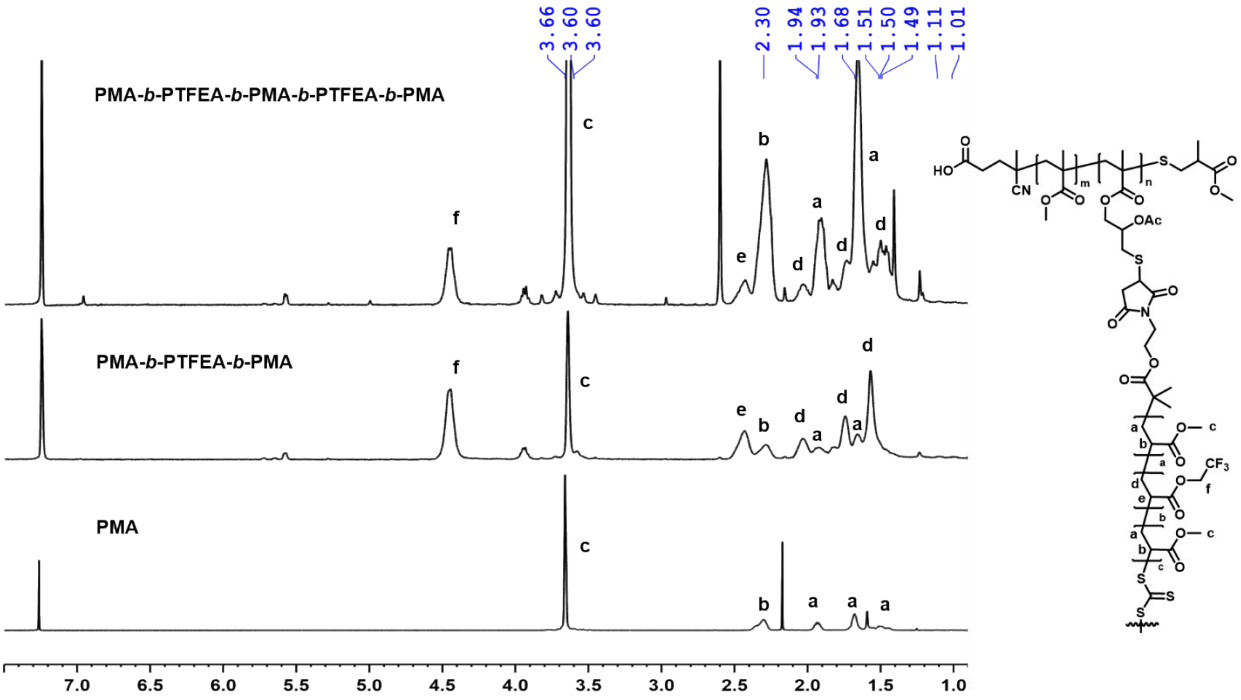


Figure S18. ^{1}H NMR ($CDCl_3$, 600 MHz) spectra of ABABA block copolymer expanded nanonetwork progression with MA and TFEA.

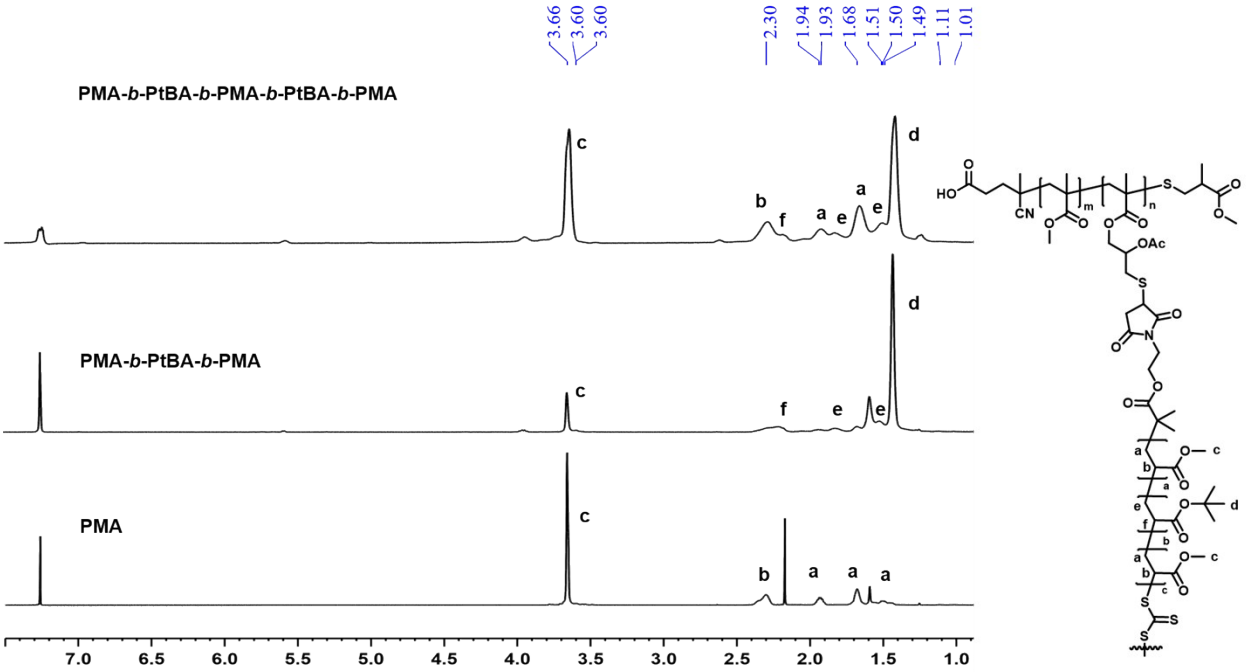


Figure S19. ^{1}H NMR ($CDCl_3$, 600 MHz) spectra of ABABA block copolymer expanded nanonetwork progression with MA and tBA.

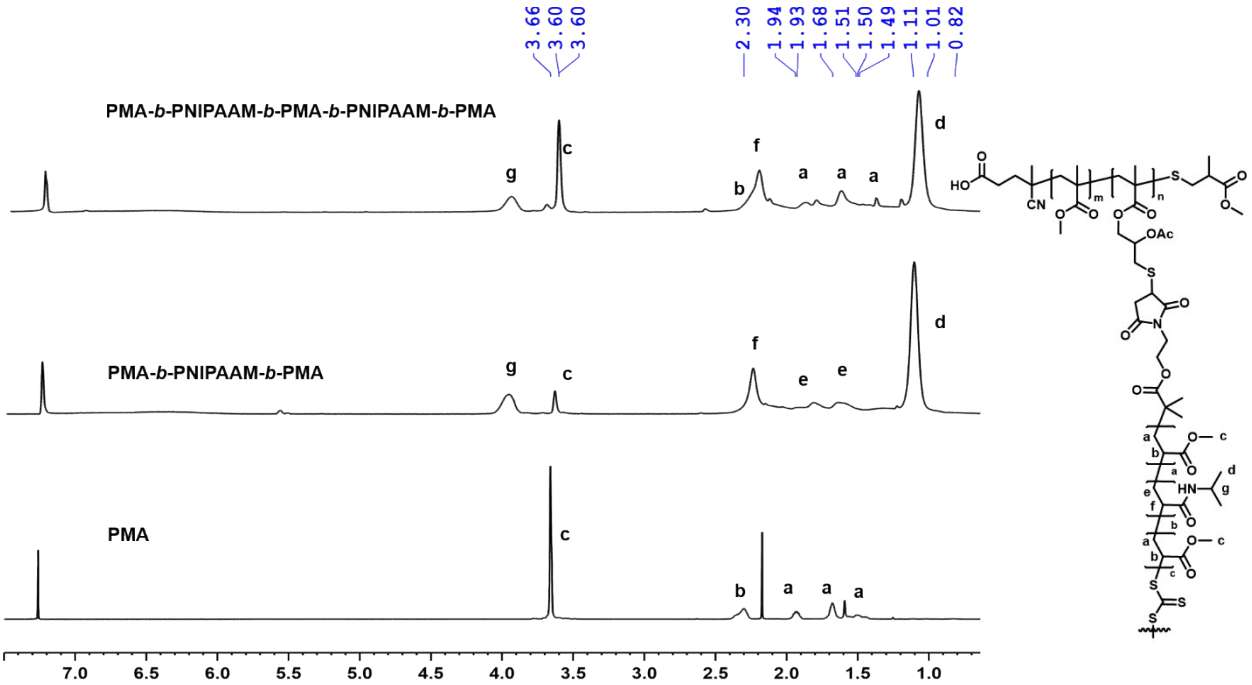


Figure S20. ^{1}H NMR ($CDCl_3$, 600 MHz) spectra of ABABA block copolymer expanded nanonetwork progression with MA and NIPAAM.

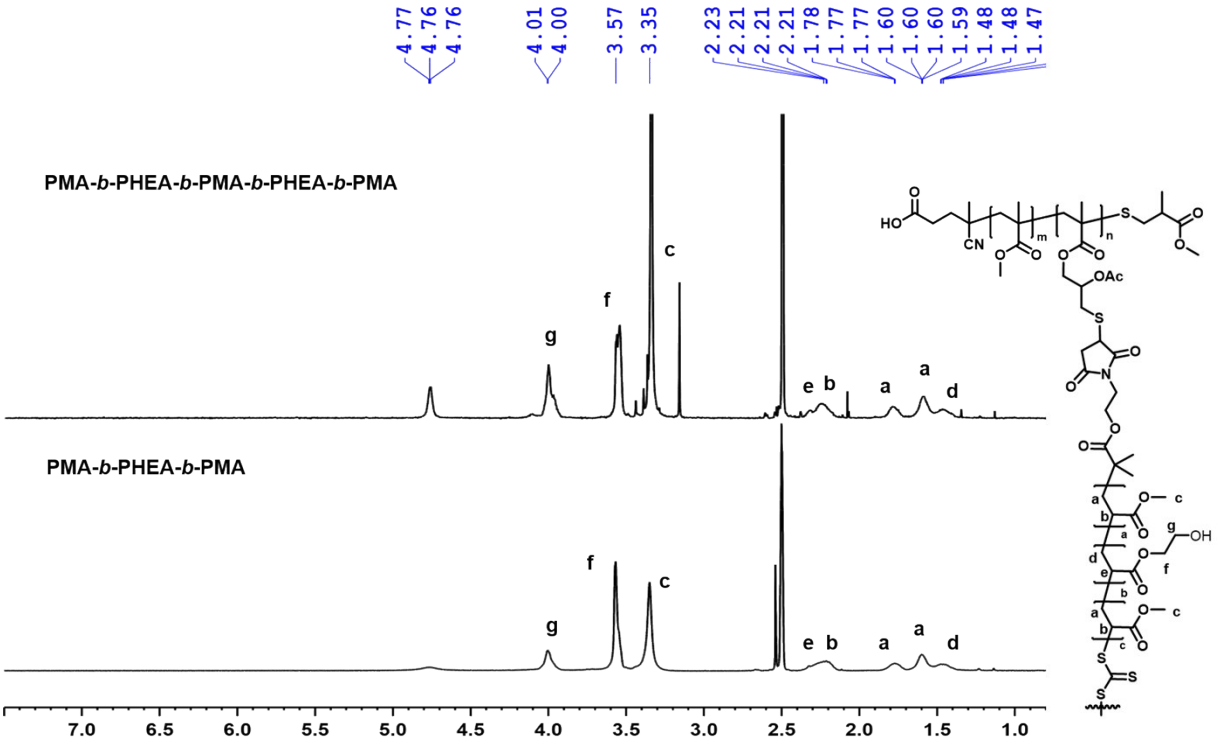


Figure S21. ^{1}H NMR (DMSO-d_6, 600 MHz) spectra of ABABA block copolymer expanded nanonetwork progression with MA and HEA.

Selected TEM Images

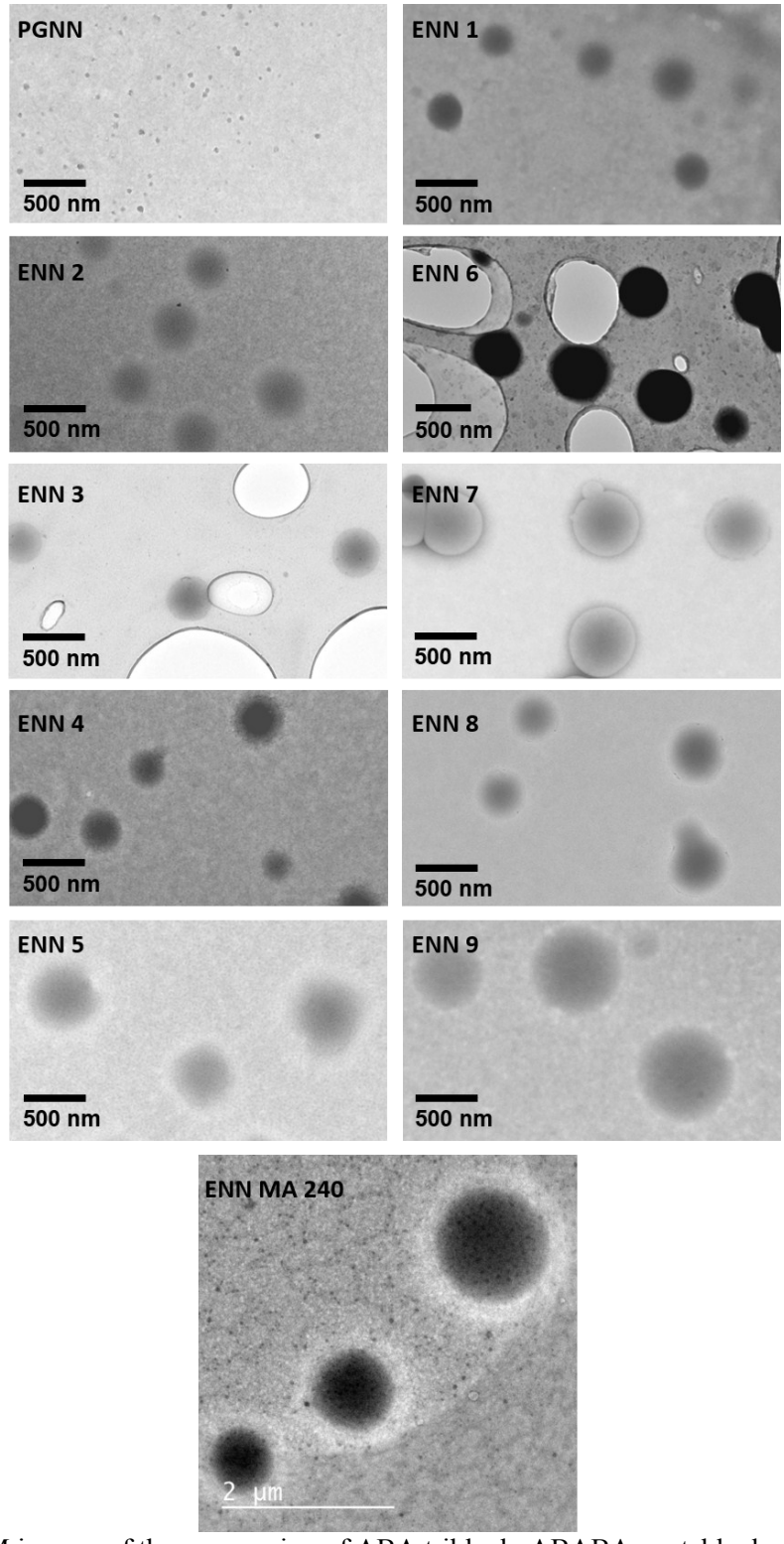


Figure S22. TEM images of the progression of ABA triblock, ABABA pentablock copolymer, and microparticle expansions.

References:

(1) Treat, N. J.; Sprafke, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Read de Alaniz, J.; Fors, B. P.; Hawker, C. J., Metal-Free Atom Transfer Radical Polymerization. J. Am. Chem. Soc. 2014, 136 (45), 16096-16101.

(2) Lampley, M. W.; Harth, E., Photocontrolled Growth of Cross-Linked Nanonetworks. ACS Macro Lett. 2018, 745-750.