Supporting Information

General Reagent Information

Monomers (acrylates and acrylamides) and solvents were purchased from Sigma-Aldrich Company. N-isopropylacrylamide (NiPAAm) was recrystallized from hexanes 3 times before use. *tert*-Butyl acrylate *(t*BA*),* ethylene glycol methacrylate (EGMEA) and N,N-dimethylacrylamide (DMA) were passed through a plug of basic alumina before use.

General Analytical Information

Gel permeation chromatography (GPC) measurements were performed on an Agilent 1260 LC system with two Shodex KD-806M GPC columns in series at 60 °C and a flow rate of 1 mL / min. Dimethyl formamide (DMF) with 0.025M LiBr was used as the eluent. The system was calibrated using poly(ethylene oxide) standards. A T-rEX refractive index detector (Wyatt) and a DAWN EOS 18 angle light scattering (MALS) detector (Wyatt) were used for polymer analysis. Relevant dn/dc values (*vide infra*) were obtained by injection of known concentrations of polymer samples. Molar masses were measured by static light scattering; values were compared to M_n values obtained by NMR. NMR spectra were recorded on a Bruker AMX 400 MHz NMR spectrometer. ^{1}H NMR signals are reported in δ units, parts per million (ppm), and were measured relative to the signal for residual chloroform (7.26 ppm) in deuterochloroform ($CDCl_3$). ^{13}C NMR signals are reported in ppm relative to deuterochloroform (77.16 ppm), and were obtained with ^{1}H decoupling.

General Material Information for Continuous Flow Setup

All tubings, connectors, nuts, ferrules, fittings and back-pressure regulators were purchased from IDEX Health and Science, unless otherwise stated. Stainless steel syringes and syringe pumps were purchased from Harvard Apparatus. The equipment configurations that were used for the flow reactions are depicted in Figures S-1 to S-3. The tubing reactors and all connecting tubing in all figures were made of Halar tubing (0.0625” OD × 0.03” ID). Connections for all reactors were made using super flangeless

ferrules (w/SST ring, 10-32 flat bottom) and super flangeless nuts (PEEK, 1/4-28 flat bottom). The T-mixers (0.04" ID) used in this work were made out of PEEK. 8W SANKYO DENKI Black light lamps emitting near ultraviolet rays (315 nm – 400 nm) with peak emission at 352 nm, were used as UV radiation source.

Experimental Procedures

Flow Setup A

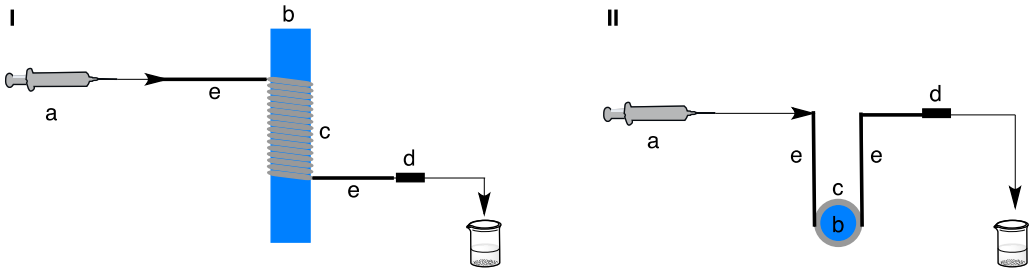
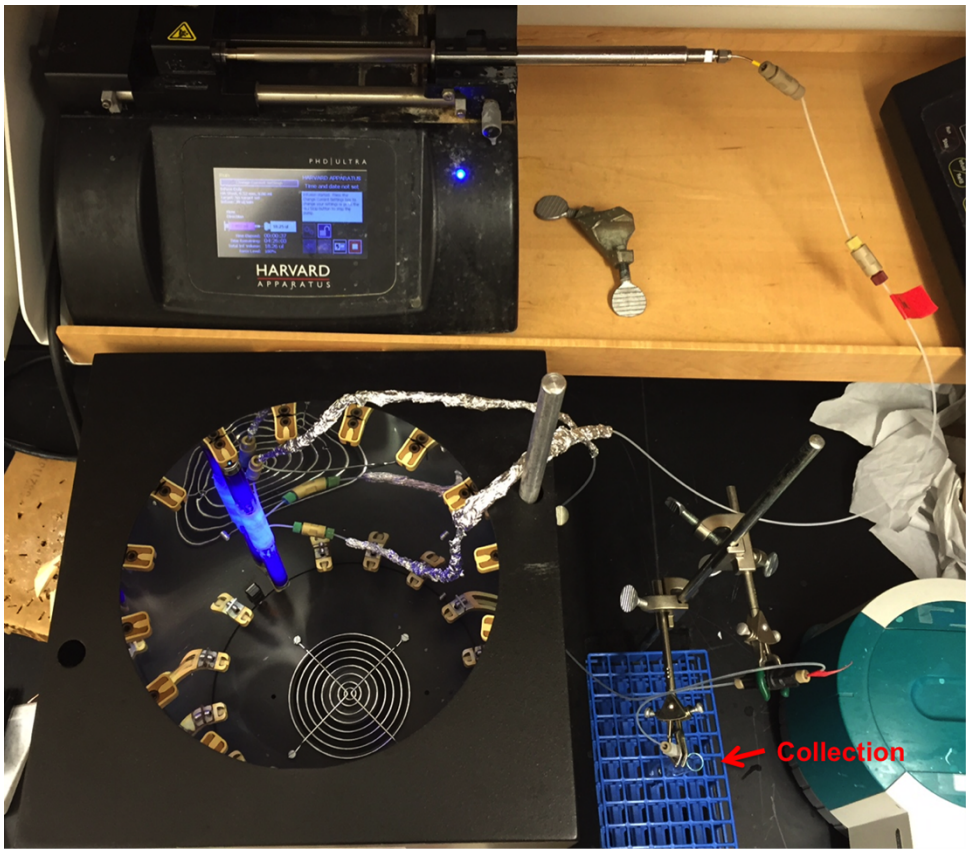


Figure S-1

I: view from the side; **II**: view from the top. a: stainless steel syringe loaded with monomer, initiator and solvent; b: UV lamp; c: tubing used as the reactor; d: back-pressure regulator (20 psi); e: connecting tubing covered with aluminium foils.



General Procedure for Flow Experiments with Setup A

A 10.0 mL oven-dried volumetric flask was charged with monomer (2.0 M), internal standards (0.1 M, DMF was used for NiPPAm, *t*BA and EGMEA, *n*-butyl benzoate was used for DMA) and trithiocarbonate **1** (8.0 mM). Anhydrous deoxygenated MeCN was added via a degassed syringe to make the solution volume 10.0 mL. After the flask was sealed with a rubber septum, the solution was deoxygenated with three freeze, pump, thaw cycles under N_2 atmosphere. The solution was loaded into an 8.0 mL degassed stainless steel syringe, and fitted to a syringe pump. Following the setup as shown in Figure S-1, the solution was introduced into the tubing reactor (For related flow rates, see following parts). After reaction, the resulting mixture was passed through a back-pressure regulator before collection. After reaching steady state (normally waiting for three times of the residence time), 1.6-2.4 mmol samples were collected into test tubes. A small aliquot of the resulting mixture was directly analyzed with NMR and GPC instruments. Results of at least two runs were shown. For dn/dc values, 0.087 was used for PNiPPAm, 0.040 was used for P*t*BA, 0.041 was used for PEGMEA, and 0.074 was used for PDMA.

Flow Setup B

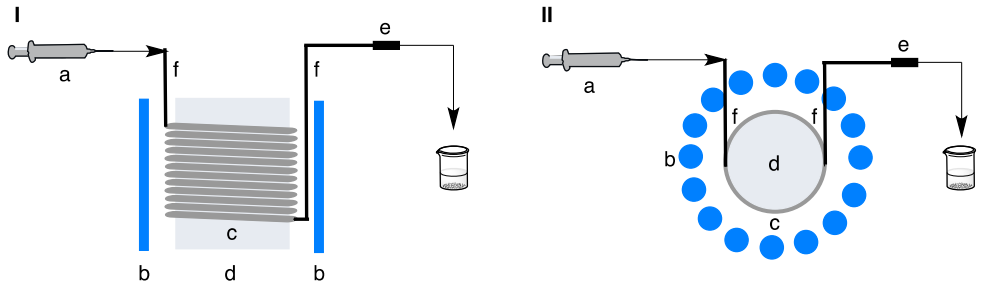
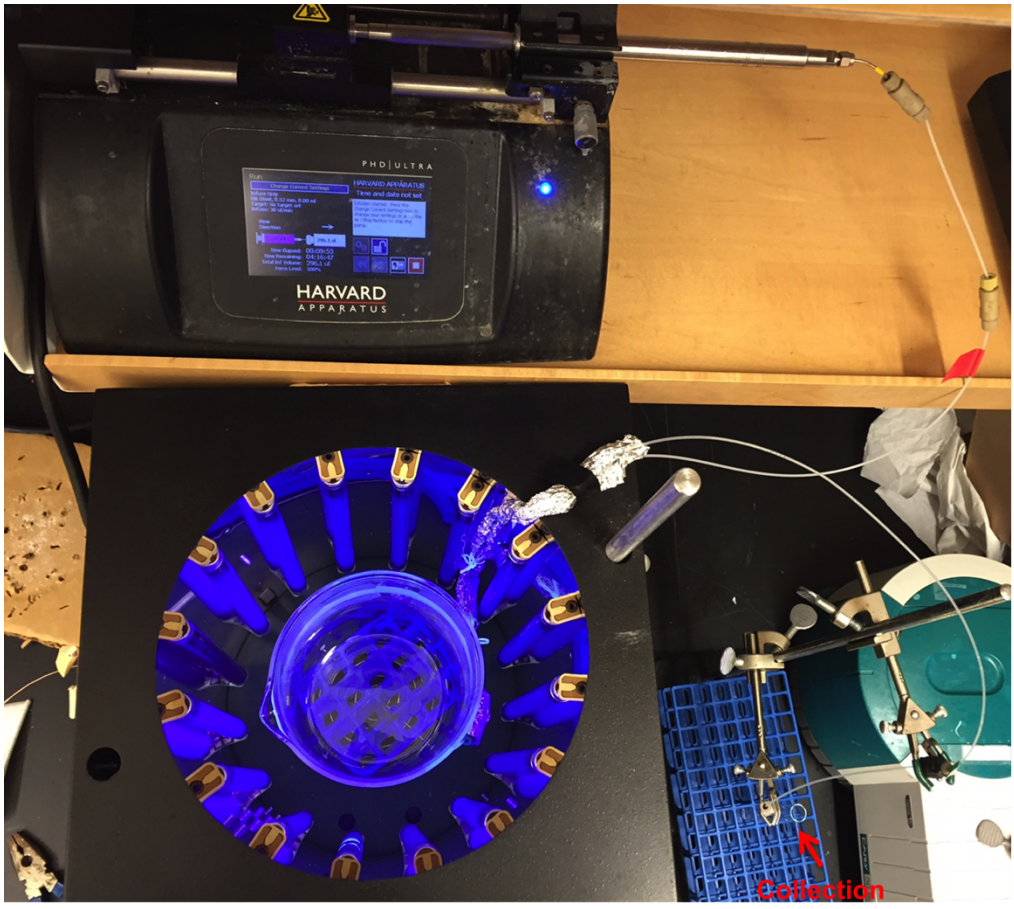


Figure S-2

I: view from the side; **II**: view from the top. a: stainless steel syringe loaded with monomer, initiator and solvent; b: UV lamp; c: tubing used as the reactor; d: glass bottle; e: back-pressure regulator (20 psi). f: connecting tubing covered with aluminium foils.



General Procedure for Flow Experiments with Setup B

A 10.0 mL oven-dried volumetric flask was charged with monomer (2.0 M), internal

standards (0.1 M, DMF was used for NiPPAm, *t*BA and EGMEA, *n*-butyl benzoate was used for DMA) and trithiocarbonate **1** (4.0 mM, or 1 mM). Anhydrous deoxygenated MeCN was added via a degassed syringe to make the solution volume 10.0 mL. After the flask was sealed with a rubber septum, the solution was deoxygenated with three freeze, pump, thaw cycles under N_2 atmosphere. The solution was loaded into an 8.0 mL degassed stainless steel syringe, and fitted to a syringe pump. Following the setup as shown in Figure S-2, the solution was introduced into the tubing reactor (For related flow rates, see following parts). After reaction, the resulting mixture was passed through a back-pressure regulator before collection. After reaching steady state (normally waiting for three times of the residence time), 1.0-2.4 mmol samples were collected into test tubes. A small aliquot of the resulting mixture was directly analyzed with NMR and GPC instruments. Results of at least two runs were shown.

Up-scaling photopolymerization experiment using Setup A

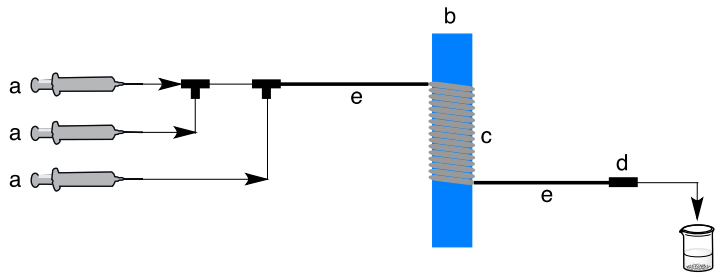


Figure S-3

a: stainless steel syringes loaded with monomer, initiator and solvent; b: UV lamp; c: tubing used as the reactor; d: back-pressure regulator (20 psi); e: connecting tubing covered with aluminium foils.

Procedures for an up-scaling photopolymerization experiment using Setup A

A 25.0 mL oven-dried volumetric flask was charged with DMA (2.0 M), internal standards (0.1 M, *n*-butyl benzoate) and trithiocarbonate **1** (8.0 mM). Anhydrous deoxygenated MeCN was added via a degassed syringe to make the solution volume 25.0 mL. After the flask was sealed with a rubber septum, the solution was deoxygenated with

three freeze, pump, thaw cycles under N_2 atmosphere. The solution was loaded into three 8.0 mL degassed stainless steel syringes (for each syringe, flow rate = 15.0 µL/min), and fitted to two syringe pumps. Following the setup as shown in Figure S-3, the solution was introduced into the tubing reactor. After reaction, the resulting mixture was passed through a back-pressure regulator to prevent backflow before collection. After reaching steady state (120 min), the resulting mixture was collected for 400 min to obtain products based on a 36.0 mmol scale. A small aliquot of the resulting mixture was directly analyzed with NMR and GPC instruments. After collection, the solution was added into Et_2O solvent with vigorously stirring. A white precipitate formed, which was filtered and dried to afford 2.95 g of desired product. For data see Table S-5.

Table S-1: Results of **Figure 3** using NiPAAm as the monomer

Entry	Flow Reactor	Flow Rate	Residence Time	Conversion	$M_{n,\,GPC}$	M_w/M_n
1	1.2 mL/Setup A	120.0 µL/min	10 min	24%	8100	1.09
2	1.8 mL/Setup A	90.0 µL/min	20 min	42%	15000	1.10
3	1.2 mL/Setup A	40.0 µL/min	30 min	60%	19100	1.09
4	1.8 mL/Setup A	45.0 µL/min	40 min	70%	21100	1.11
5	2.1 mL/Setup A	42.0 µL/min	50 min	77%	24200	1.18

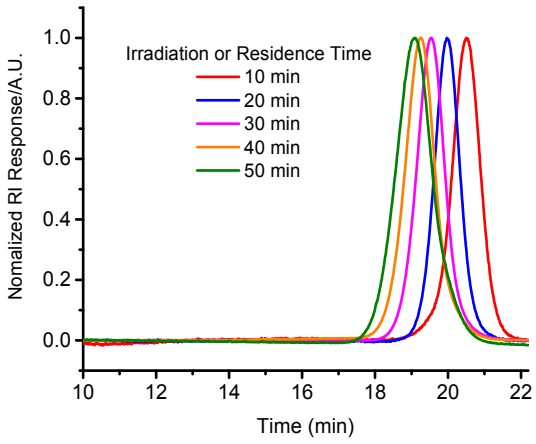


Table S-2: Results of Figure 6 using NiPAAm as the monomer

Entry	Flow Reactor	Flow Rate	Residence Time	Conversion	$M_{n,\,GPC}$	M_w/M_n
1	1.2 mL/Setup B	60.0 µL/min	20 min	31%	19400	1.11
2	1.2 mL/Setup B	30.0 µL/min	40 min	50%	26900	1.10
3	2.4 mL/Setup B	40.0 µL/min	60 min	65%	37000	1.15
4	2.4 mL/Setup B	26.7 µL/min	90 min	75%	41600	1.18

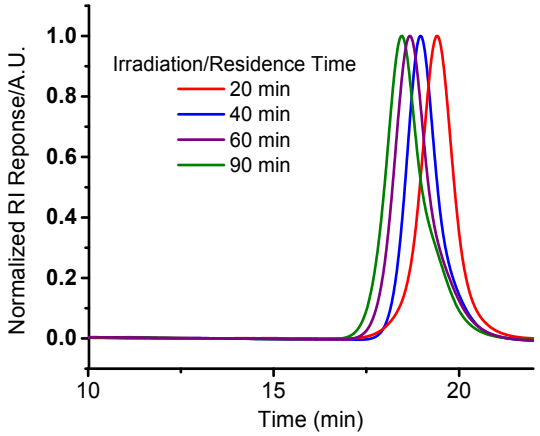


Table S-3: Results in Table 2 using *t*BA as the monomer

Entry	Flow Reactor	Flow Rate	Residence Time	Conversion	$M_{n,\,GPC}$	M_w/M_n
1	1.8 mL/Setup A	30.0 µL/min	60 min	81%	29800	1.21
2	2.4 mL/Setup B	26.7 µL/min	90 min	82%	54200	1.19

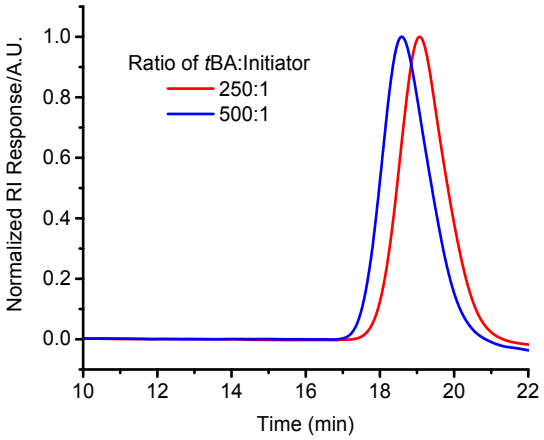


Table S-4: Results in Table 2 using EGMEA as the monomer

Entry	Flow Reactor	Flow Rate	Residence Time	Conversion	$M_{n,\,GPC}$	M_w/M_n
1	1.8 mL/Setup A	30.0 μL/min	60 min	88%	30300	1.21
2	2.4 mL/Setup B	30.0 μL/min	80 min	81%	55800	1.17

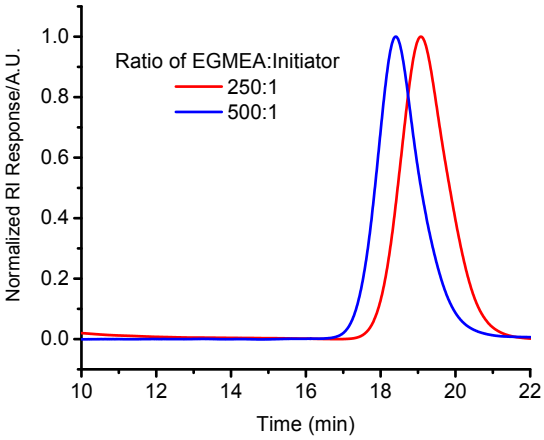


Table S-5: Results in Table 2 using DMA as the monomer

Entry	Volume of Flow Reactor	Flow Rate	Residence Time	Conversion	$M_{n,\,GPC}$	M_w/M_n

1	1.8 mL/ Setup A	45.0 µL/min	40 min	87%	25500	1.11
2	1.8 mL/Setup A	15.0 µL/min × 3	40 min	87%	24900	1.11
3	2.4 mL/ Setup B	30.0 µL/min	80 min	84%	43300	1.18
4	1.2 mL/ Setup B	30.0 µL/min	40 min	55%	105800	1.22

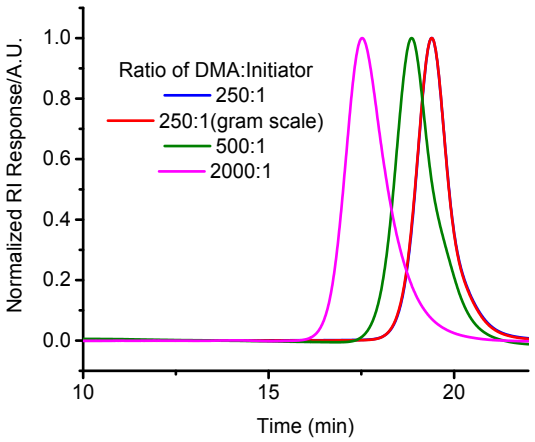
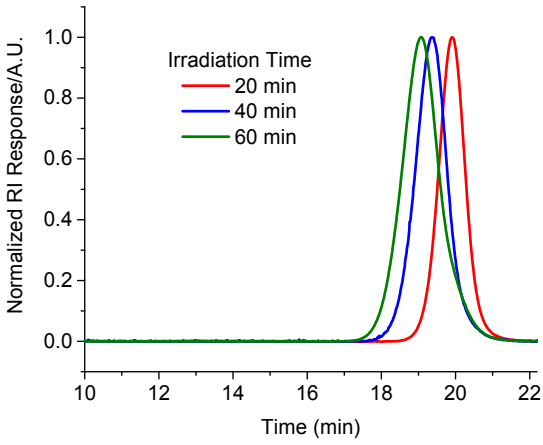


Table S-6: Results for "on"/ "off" experiments in Figure 4 using NiPPAm as monomer

Entry	Conversion	$M_{n,\,GPC}$	M_w/M_n
1	40%	14400	1.10
2	67%	19700	1.12
3	81%	24300	1.21

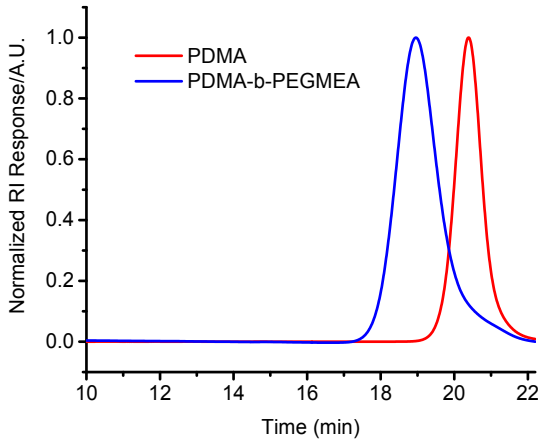


Procedure of synthesizing block polymers using a combination of Setup A and B

Two 10.0 mL oven-dried volumetric flask was charged with DMA (2.0 M) and trithiocarbonate **1** (20.0 mM). Anhydrous deoxygenated MeCN was added via a degassed syringe to make each of the solution volume 10.0 mL. After flasks were sealed with rubber septum, the solutions were deoxygenated with three freeze, pump, thaw cycles under N_2 atmosphere. The solutions were loaded into two 8.0 mL degassed stainless steel syringes, and fitted to a syringe pump. Following the Setup A as shown in Figure S-1, the solution was introduced into the tubing reactor (volume of tubing reactor = 1.2 mL, flow rate = 15.0 μL/min×2, residence time = 40 min). After reaction, the resulting mixture was passed through a back-pressure regulator before reaching the outlet. After reaching steady state (120 min), the reaction mixture was collected for 300 min to obtain PDMA based on 18.0 mmol DMA. The collected solution was added into Et_2O solvent with vigorously stirring. A light yellow precipitate formed, which was filtered and dried to afford 1.45 g PDMA, which was analyzed by GPC. $M_{n,\,GPC}$ = 10200, M_w/M_n = 1.06.

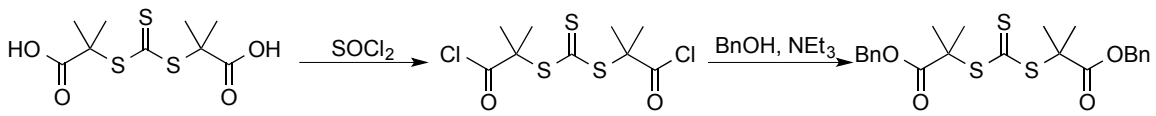
A 10.0 mL oven-dried volumetric flask was charged with EGMEA (2.0 M), PDMA (8.0 mM). Anhydrous deoxygenated MeCN was added via a degassed syringe to make the solution volume 10.0 mL. After the flask was sealed with a rubber septum, the solution was deoxygenated with three freeze, pump, thaw cycles under N_2 atmosphere. The solution was loaded into a 8.0 mL degassed stainless steel syringe, and fitted to a syringe pump. Following the Setup B as shown in Figure S-2, the solution was introduced into

the tubing reactor (volume of tubing reactor = 1.8 mL, flow rate = 30.0 μL/min, residence time = 60 min). After reaction, the resulting mixture was passed through a back-pressure regulator before collection. After reaching steady state, the reaction mixture was collected for 80 min to obtain PDMA-*block*-PEGMEA on 4.8 mmol scale. The collected solution was added into cold Et_2O solvent with vigorously stirring. A light yellow precipitate formed, which was filtered and dried to afford 612 mg PDMA-*block*-PEGMEA, which was analyzed by GPC. $M_{n,\,GPC}$ = 34900, M_w/M_n = 1.17.



Synthesis of dibenzyl 2,2'-(thiocarbonylbis(sulfanediyl))bis(2-methylpropanoate)

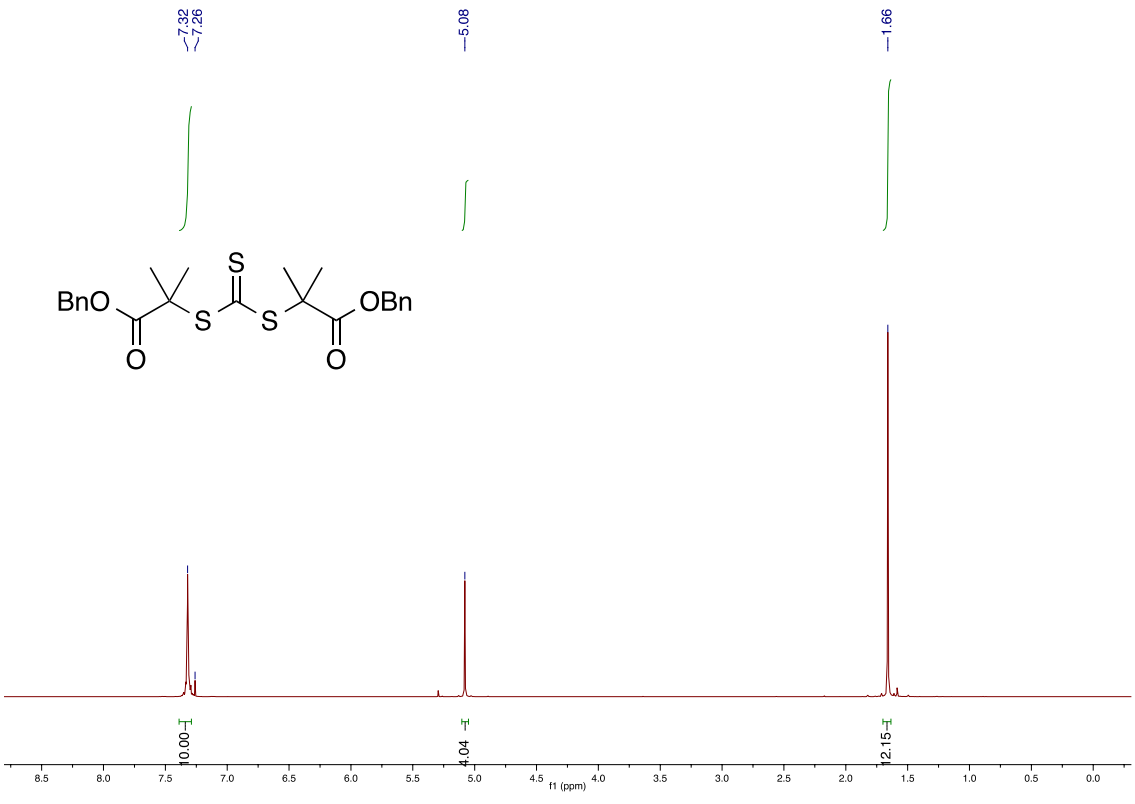
For the synthesis of the S,S-bis(a,a'-dimethyl a"-acetic acid)trithiocarbonate **1**, see: J. T. Lai, D. Filla, R. Shea, *Macromolecules* **2002**, *35*, 6754.

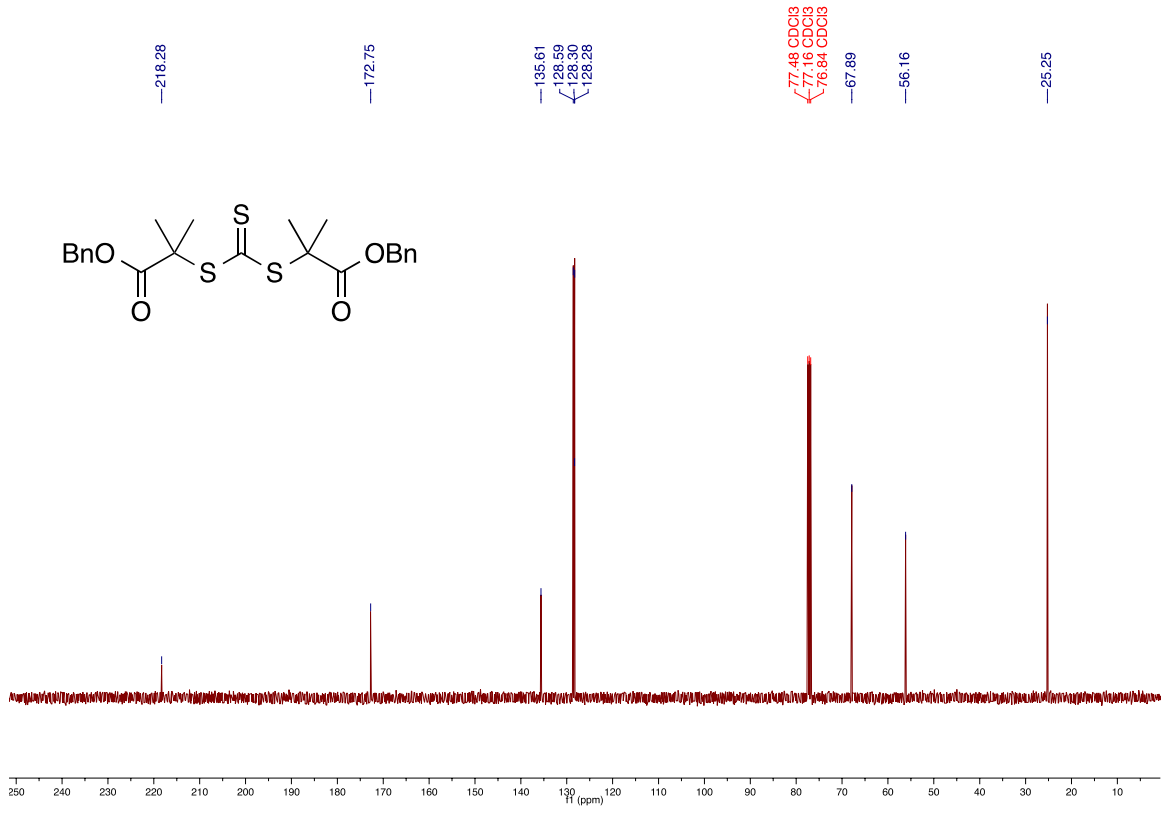


1 **2** **3**

Synthesis of **2**: An oven-dried round bottom flask was charged with a magnetic stir bar and **1** (1.41 g, 5.0 mmol). 6 mL $SOCl_2$ was added dropwise via syringe. Then, the mixture was stirred at 60°C for 3 hours. The mixture was cooled down to room temperature, and the excess $SOCl_2$ was removed under reduced pressure. Yellow solid of **2** was obtained, which was dissolved in 10 mL anhydrous DCM and directly used in the next step without further purification.

Synthesis of **3**: An oven-dried round bottom flask equipped with a magnetic stir bar was charged with BnOH (1.19 g, 11.0 mmol), 1.5 mL anhydrous triethylamine and 15 mL anhydrous DCM, and was cooled to 0°C. The pre-prepared solution of **2** in DCM was added dropwise via syringe at 0°C with stirring. After addition, the mixture was stirred at room temperature overnight. After reaction, the mixture was concentrated under vacuum. Then, it was treated with EtOAc and H_2O. The separated water layer was extracted with EtOAc for three times. The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under vacuum. The crude mixture was purified by flash column chromatography (0-5 % EtOAc in hexanes) to afford the title compound **3** (1.04 g, 45 % yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.28 (m, 10 H), 5.08 (s, 4 H), 1.66 (s, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 218.3, 172.7, 135.6, 128.6, 128.3, 128.2, 67.9, 56.2, 25.2 ppm.




218.28
172.75
135.61
128.59
128.30
128.28
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.89
56.16
25.25
BnO
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S
S
S
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250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)