A novel smart polymer responsive to CO_2

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Detailed Synthesis and Characterizations

Materials

P-chloromethylstyrene (CMS) (Aldrich, 90%) was purified by vacuum distillation from CaH_2, and 2,2-azoisobutyronitrile (AIBN) (Aldrich, 98%) was recrystallized from diethylether prior to use. The chain transfer agent (CTA), S-1-dodecyl-S'-(α,α'-dimethyl -α''-aceticacid)trithiocarbonate, was synthesized following a previously reported procedure.[1] Tetrahydrofuran (THF) (Guangdong Guanghua Chemical Co. Ltd, 99.8%) was dried and distilled over benzophenone-Na. N,N-dimethylacetamide dimethyl acetal (Aldrich, 90.0%), *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine (PMDTA) (Aldrich, 99.0%) and propargyl amine (Shanghai Rainbow Chemical Co., Ltd., 99.3%) were used as received. All other reagents were purchased from Shanghai Chemical Reagent Co., Ltd., and used as received unless otherwise specified.

Characterizations

^{1}H NMR spectra were recorded at 25 °C on a Bruker AV300 NMR spectrometer at 300 MHz. Chemical shifts (δ) are reported in parts per million (ppm) with reference to the residual protons of the deuterated solvents.

Infrared spectra were registered on a Nicolet MX-1E FTIR (USA) spectrophotometer in the scanning range of 4000–400 cm^{-1} using KBr pellet method or paraffin liquid cell.

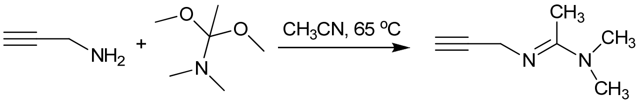
Relative molecular weight and molecular weight distribution were determined by one of the following two gel permeation chromatography (GPC) systems depending on the solubility of the polymers. The first one is equipped with a waters model 1515 pump, a model 2410 refractive index detector, and an OH-pak KB-803 column operated at an oven temperature of 25 °C. THF was used as the mobile phase at a flow rate of 0.8 $ml\cdot min^{-1}$, and the column was calibrated using poly(ethylene oxide) (PEO) as standard in this case. The other is PL GPC50 with a refractive index detector, and the columns (7.5 × 300 mm PLgel Mixed-C) were eluted by DMF and calibrated with poly(methylmethacrylate) (PMMA) standard. Analysis was performed at 40 ^{o}C with flow rate of 1.0 $ml\cdot min^{-1}$.

Conductivity of the wet DMF solution of amidine-based polymer was measured with a DDS-11A conductometer (Chengdu Fangzhou Instrument) at 25 °C, and average values were calculated from three runs of a certain measurement.

The X-ray photoelectron spectroscopy (XPS) experiments were performed on a Kratos XSAM800 XPS system (Kratos Ltd.). The measurement parameters are: photon energy (Al K_α) = 1486.6 eV, P = 12 KW × 1 mA.

Preparation of N'-Propargyl-N,N-dimethylacetamidines (PDAA)

To a CH_3CN (8.0 ml) solution of N,N-dimethylacetamide dimethyl acetal (2.00 g, 15.00 mmol) was added propargylamine (0.82 g, 15.00 mmol) via a syringe. The reaction mixture was stirred under N_2 at 65 °C for 1.5 h. After removal of the solvent, the crude product was purified by basic Al_2O_3 chromatography using CH_2Cl_2/CH_3OH (10:1) as eluent to give the final compound as a yellow liquid (1.32 g, 10 mmol, 71.0%). As PDAA can react with CO_2 in the air, it is necessary to keep it under argon or N_2. ^1H NMR ($CDCl_3$): δ 2.21 (s, 3H), 2.28 (t, J = 2.4Hz, 1H), 3.11 (s, 6H), 4.10 (d, J = 2.7Hz, 2H). FI-IR: 2110.3 cm^{-1} (C≡C), 1639.5 cm^{-1} (C=N).



Scheme S1. Synthesis of N'-propargyl-N,N-dimethylacetamidines (PDAA).

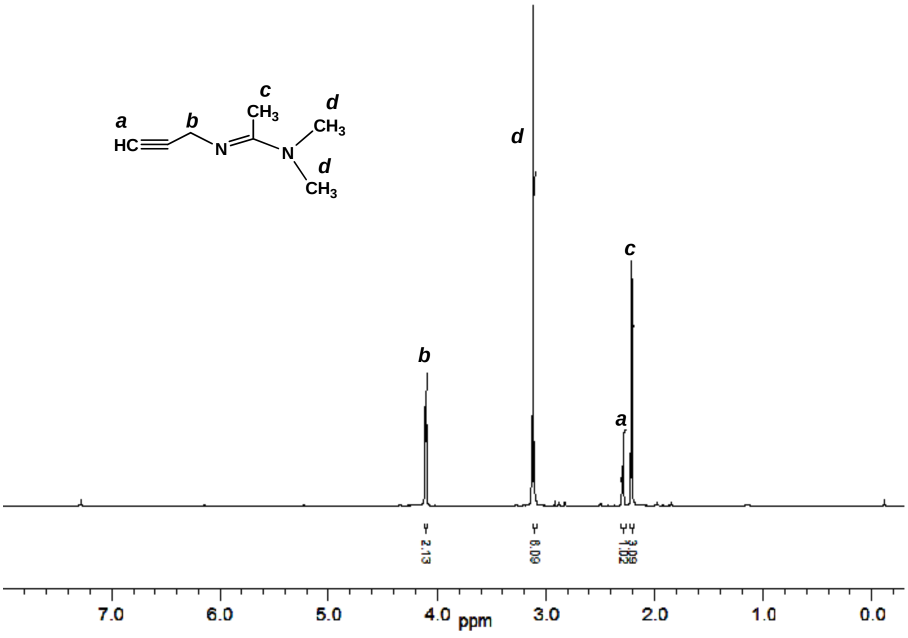


Figure S1. ^1H NMR spectrum of N'-propargyl-N,N-dimethylacetamidines in $CDCl_3$.

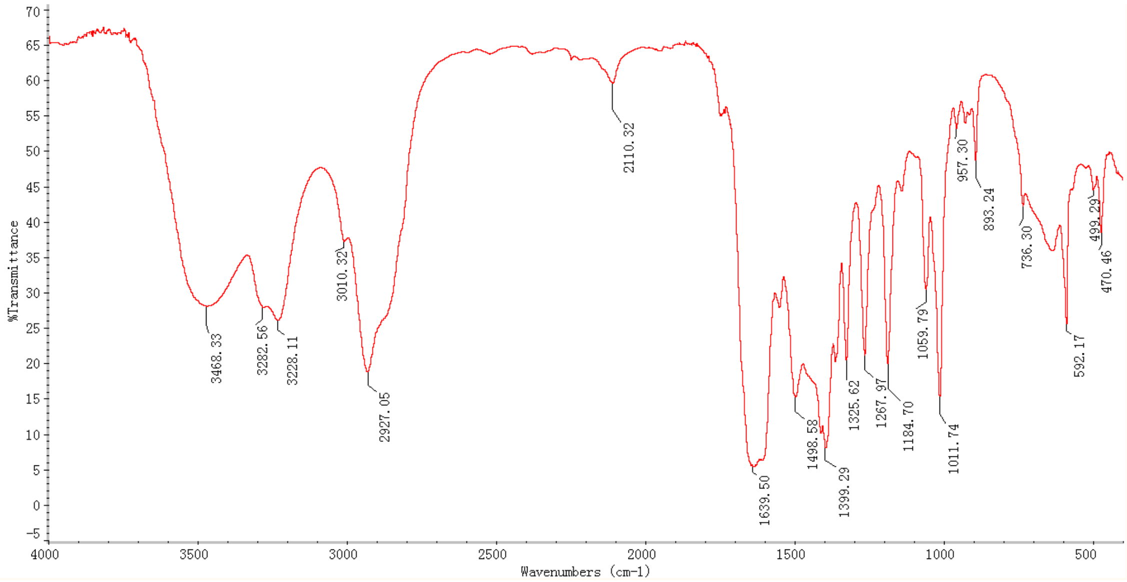
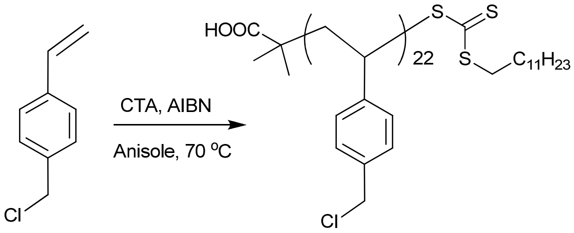


Figure S2. IR spectrum of N'-propargyl-N,N-dimethylacetamidines (paraffin liquid cell procedure).

Preparation of poly(4-chloromethylstyrene) (PCMS) by RAFT polymerization

A mixture of 4-chloromethylstyrene (5.00 g, 32.78 mmol), (S)-1-dodecyl-(S')-(α,α'-dimethyl -α''aceticacid)-trithiocarbonate (DDMAT) (238.00 mg, 0.656 mmol), 2,2'-azobis(isobutyronitrile) (AIBN) (21.50 mg, 0.131 mmol) and anisole (2.0 ml) was degassed by three freeze/thaw cycles, sealed under argon, and heated at 70 °C for 24 h. The polymerization was stopped by immerging the reaction tube into liquid nitrogen for about 5 minutes. Then, the product mixture was diluted by roughly the same volume of dry THF, and the final product was gained via precipitation in *n*-hexane followed by filtration over a G4 frit and drying under vacuum. Yield: 4.2 g (84%). THF-GPC: M_n = 3726 g·mol^{-1}, PDI = 1.27. The degree of polymerization (n) was calculated out based on the obtained molecular weight. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09–6.49 (arom. C*H* of styrenic ring), 4.51 (CH_2Cl), 1.56 and 1.38 (C*H* and CH_2 of polymer chain).



Scheme S2. RAFT polymerization of 4-chloromethylstyrene to produce PCMS.

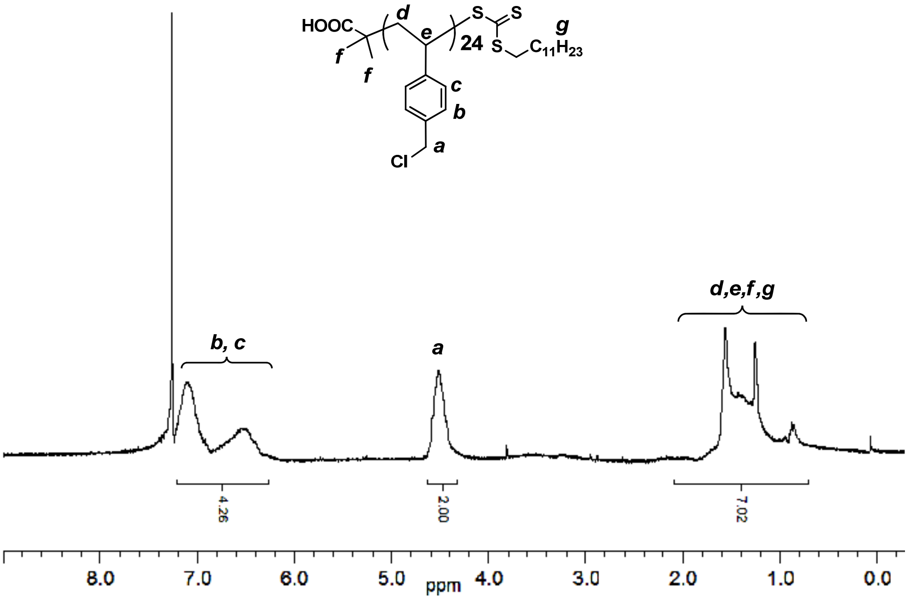


Figure S3. ^{1}H NMR spectrum of PCMS in $CDCl_3$.

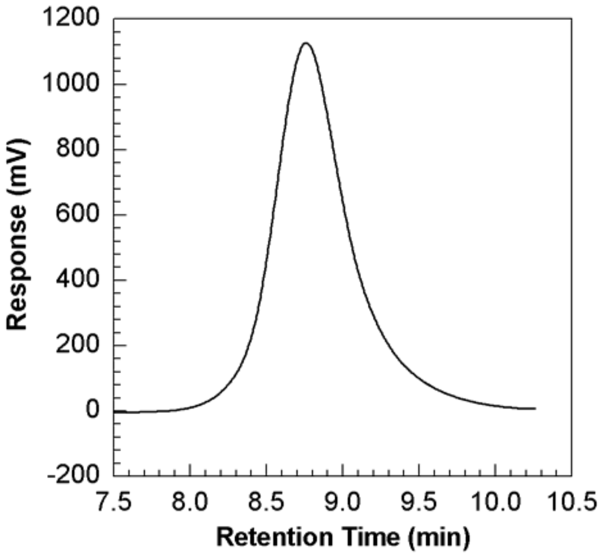
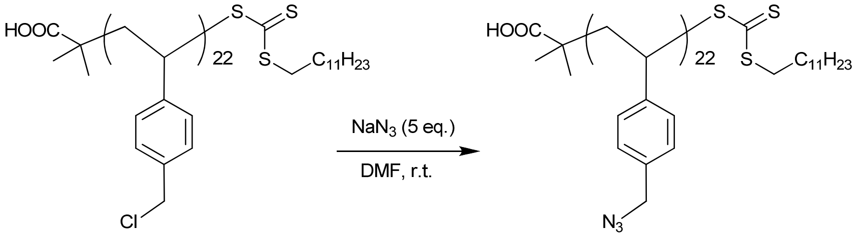


Figure S4. GPC chromatogram for PCMS.

Preparation of Poly(p-azidomethylstyrene) (PAMS)

PCMS (2.00 g, 0.54 mmol) was dissolved in 30 ml dry DMF, and then NaN_3 (3.86 g, 65.50 mmol) was added. The reaction mixture was stirred at room temperature for 2 days and then precipitated in excess of methanol. The obtained product was redissolved in dichloromethane and reprecipitated in methanol. The resultant solid was collected by filtration and dried overnight in a vacuum oven for 24 h to give PAMS. Yield: 1.8 g (90%). The chemical shifts of the benzylic protons were changed from 4.51 ppm in PCMS to 4.27 ppm in PAMS, indicating that all chloro groups have been converted into azido units. THF-GPC: $M_n = 5240$ g·mol^{-1}, PDI = 1.47. ^1H NMR ($CDCl_3$, 300 MHz), δ 7.01 and 6.51 (arom. C*H* of styrenic ring), 4.27 (CH_2N_3), 1.72 and 1.45 (C*H* and C*H*$_2$ of polymer chain). FI-IR: 2094.3 cm^{-1} ($-N_3$).



Scheme S3. Postmodification of PCMS into PAMS.

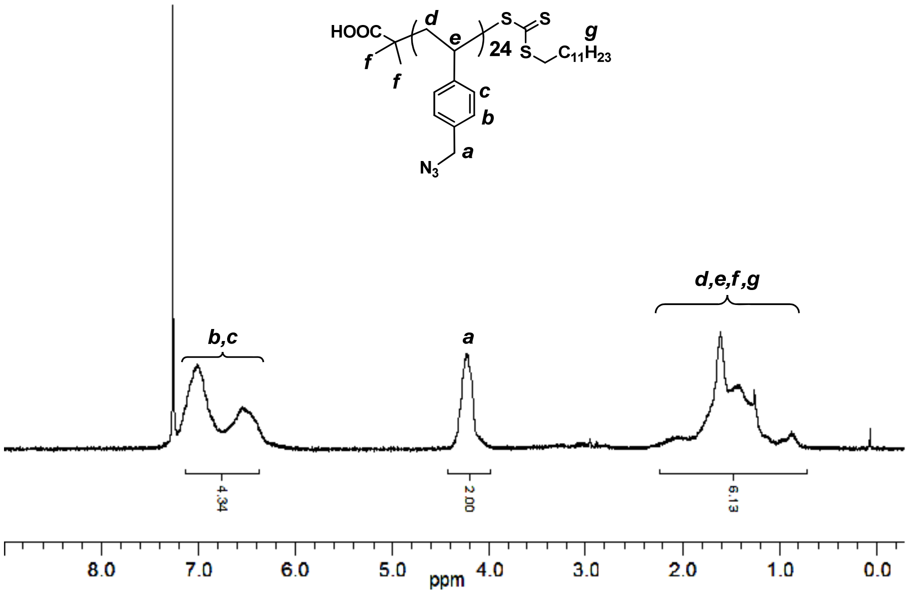


Figure S5. ^{1}H NMR spectrum of PAMS in $CDCl_3$.

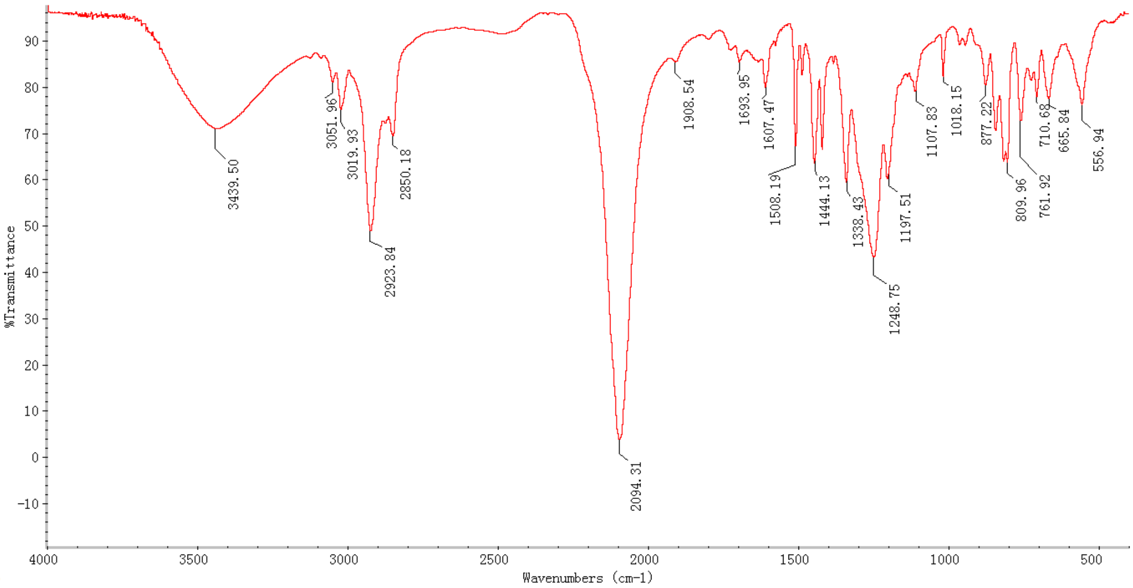


Figure S6. IR spectrum of PAMS (KBr pellet method).

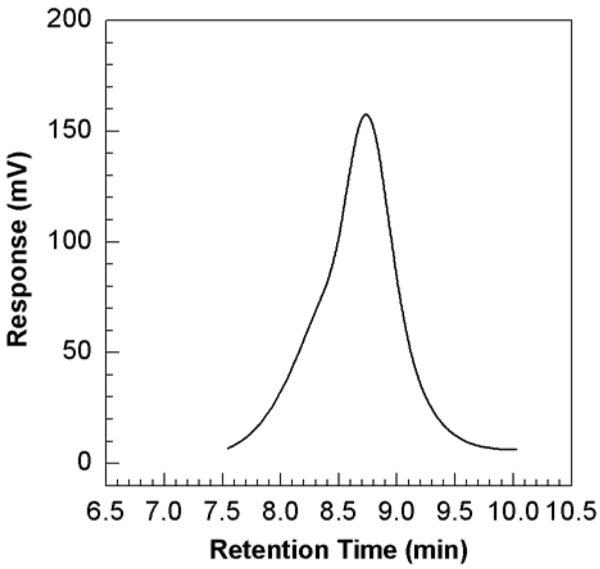
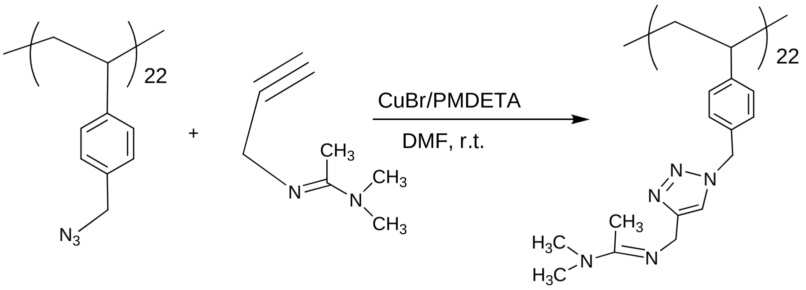


Figure S7. GPC chromatogram for PAMS.

Preparation of amidine-based polymer by "click" reaction

To a solution of PAMS (1.00 g, 0.26 mmol) and PDAA (1.30 g, 10.50 mmol) in 20 ml DMF, the catalyst CuBr (1.22 g, 8.50 mmol) and PMDETA (1.47 g, 8.50 mmol) were added. The reaction vessel was sealed and the mixture was degassed by doing three freeze-pump-thaw cycles. The solution was stirred under argon at room temperature overnight. At the end of this period, the polymer solution was passed through a basic alumina column several times to remove copper salt. Finally, the polymer solution was precipitated into ether. After filtration, the polymer was dried in a vacuum oven. Yield: 1.2 g (70 %). The chemical shifts of the benzylic protons were changed from 4.27 ppm in PAMS to 5.37 ppm in the amidine-based polymer, indicating that the click reaction between PDAA and PAMS was accomplished. DMF-GPC: Mn = 10759 g·mol^{-1}, PDI = 1.15. FI-IR: 1645 cm^{-1} (C=N).



Scheme S4. Synthesis of amidine-based polymer by "clicking" PDAA onto PAMS.

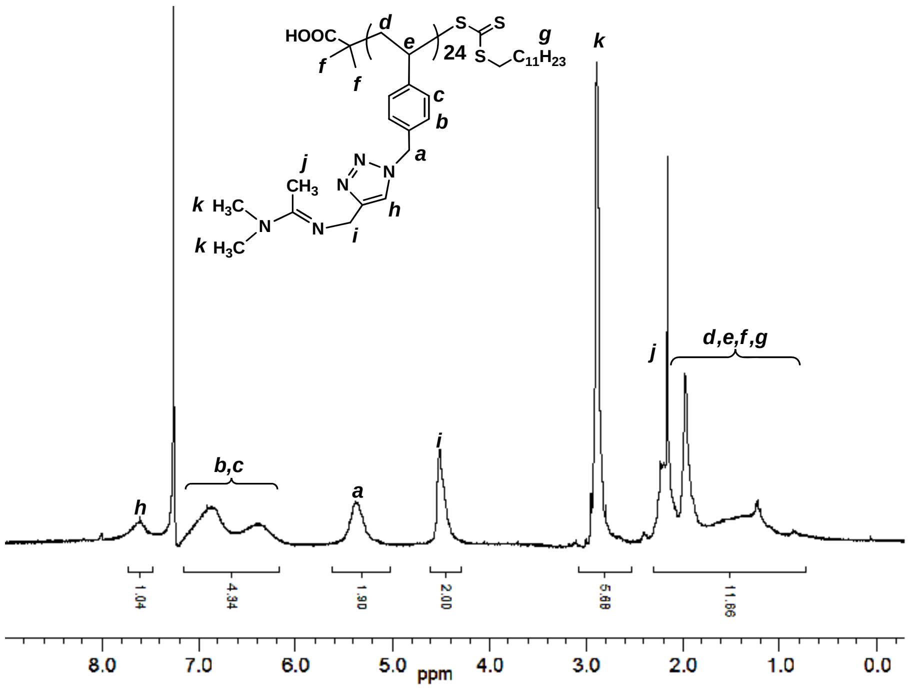


Figure S8. ^{1}H NMR (300 MHz) spectrum of the amidine-based polymer in $CDCl_3$.

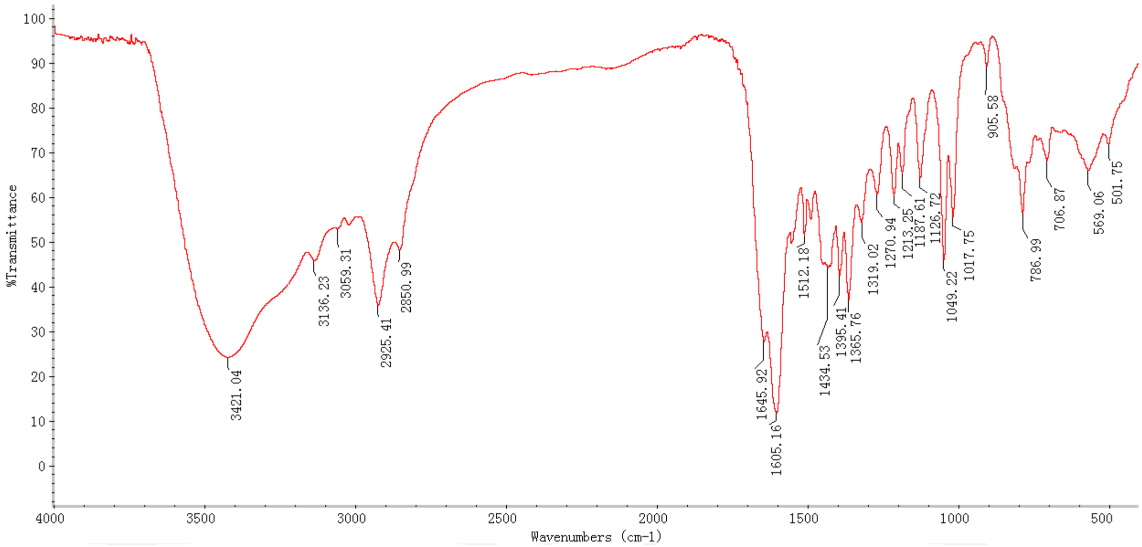


Figure S9. IR spectrum of the amidine-based polymer (KBr pellet method).

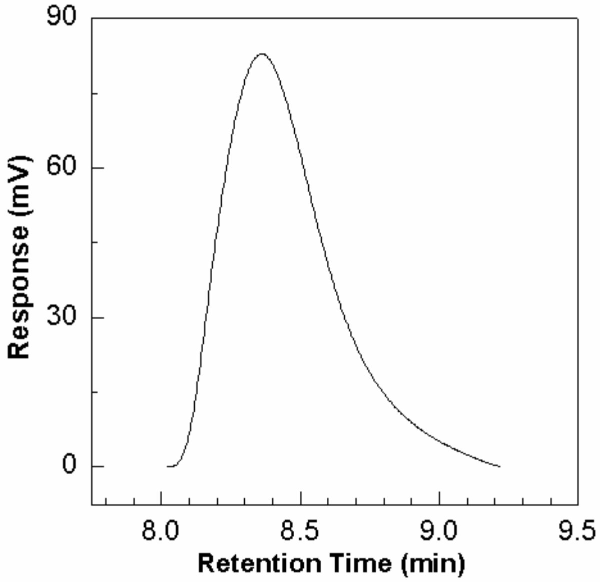


Figure S10. GPC chromatogram for the amidine-based polymer.

XPS spectrum of the amidine-based polymer

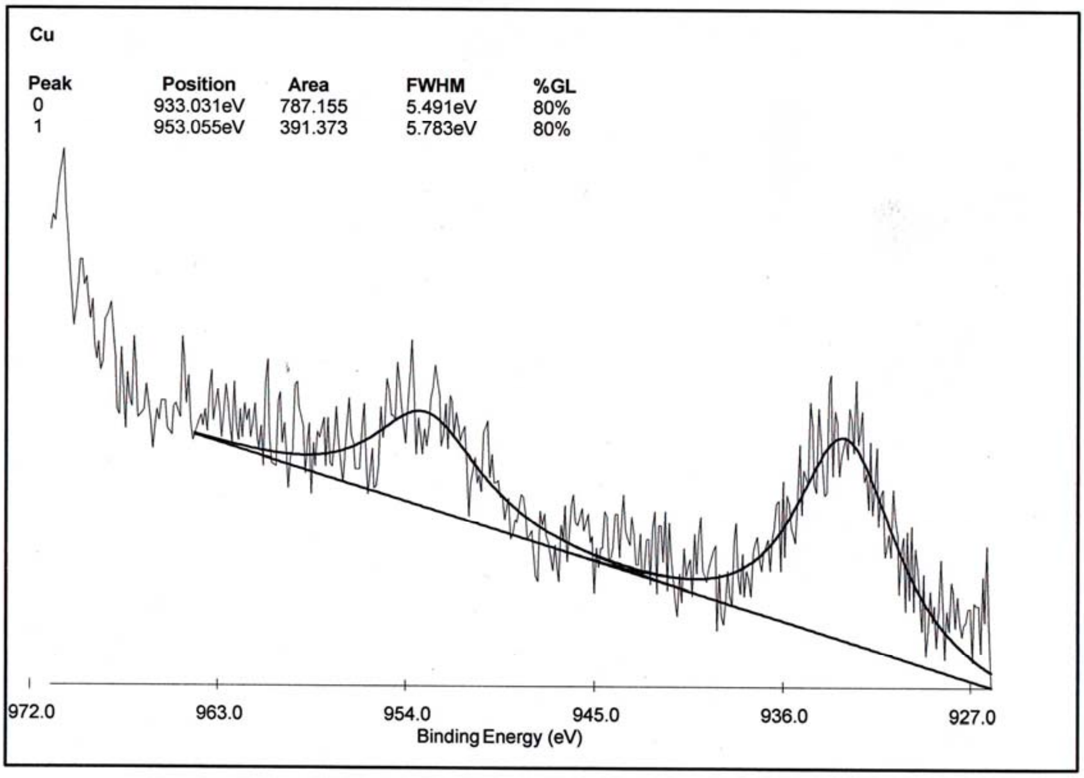


Figure S11. XPS spectrum of the amidine-based polymer. The binding energy ranges from 927 to 972 ev.

From the XPS spectrum of amidine-based polymer samples (Fig. S11), it can be seen that the binding energy of 933 and 953 are the peaks of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ respectively, which indicates that amidine-based polymer trapped copper ions.

Reference

1. J. T. Lai, D. Filla, R. Shea, *Macromolecules*, 2002, **35**, 6754.