Electronic Supporting Information

Thioamides on Radical-Chain Growth Monomers: Post-polymerization Transformation for Tailored Functional Polymers

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1 General Information

1.1 Materials

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used as received. Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol prior to use, and methyl methacrylate (MMA) was purified by passing through basic alumina to remove inhibitor before polymerization. Solvents were reagent grade. Solvents, including THF, DCM, and DMF were dried via a Glass Contours Inc. solvent purification system. Analytical thin-layer chromatography (TLC) and flash chromatography of all reactions were performed on silica gel (40 µm) purchased from Grace Davison.

1.2 Experimental

NMR Spectroscopy: ^{1}H and ^{13}C NMR spectra for all compounds were acquired in deuterated solvents (as indicated) on a Bruker Spectrometer at the field strengths reported in the text. The chemical shift data are reported in units of δ (ppm) relative to residual solvent.

UV-Visible Spectroscopy: Absorbance measurements were carried out using a Thermo Scientific NanoDrop™ 1000 spectrophotometer. Metal ion concentrations in pre- and post-adsorption supernatants were quantified by measuring the absorbance at the characteristic λ_{max} of each metal ion according to the Beer–Lambert Law ($A = \varepsilon bc$). Calibration curves were constructed from serial dilutions of standard metal ion solutions of known concentration measured under identical conditions. The extent of adsorption was determined from the decrease in absorbance relative to an unadsorbed reference sample.

Liquid Chromatography: LC-MS data was collected an Acquity UPLC BEH C18 (1.7μm) column on a Waters Acquity UPLC H-Class LC-MS system equipped with detection using a dual-wavelength TUV detector and ESI ionization with QDa mass detection. LC-MS was performed using water and acetonitrile as eluents, both contained 0.1% TFA.

Mass Spectrometry: HRMS data was collected on either an Agilent QTOF 6540 MSMS or Agilent LCTOF 6230, both with ESI ionization and TOF detection. Chemical Formulas found from HRMS data were obtained via Agilent MassHunter software equipped with the HRMS QTOF.

Size-Exclusion Chromatography: Molecular weights and dispersities were determined by size-exclusion chromatography (SEC) on a Waters system equipped with an isocratic solvent manager (ACQ-ISM), UV detector (ACQ-UV), refractive index detector (ACQ-RI), and five ethylene-bridged hybrid (BEH) packed columns connected in series (1 x XT900A APC, 300,000-2,000,000; 1 x XT450A APC, 20,000-400,000; 2 x XT200A APC, 3,000-70,000; 1 x XT45A APC, 200-5,000). Tetrahydrofuran (THF) was used as the eluent at 25 $^{\circ}$C with a flow rate of 0.8 mL/min. The SEC system was calibrated using narrowly dispersed polystyrene (PS) and poly(methyl methacrylate) (PMMA) standards. Samples were prepared by dissolving approximately 5 mg of polymer in 1 mL of THF and filtering the solution through a 0.45 μm PTFE syringe filter prior to injection.

X-ray photoelectron spectroscopy: XPS measurements were performed using a Kratos Amicus/ESCA 3400 instrument. Samples were irradiated with unmonochromated Mg Kα X-rays at a source power of 240 W (12 kV), and the emitted photoelectrons were collected at a perpendicular take-off angle to the sample surface. Survey spectra were acquired to identify the elemental composition of the sample surface, and high-resolution narrow scans were collected over the binding energy regions of interest to determine the chemical state of each element. Binding energy calibration was carried out by referencing the adventitious carbon C 1s peak to 284.8 eV. Spectral deconvolution and baseline subtraction (Shirley background) were performed using CasaXPS software.

Scanning Electron Microscope: The morphology of the cross-linked thioamide polymeric adsorbent was observed through scanning electron microscopy (SEM, FEI Quanta 250). The applied voltage was 10 kV, and the fracture surface of the samples was sputter-coated with iridium (2 nm) before SEM observation.

2 Synthesis of Thioimidate Monomers

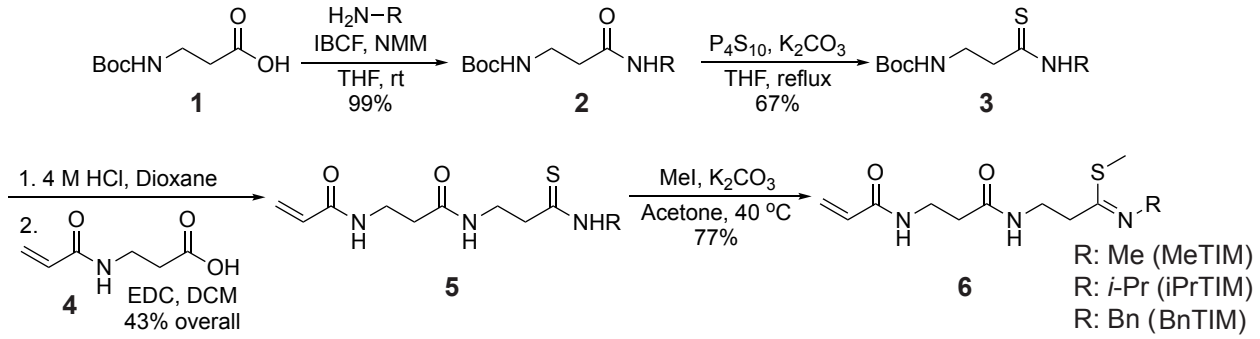
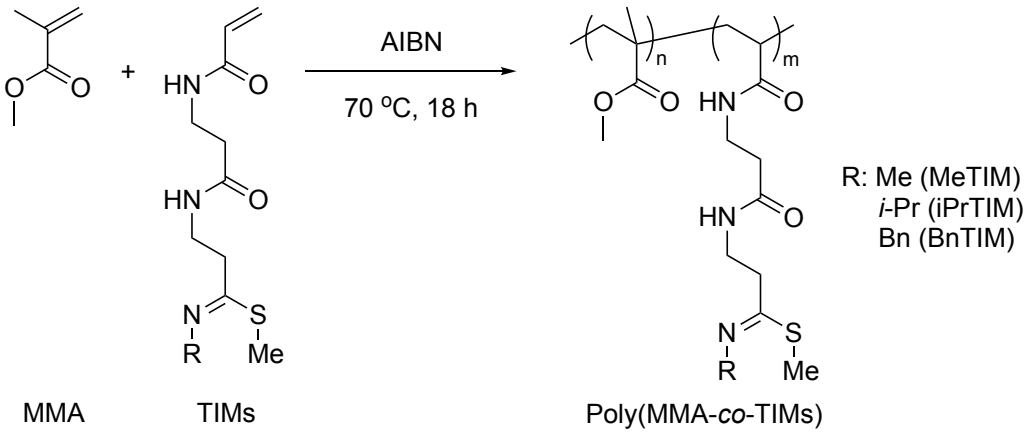


Figure S1: Synthesis of thioimidate monomers (TIMs).

Thioimidate (TIM) monomers were prepared according to our previously reported procedure starting from 3-((*tert*-butoxycarbonyl)amino) propanoic acid (**1**). Briefly, **1** was first converted into the corresponding **2** amide intermediates using standard coupling conditions. These intermediates were then subjected to thionation with phosphorus pentasulfide in the presence of a base in an anhydrous solvent to furnish the corresponding thioamides (**3**). After acidic Boc-deprotection, the resulting thioamides (**3**) were coupled with the appropriate acid components *N*-acryloyl β-alanine ((**4**)) under carbodiimide-mediated conditions to afford the targeted thioamide monomers (**5**). Subsequent alkylation with iodomethane provided the thioimidate (TIMs) monomers (**6**). The crude products were isolated by standard aqueous workup and purified by column chromatography to give analytically pure materials.[1]

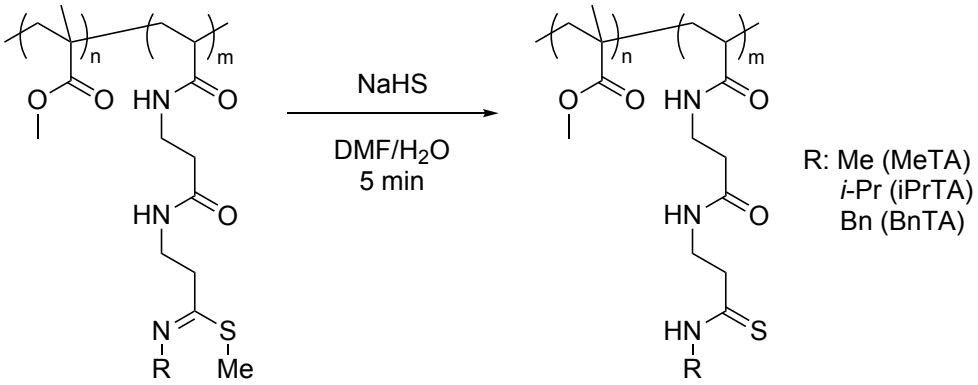
3 Polymerization of Thioimidate-Containing Monomers and Convertion into Thioamide

3.1 Synthesis of Poly(MMA-*co*-TIMs)



Poly(MMA-*co*-TIMs) was synthesized via free radical polymerization of MMA and TIMs monomers. MMA, TIMs, AIBN (Monomer/TIMs/Initiator: 50/50/1 and 100/100/1), and DMF (10 mL) were placed in glass reactor. The mixture was degassed by three freeze−pump−thaw cycles and heated to 70 °C for 18 h. After the reaction, the mixture was quenched in dry ice, precipitated into cold diethyl ether to remove residual monomer and low-molecular-weight oligomeric fractions, redispersed in fresh cold diethyl ether, and the resulting yellowish polymer was collected by filtration and dried under vacuum.

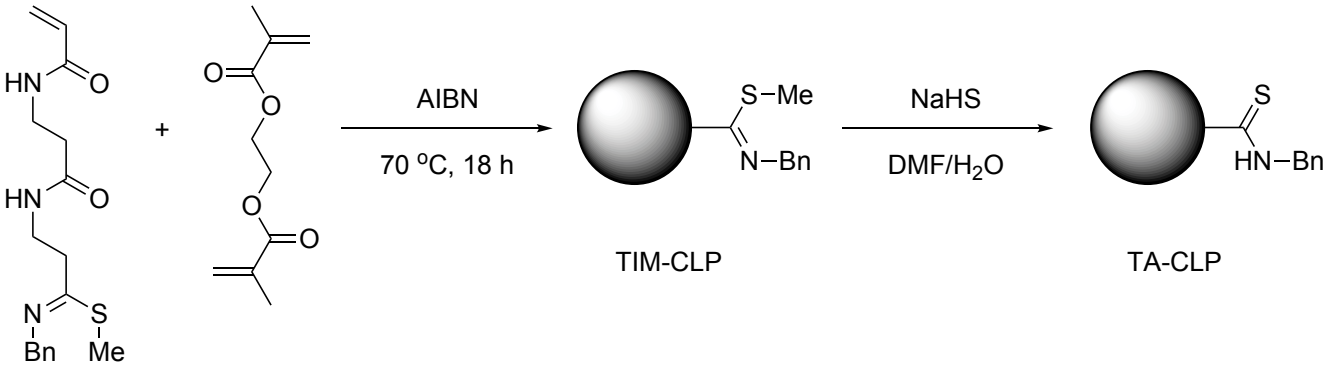
3.2 Synthesis of Poly(MMA-*co*-TAs)



Poly(MMA-*co*-TIMs) Poly(MMA-*co*-TAs)

Poly(MMA-*co*-TIMs) were dissolved in anhydrous DMF (0.1 M) and was added to a solution of NaHS in degassed water such that the final solution was 20% water and 1 M NaHS. This post-polymerization step liberates methyl mercaptan (methanethiol, CH_3SH) as a volatile by-product, so all reactions were carried out in closed vessels under fume-hood conditions. After the reaction, the mixture was precipitated into cold diethyl ether, and obtained polymers were dried in a vacuum oven. The polymers were analyzed by ^{1}H NMR.

3.3 Synthesis of Cross-linked Thioamide Polymeric Adsorbent



BnTIM EGDMA TIM-CLP TA-CLP

In 20 mL vial equipped with magnetic stir bar, BnTIM and EGDMA were dissolved in anhydrous DMF with AIBN initiator (BnTIM/EGDMA/Initiator: 100/20/1). The resulting reaction mixture was degassed by bubbling nitrogen gas through the solution for 5 minutes to remove dissolved oxygen. The vial was sealed, and heated at 70 °C for 16 hours. The reaction was terminated by cooling the vial in an ice bath to room temperature. The crude polymer was broken into small pieces and washed with DMF and methanol and dried in a vacuum oven at 60°C for 48 hours to afford the purified cross-linked thioimidate polymer as a yellow solid (88% yield).

The cross-linked thioimidate polymer was first immersed in anhydrous DMF. An aqueous NaHS solution was then added to this solution. This post-polymerization step liberates methyl mercaptan (methanethiol, CH_3SH) as a volatile by-product, so all reactions were carried out in closed vessels under fume-hood conditions. After the reaction, cross-linked thioamide polymeric adsorbent was washed thoroughly with DMF and methanol and dried in a vacuum oven. The polymers were analyzed by XPS and SEM.

4 Procedures for Gold Capture Test

4.1 Purification of Polymers Prior to Gold Capture

After NaHS treatment, the linear poly(MMA-*co*-TAs) and thioamide-containing cross-linked polymers (TA-CLP) samples were thoroughly washed to remove residual sulfide before use in adsorption experiments. The standard methylene blue colorimetric method for aqueous sulfide was used to monitor residual free sulfide,[2] and the washing procedure was repeated at least three times until no absorption was observed at 660 nm. Polymer batches that showed no detectable sulfide under these conditions were dried and used in the subsequent Au^{3+} adsorption experiments.

4.2 Batch Adsorption Experiments

Poly(MMA-*co*-BnTA) (16 mg) was added into 10 mL aqueous solution of $CuCl_2 \cdot 2\,H_2O$, $FeCl_3 \cdot 6\,H_2O$, $HAuCl_4 \cdot xH_2O$ or $PtCl_4$ ($[M^{n+}]$ = 100 mg/L, with 5 wt% HNO_3). After stirring at room temperature for 2 h, the suspensions were centrifuged for 10 min at a spin rate of 10,000 rpm, and the solid was separated by filtration through a filter membrane with an aperture of 0.22 μm. The residual concentrations of Cu^{2+}, Fe^{3+} and Au^{3+} in the supernatants were quantified by UV-Vis spectrophotometer using their characteristic absorptions in acidic solution, while Pt was determined spectrophotometrically as the Pt(IV) chloro complex generated from $PtCl_4$ by monitoring the $[PtCl_6]^{2-}$ species under acidic chloride conditions.

Poly(MMA-*co*-TIMs) and poly(MMA-*co*-TAs) (16 mg) were added into 10 mL aqueous solution of $AuCl_3$ ($[Au^{3+}]$ = 100 mg/L, with 5 wt% HNO_3). After stirring at room temperature for 10 min, 30 min, 1 h and 2 h, the suspensions were centrifuged for 10 min at a spin rate of 10,000 rpm, and the solid was separated by filtration through a filter membrane with an aperture of 0.22 μm. The remaining concentration of Au^{3+} in the supernatant was then measured using a UV-Vis spectrophotometer at a wavelength of 312 nm to calculate the extraction efficiency.

In a 10 mL aqueous solution of $AuCl_3$ ($[Au^{3+}]$ = 100 mg/L, with 5 wt% HNO_3), 1, 4, 8, or 16 mg of copolymer poly(MMA-*co*-TIMs) and poly(MMA-*co*-TAs) were added respectively. After stirring at room temperature for 2 h, the suspensions were centrifuged for 10 min at a spin rate of 10,000 rpm, and the solid was separated by filtration through a filter membrane with an aperture of 0.22 μm. The remaining concentration of Au^{3+} in the supernatant was then measured using a UV-Vis spectrophotometer at a wavelength of 312 nm to calculate the extraction efficiency.

A series of Au^{3+} adsorption isotherm experiments was carried out using aqueous $AuCl_3$ solutions in 5 wt% HNO_3 with initial concentrations ranging from 10 to 100 μg/mL. For each experiment, a defined amount of TA-CLP adsorbent was added to 10 mL Au^{3+} solution and stirred at room temperature for 2 h to reach adsorption equilibrium, as confirmed by preliminary kinetic tests. After adsorption, the mixtures were centrifuged at 10,000 rpm for 10 min, and the supernatants were carefully collected. The residual Au^{3+} concentration in the supernatant was determined using a UV–Vis spectrophotometer. The equilibrium adsorption capacity q_e (mg/g) for each initial concentration was calculated from the difference between the initial and equilibrium Au^{3+} concentrations. The resulting C_e/q_e versus C_e data were fitted to the Langmuir isotherm model to obtain the maximum adsorption capacity (q_m) and Langmuir constant (K_m). To extract the Langmuir parameters for Au^{3+} binding, the equilibrium data within this concentration window were fitted using the linearized Langmuir equation,

$$\frac{C_e}{q_e} = \frac{1}{q_m K_m} + \frac{C_e}{q_m} \tag{1}$$

where C_e is the equilibrium Au^{3+} concentration (g/mL), q_e is the equilibrium adsorption capacity (g/mg), q_m is the maximum adsorption capacity (g/mg), and K_m is the Langmuir adsorption constant (mL/mg).

Linear regression analysis of the Langmuir isotherm plot of C_e/q_e versus C_e plot gave an excellent correlation coefficient (R^2=0.9877), from which K_m=5.45x10^{-2} mL/μg and q_m=38.17 μg/mg were obtained, indicating that the Langmuir model provides a very good description of Au^{3+} adsorption on TA-CLP under the examined conditions and is consistent with predominantly monolayer adsorption on a relatively homogeneous surface.

The thermodynamic favorability of adsorption was further assessed using the dimensionless Langmuir separation factor (equilibrium parameter) R_L, defined as

$$R_L = \frac{1}{1 + K_m C_0} \tag{2}$$

where C_0 is the initial Au^{3+} concentration (g/mL). According to the standard criteria, R_L > 1 indicates unfavorable adsorption, R_L = 1 indicates

linear adsorption behavior, $0 < R_L < 1$ indicates favorable adsorption, and $R_L = 0$ indicates irreversible adsorption. The calculated R_L values for Au^{3+} adsorption on TA-CLP across the studied concentration range (Table S2) all lie between 0 and 1, confirming that Au^{3+} uptake on TA-CLP occurs under thermodynamically favorable conditions within the experimental system.

4.3 Column Adsorption Experiments

TA-CLP (20 mg) was packed into a glass column with an inner diameter of 4 mm and a packed bed height of 20 mm to evaluate the dynamic adsorption performance for Au^{3+}. An aqueous Au^{3+} solution was pumped through the column in down-flow mode at a constant flow rate of 1 mL/min using a peristaltic pump. The Au^{3+} concentration was determined by UV–Vis spectroscopy.

5 NMR and FTIR Spectra

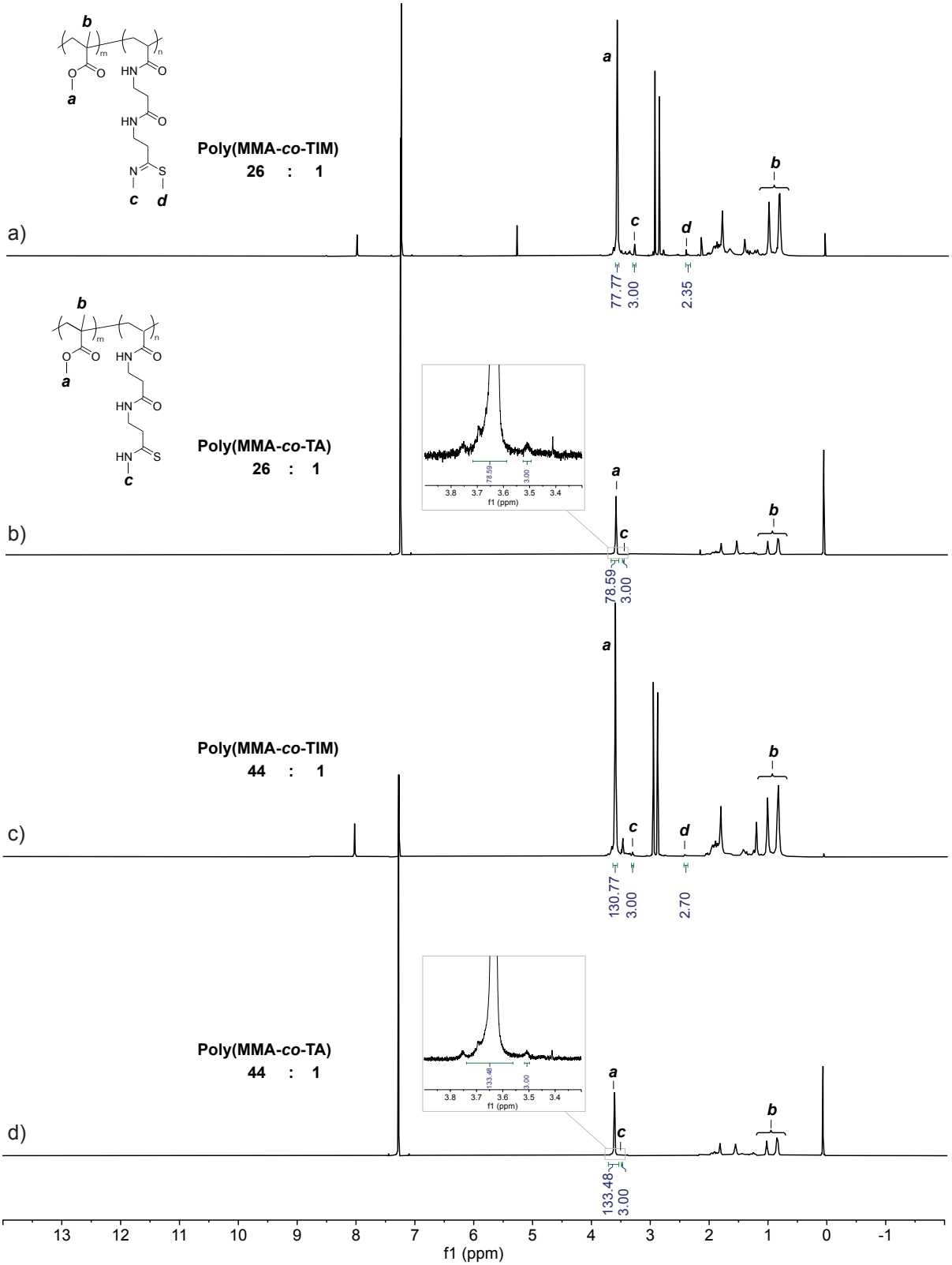


Figure S2: ^{1}H NMR spectra of poly(MMA-*co*-MeTIM) and poly(MMA-*co*-MeTA) copolymers prepared with different initial monomer feed ratios and subsequent conversion. (a) Poly(MMA-*co*-MeTIM) synthesized with a feed ratio of MMA/TIM/initiator = 50/50/1.[1] (b) Poly(MMA-*co*-MeTA) obtained from (a) after post-polymerization conversion. (c) Poly(MMA-*co*-MeTIM) synthesized with a feed ratio of MMA/TIM/initiator = 100/100/1.[1] (d) Poly(MMA-*co*-MeTA) obtained from (c) after post-polymerization conversion. (600 MHz, $CDCl_3$).

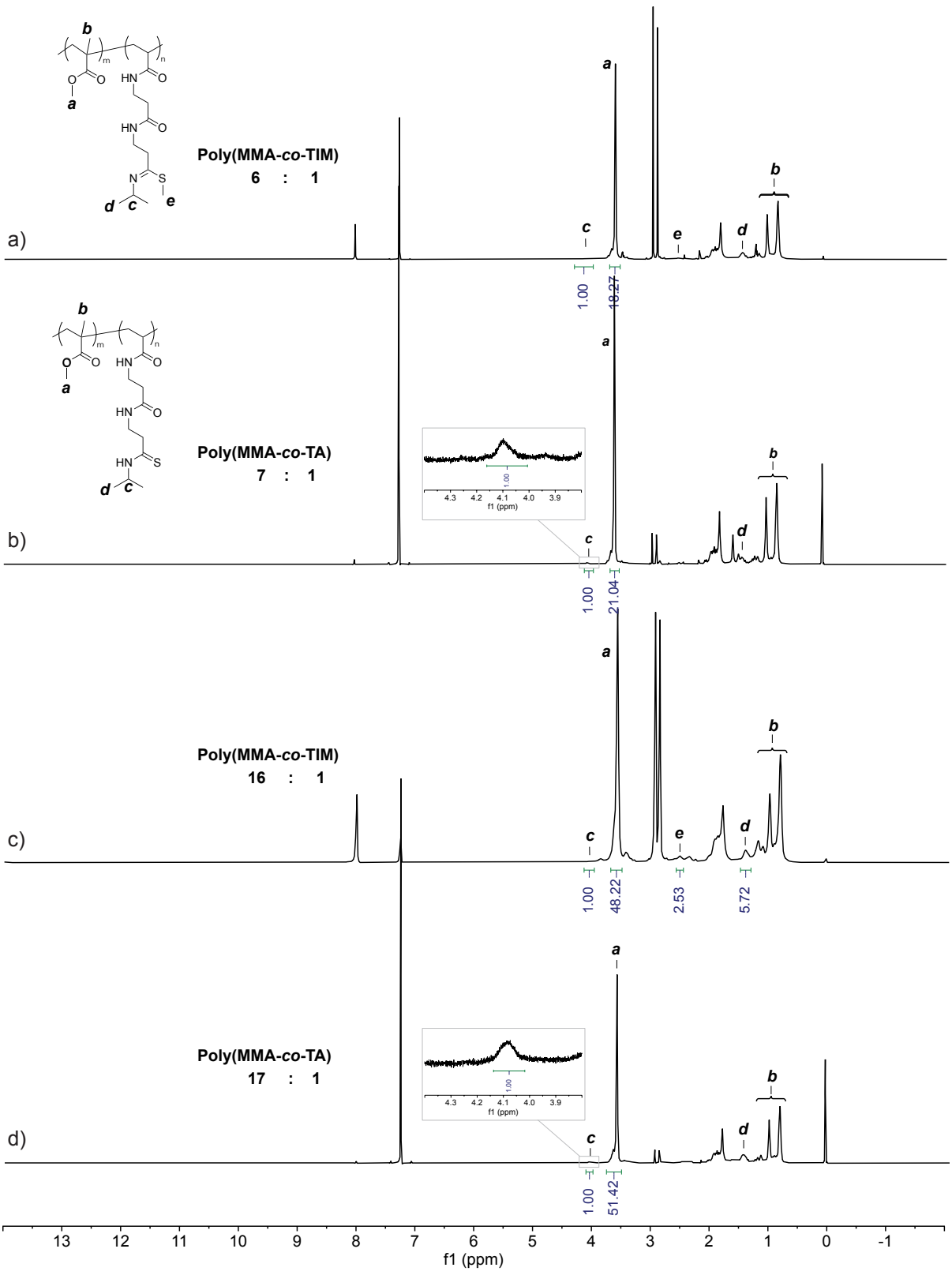


Figure S3: ^{1}H NMR spectra of poly(MMA-*co*-iPrTIM) and poly(MMA-*co*-iPrTA) copolymers prepared with different initial monomer feed ratios and subsequent conversion. (a) Poly(MMA-*co*-MeTIM) synthesized with a feed ratio of MMA/TIM/initiator = 50/50/1.[1] (b) Poly(MMA-*co*-iPrTA) obtained from (a) after post-polymerization conversion. (c) Poly(MMA-*co*-iPrTIM) synthesized with a feed ratio of MMA/TIM/initiator = 100/100/1.[1] (d) Poly(MMA-*co*-iPrTA) obtained from (c) after post-polymerization conversion. (600 MHz, $CDCl_3$).

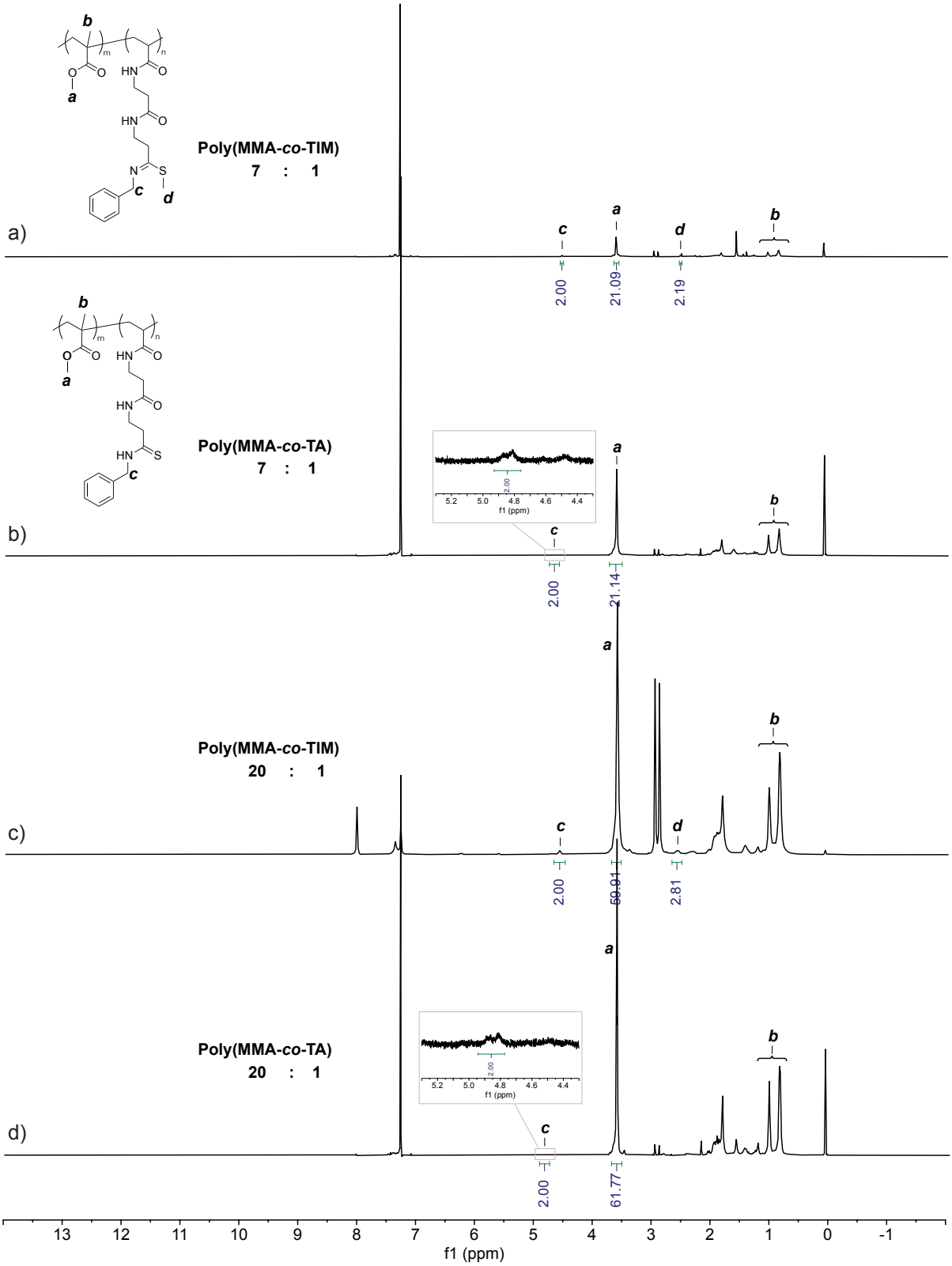


Figure S4: ^{1}H NMR spectra of poly(MMA-*co*-BnTIM) and poly(MMA-*co*-BnTA) copolymers prepared with different initial monomer feed ratios and subsequent conversion. (a) Poly(MMA-*co*-BnTIM) synthesized with a feed ratio of MMA/TIM/initiator = 50/50/1.[1] (b) Poly(MMA-*co*-BnTA) obtained from (a) after post-polymerization conversion. (c) Poly(MMA-*co*-BnTIM) synthesized with a feed ratio of MMA/TIM/initiator = 100/100/1.[1] (d) Poly(MMA-*co*-BnTA) obtained from (c) after post-polymerization conversion. (600 MHz, $CDCl_3$).

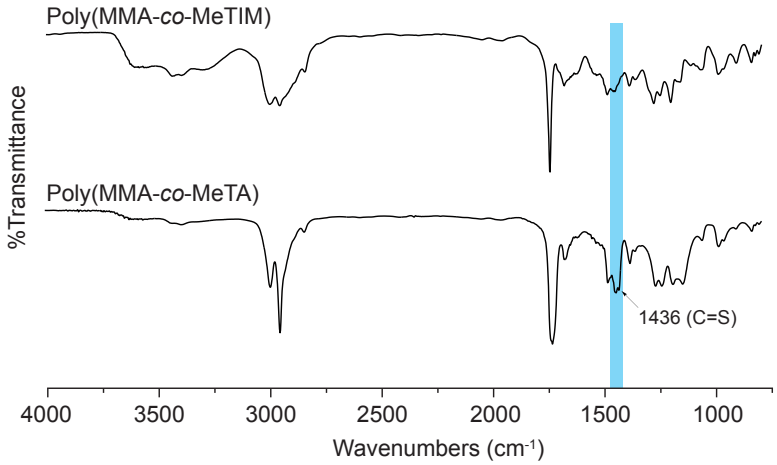


Figure S5: FTIR spectra of poly(MMA-*co*-MeTIM) and poly(MMA-*co*-MeTIM)

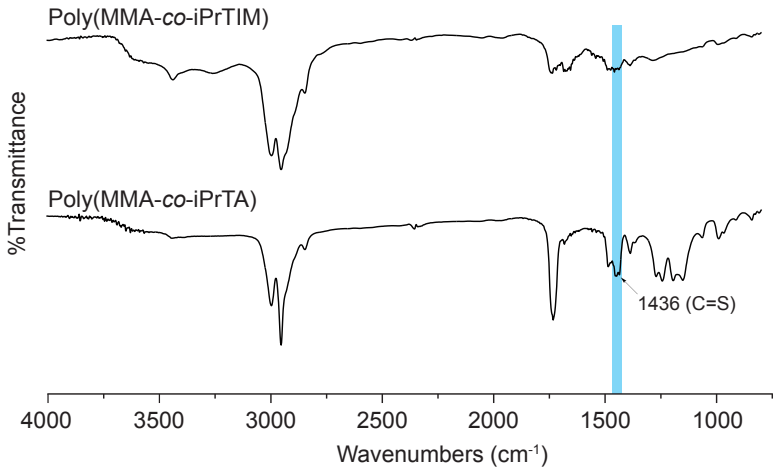


Figure S6: FTIR spectra of poly(MMA-*co*-iPrTIM) and poly(MMA-*co*-iPrTA)

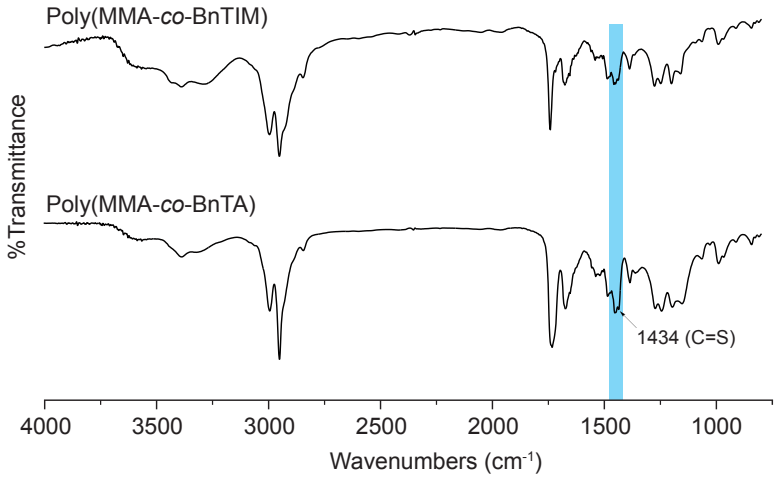


Figure S7: FTIR spectra of poly(MMA-*co*-BnTIM) and poly(MMA-*co*-BnTIM).

6 Supplementary Figures and Tables

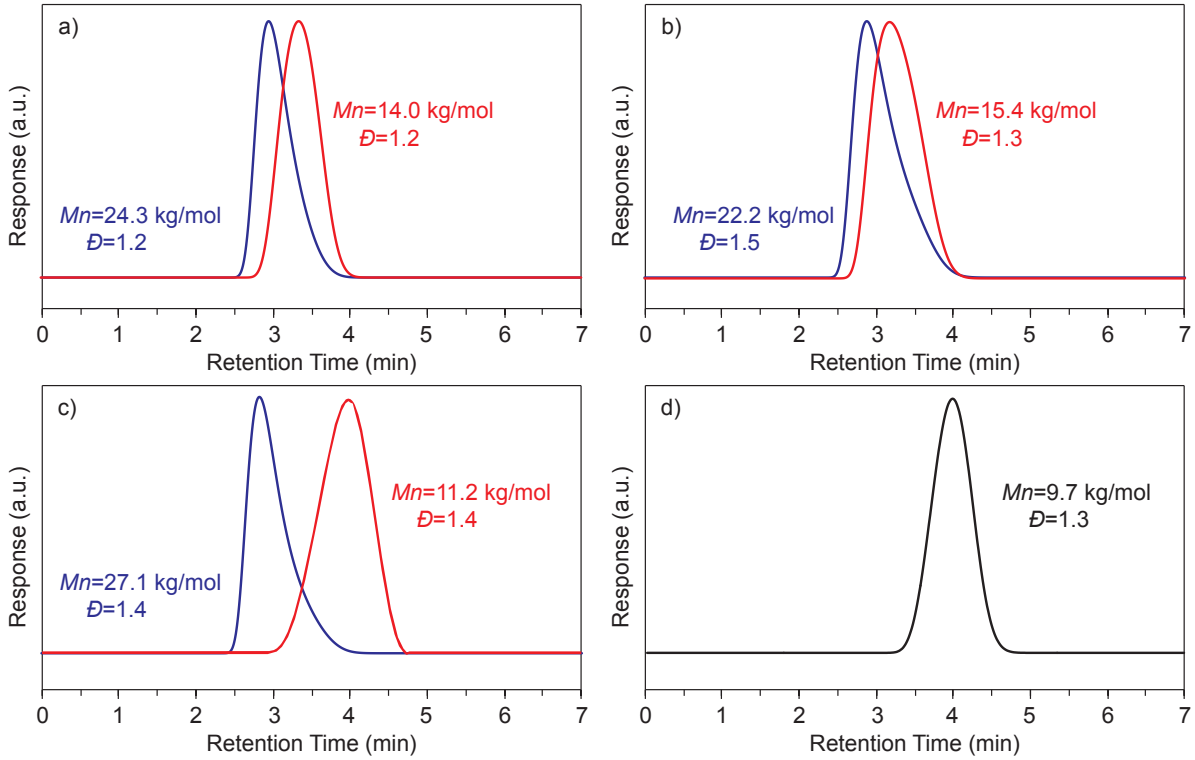


Figure S8: SEC traces of thioimidate containing copolymers, (a) poly(MMA-*co*-MeTIM), (b) poly(MMA-*co*-*i*-PrTIM), (c) poly(MMA-*co*-BnTIM) with varying MMA/TIM/In ratios (50/50/1: red, 100/100/1: blue).[1] (d) SEC traces of poly(MMA-*co*-BnTA) was obtained by the reaction of poly(MMA-*co*-BnTIM) ($M_{n,SEC}$=11.2 k.mol^{-1}, *Đ*=1.4) with NaHS. SEC was performed in THF, using PMMA standards.

Table S1: Atomic concentration of cross-linked polymers as determined by XPS analysis.

	Atomic concentration (%)				
entry	O	N	C	S	Au
TIM-CLP	17.76	2.16	79.84	0.23	-
TA-CLP	18.34	2.32	78.98	0.36	-
TIM-CLP@Au	19.98	2.35	77.74	0.17	0.39
TA-CLP@Au	18.26	2.77	77.26	0.48	1.23

Table S2: R_L values of adsorbent based on the Langmuir equation.

Initial concentration of Au^{3+} (μg/mL)	R_L
10	0.65
20	0.48
40	0.31
60	0.23
80	0.19
100	0.16

7 References

(1) Kinali-Demirci, S.; Demirci, S.; Byerly-Duke, J.; VanVeller, B. Radical Reactivity of Thioimidates for Diversified Polymeric Amidines with Tunable Properties. *Angewandte Chemie International Edition* **2025**, e202509727.

(2) Cline, J. D. Spectrophotometric determination of hydrogen sulfide in natural waters 1. *Limnology and Oceanography* **1969**, *14*, 454–458.