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# Pyridinyl Polythioether via a One-Pot Thiolactone Ring-Opening and Thiol-Phenylsulfone Click Polymerization: Synthesis, Fluorescence, and Degradation Behavior

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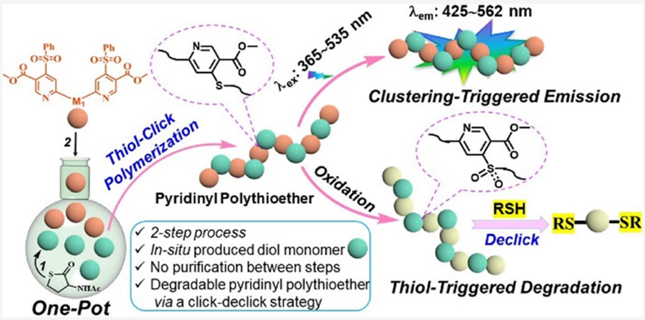
**ABSTRACT:** In this study, we synthesized a heteroaromatic thioether-containing polymer through the ring-opening of *N*-acetyl homocysteine thiolactone (NHTL) and thiol-heteroaromatic sulfone click polymerization in a one-pot approach. A dithiol monomer, produced in situ via NHTL ring-opening, was polymerized with a bis(phenylsulfone)-containing monomer through the click step-growth polymerization, resulting in the generation of a thermally stable polymer with pyridinyl thioether moieties in its main chain. The obtained polymer demonstrated clustering-triggered emission behavior due to electron-rich N, O, and S heteroatoms in the polymer structure. It was explored as a fluorescent polymeric probe to detect $Cu^{2+}$ ions in the visible region. With $H_2O_2/Na_2WO_4$ as the oxidative reagent, thioether moieties in the polymer backbone were converted to sulfoxide/sulfone moieties. The resulting oxidized polymer underwent degradation through a declick reaction with a monothiol-containing compound. After the declick reaction of 2-mercaptoethanol and the oxidized polymer, a small molecule readily separated from the degradation product was recycled as a diol monomer to prepare polyurethane with a diisocyanate monomer. The pyridinyl thioether-containing polymer with clustering-triggered emission behavior exhibits potential as a new degradable material that can address environmental concerns and enhance sustainability in various applications.



## INTRODUCTION

The widespread applications of nondegradable synthetic polymers have led to global pollution. There is an increasing demand for degradable polymers to address environmental concerns. Over past decades, various degradable polymers have been developed by incorporating cleavable groups or dynamic covalent bonds into polymer structures.[1−5] Backbone degradable polymers are highly desirable for biomaterials,[6−8] nanomaterials,[9] transient electronics,[10,11] and environmental applications.[12] It is a promising strategy to accelerate degradation by inserting heteroatom-containing weak bonds into the polymer backbone.[13]

Click polymerization demonstrates distinctive advantages in preparing degradable polymeric materials because of the high efficiency and modular character of click reactions.[14] The versatile toolbox of click chemistry enables the creation of various heteroatom-containing linkages between clickable monomer units. Based on hydroxyl-alkyne and amine-alkyne click polymerizations, Tang and Qin's group developed dynamic polymers and acid-degradable polymers, including poly(vinyl ether)s, poly(vinylene ether ketone)s, and hyperbranched poly($\beta$-aminoacrylate)s.[15−20] The resulting dynamic poly($\beta$-aminovinylsulfone) and poly($\beta$-enaminone) were able to undergo amine exchange to induce polymer degradation.[15,16] The thermally reversible nature of the maleimide-furan Diels−Alder click cycloaddition makes it an attractive approach for the preparation of various polymer architectures with temperature-responsive degradation, self-healing properties, or recyclability.[21] The sulfur(VI)−fluoride exchange (SuFEx) click polymerization has enabled the synthesis of unique classes of polymers containing $-SO_2-$ linkers.[22] Xu and Lu's group prepared aryl polysulfonates through SuFEx click step-growth polymerization of bisalkylsulfonyl fluoride and bis(aryl silyl ether) and found that the resulting polysulfonates gradually decomposed into oligomers using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst.[23] The polysulfonimidate derived from the disulfonimidoyl fluoride and diphenolate demonstrated dynamic covalent chemistry with other phenols and degraded within 48 h in refluxing tetrahydrofuran (THF) containing DBU with phenol or *p*-OMe-phenol.[24] Aromatic polysulfamides obtained by SuFEx

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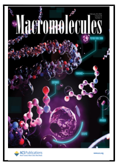

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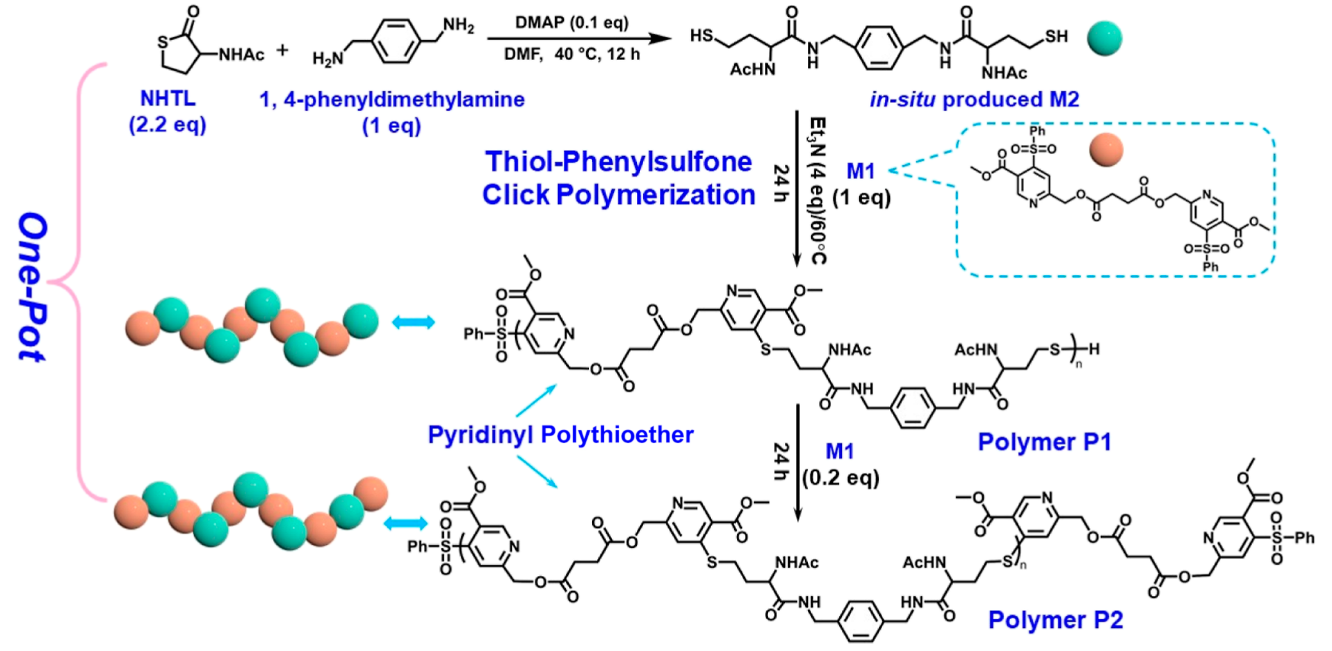
**Scheme 1. Outline for the Synthesis of Pyridinyl Polythioethers P1 and P2 by NHTL Ring Opening and Subsequent Thiol-Phenylsulfone Click Polymerization in a One-Pot Approach**



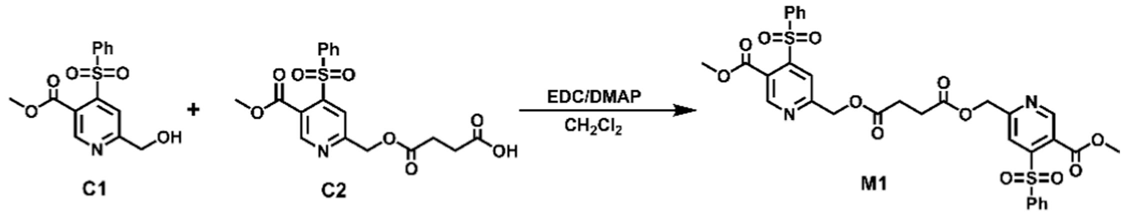
click polymerization could be depolymerized upon heating in basic or acidic aqueous solution and recycled back to their constituting monomers.[25,26] Sharpless and co-workers[27] utilized AB-type aryl silyl ether-fluorosulfates to synthesize sulfate-linked polymer polysulfates via the chain-growth SuFEx polycondensation. The resulting electron-deficient polysulfates underwent complete degradation under alkaline conditions.

Sulfur (S)-containing polymers have attracted growing attention in recent years owing to their unique features, including high light refractivity, mechanical properties, electrochemical properties, photophysical properties, and coordination ability with metal ions.[28−32] Due to the high reactivity of thiol to alkenes/alkynes, epoxies, isocyanates, and halogens, thiol-based click reactions have provided a versatile strategy to construct thioether-containing polymers with diverse architectures under mild conditions.[33−35] Incorporating S atoms into polymer structures can also impart polymers with degradation. The poly($\beta$-thioester)s synthesized by the thiol-Michael addition of dithiols and diacrylates exhibited hydrolytic degradation in acidic or alkaline environments.[36] Recently, the nucleophilic aromatic substitution of heteroaromatic methylsulfones by thiols has emerged as an attractive coupling reaction for specific bioconjugation of peptides and proteins,[37−39] preparation of antibody-drug conjugates,[40] and fabrication of hydrogels for cell encapsulation.[41,42] Similarly, Su's group developed the reaction of phenylsulfonated pyridine derivatives and thiols for site-specific labeling of proteins.[43,44] The nucleophilic aromatic substitution of a phenylsulfonyl group on the 4-position of pyridine by a thiol leads to the generation of a stable pyridinyl-thioether product, releasing a phenylsulfonate anion as a leaving group. The click reaction of thiols and heteroaromatic sulfones is characterized by high reactivity and specific selectivity toward thiols. The reaction rate can be regulated by adjusting the electron-deficient character of the heteroaromatic substrate bearing the sulfonyl group.[45] Additionally, the heteroaryl-thioether linkages formed are irreversible and highly stable, as compared to thiol-maleimide adducts that are prone to hydrolysis and exchange reactions with reactive thiols through the retro-Michael reaction.[37,46]

In our previous study, we found that thioether moieties at the 4-position of the pyridyl ring could be oxidized to sulfoxides and/or sulfones, both of which were able to undergo base-catalyzed nucleophilic substitution reactions with other thiols.[47] The two-step reaction provides an efficient approach to breaking the initially formed thioether bonds. Based on the thioether oxidation and thiol-phenylsulfone substitution reaction, we have developed a click-declick strategy to obtain cleavable block copolymer and star-like polymer. In the click-declick strategy, the clickable units are linked through temporary covalent bonds formed by a click reaction, while the resulting bonds can undergo efficient and selective cleavage by a declick reaction.[48] This protocol allows the fabrication of novel degradable and recyclable polymers, which remain stable during use and storage but can readily degrade upon activation triggered by unusual stimuli, such as chemical, mechanical, and light stimuli.[49−52]

Herein, a main-chain degradable polymer pyridinyl polythioether was developed through a click-declick strategy based on thioether oxidation and a thiol−click reaction. We employed a one-pot approach to preparing pyridinyl polythioether (Scheme 1). The ring-opening of *N*-acetyl homocysteine thiolactone (NHTL) and click step-growth polymerization were conducted sequentially in the same pot. A dithiol monomer was produced in situ by the NHTL ring-opening with a diamine to polymerize with a bis(phenylsulfone)-containing monomer via the thiol-phenylsulfone click step-growth polymerization. The resulting thermally stable pyridinyl polythioether (polymer P2) with pyridinyl thioethers on its main chain demonstrates clustering-triggered emission (CTE) behavior and can be used as a fluorescent probe to detect $Cu^{2+}$ ions in the visible region. After P2 was treated with $H_2O_2/Na_2WO_4$, the polymer degradation was investigated through a declick reaction with

**Scheme 2. Synthesis of Monomer M1**



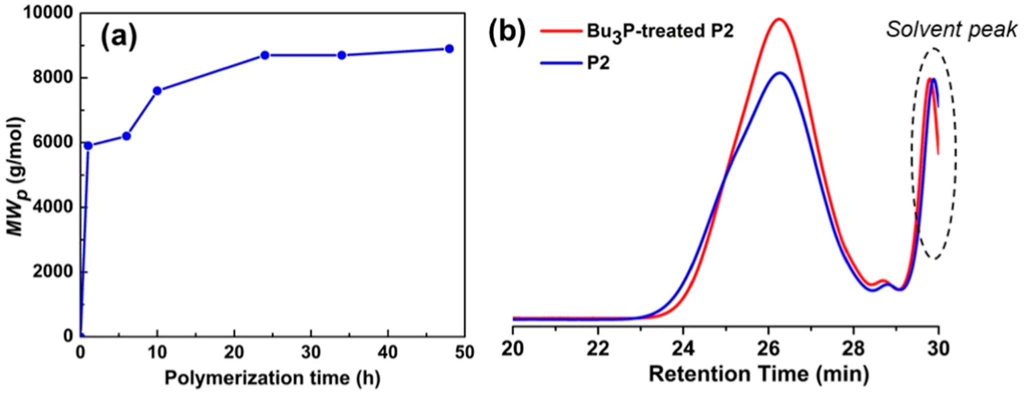


**Figure 1.** (a) Dependence of the peak molecular weight ($MW_p$) of P1 on polymerization time. (b) SEC curves of P2 and $Bu_3P$-treated P2.

a monothiol-containing compound. The degradation product separated from the reaction with 2-mercaptoethanol was recycled as a diol monomer to prepare polyurethane (PU). It is anticipated that the synthesized pyridinyl polythioether with CTE characteristics and on-demand degradability has potential applications as a novel type of degradable material.

## EXPERIMENTAL SECTION

**Synthesis of a Bis(phenylsulfone)-Containing Monomer M1.** As shown in Scheme 2, the bis(phenylsulfone)-containing monomer M1 was synthesized by an esterification reaction of compounds 1 (C1) and 2 (C2). Using methyl 4-bromo-6-methylnicotinate as the starting reagent, C1 and C2 were prepared according to our previous paper.[53] Briefly, C1 (2.53 g, 8.18 mmol), C2 (4.00 g, 9.82 mmol), 1-ethyl-3-(3-dimethylpropylamine) carbodiimide hydrochloride (EDC, 1.73 g, 9.00 mmol), and 4-dimethylaminopyridine (DMAP, 0.1 g, 0.82 mmol) were dissolved in $CH_2Cl_2$ and stirred for 12 h at 25 °C. After the reaction solution was concentrated by a rotary evaporator, the crude product was purified by silica gel column chromatography using ethyl acetate as the eluent to yield monomer M1 as a white solid (5.56 g, 97.6% yield). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.83 (s, 2H), 8.06−7.97 (m, 6H), 7.67−7.59 (t, 2H), 7.58−7.52 (t, 4H), 5.39 (s, 4H), 3.95 (s, 6H), 2.87 (s, 4H) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$: 172.24, 165.33, 160.58, 151.39, 148.91, 140.40, 134.98, 130.54, 128.46, 125.65, 120.16, 66.11, 54.04, 28.94 ppm. HRMS ($[C_{32}H_{28}N_2O_{12}S_2 + H]^+$): calcd 697.1162; found, 697.1153. NMR spectra and the HRMS spectrum of M1 are shown in Figure S1.

**Synthesis of Pyridinyl Polythioethers P1 and P2 via Ring-Opening of NHTL and Click Polymerization.** The pyridinyl poly(thioether)s were prepared through a one-pot approach, as shown in Scheme 1. Typically, NHTL (108.3 mg, 0.68 mmol), 1, 4-phenyldimethylamine (42.1 mg, 0.31 mmol), and DMAP (3.8 mg, 0.031 mmol) were dissolved in dry *N*,*N*-dimethylformamide (DMF, 3.0 mL). After three freeze−pump−thaw cycles, the solution was stirred at 40 °C for 12 h to obtain dithiol monomer M2 in situ. Then, M1 (215.4 mg, 0.31 mmol) and triethylamine (TEA, 0.17 mL) were added into the solution under an Ar atmosphere. After three freeze−pump−thaw cycles, the click polymerization was carried out for 24 h at 60 °C under an Ar atmosphere to obtain P1 polymer.

For the preparation of P2 polymer, a second batch of M1 (43.1 mg, 0.062 mmol) was added after a 24 h click polymerization of M1 and M2. Before adding M1, an aliquot of the polymer solution was withdrawn to determine the thiol content and molecular weight. The reaction continued for another 24 h at 60 °C to prepare P2. After polymerization, the P2 solution was purified by dialysis against THF for 2 days. Then, the P2 solution was precipitated into an excess of the mixed solution of methanol and water (1/1, v/v) and centrifuged. The obtained P2 polymer was dried overnight under a vacuum at 30 °C.

**Oxidation of Polymer P2.** Briefly, P2 (142.1 mg), $H_2O_2$ (600 $\mu$L, 5.85 mmol), and $Na_2WO_4 \cdot 2H_2O$ (51 mg, 0.146 mmol) were dissolved in dry DMF (3.0 mL). The solution was stirred at 30 or 40 °C for 24 h and then concentrated on a rotary evaporator. The resulting oxidized polymer OP2 was precipitated in water, centrifuged, and dried overnight under a vacuum at 30 °C, yielding a white solid.

**Degradation of OP2.** The degradation of OP2 was conducted in the presence of various thiols, including 2-mercaptoethanol (2-ME), methyl thioglycolate, and *N*-acetyl-L-cysteine methyl ester. Typically, OP2 (3 mg), 2-ME (2.04 $\mu$L, $29.3 \times 10^{-3}$ mmol), and TEA (2.44 $\mu$L, $17.6 \times 10^{-3}$ mmol) were dissolved in DMF (200 $\mu$L). The solution was stirred for 24 h at 35 °C. After the solvent was removed, the degradation product was dried under vacuum and characterized by size exclusion chromatography (SEC).

**Chemical Recycling of OP2.** The degradation product from the reaction of OP2 (52 mg) and 2-ME (39.6 mg) was dispersed in $CH_2Cl_2$. Then, the dispersion was centrifuged to separate the supernatant. The supernatant was washed with a saturated $NaHCO_3$ solution, saturated NaCl solution, and water in order. The organic phase was collected and dried with anhydrous $MgCl_2$. The solvent was removed to afford light-yellow solid S1. The polymerization of S1 and hexamethylene diisocyanate was carried out for 48 h in DMF at 50 °C using dibutyltin dilaurate (DBTL) as the catalyst.

**Fluorescence Detection Studies.** NaCl, KCl, $MgCl_2$, $CaCl_2$, $CuCl_2$, $ZnCl_2$, $NiCl_2 \cdot 6H_2O$, $AgNO_3$, $(CH_3COO)_2Mn \cdot 4H_2O$, and $(CH_3COO)_2Pb \cdot 3H_2O$ were used for detection studies. The stock solutions of metal ions, $Na^+$, $Mg^{2+}$, $K^+$, $Ca^{2+}$, $Mn^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Ag^+$, and $Pb^{2+}$, were made at a concentration of 5 mM in deionized water. The appropriate concentrations for fluorescence measurements were obtained by diluting the metal ion stock solutions. The solution

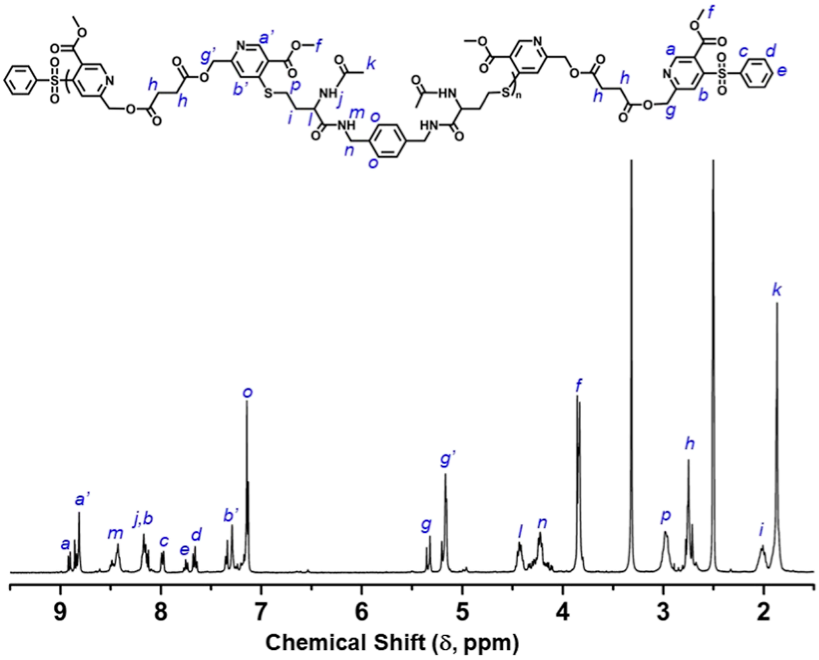


**Figure 2.** $^1$H NMR spectrum of polymer P2 in DMSO-$d_6$.

of P2 (2.5 mg/mL) was prepared in DMF. After addition of 20 $\mu$L of various metal ion solutions to 0.6 mL of P2/DMF solution, the fluorescence emission spectra were collected at an excitation wavelength of $\lambda_{ex}$ 510 nm.

## ■ RESULTS AND DISCUSSION

**Synthesis of Pyridinyl Polythioethers in a One-Pot Approach.** The pyridinyl polythioethers were synthesized through the combined NHTL ring-opening and thiol-phenylsulfone click step-growth polymerization in a one-pot approach (Scheme 1). NHTL serves as a latent thiol reagent as it can generate a thiol group by a ring-opening reaction with nucleophiles such as amines and alcohols via an addition–elimination mechanism.[54] Herein, a diamine compound 1, 4-phenyldimethylamine was selected as a nucleophile to react with NHTL to form a dithiol monomer M2 in situ. The ring-opening reaction was carried out in DMF at 40 °C for 12 h under Ar. The complete consumption of 1, 4-phenyldimethylamine was confirmed by the disappearance of the $^1$H NMR signal corresponding to benzylic protons at $\delta$ 3.67 ppm (Figure S2). Subsequently, monomer M1 and catalyst TEA were added directly to the reaction flask of NHTL and 1, 4-phenyldimethylamine. The click step-growth polymerization of M1 and M2 monomers was based on the nucleophilic substitution reaction between the thiol and the phenylsulfonyl group. M1 and the in situ produced M2 polymerized at a 1:1 stoichiometric ratio to generate polymer P1 with one thiol and one phenylsulfone terminal. SEC was used to trace the molecular weight (MW) of P1 at specific intervals. As shown in Figure 1a, the peak MW increased with polymerization time over 24 h and then reached a plateau. After 24 h click polymerization, an aliquot of the polymer P1 solution was withdrawn to react with 2, 2′-dithiodipyridine (DTP). After the coupling reaction, the UV–vis spectrum revealed a peak at $\lambda$ 375 nm (Figure S3), corresponding to the characteristic absorption of pyridine-2-thione.[55] The production of pyridine-2-thione is ascribed to the thiol–disulfide exchange reaction between P1 and DTP, confirming that P1 contains a thiol terminal.

To obtain the polymer P2 bearing two phenylsulfone terminals, a second batch of M1 (0.2 equiv) was added to the flask after 24 h polymerization of M1 and M2. This reaction continued for another 24 h to yield polymer P2 and then an aliquot of P2 solution was immediately withdrawn to be characterized by SEC and to determine the thiol content. Compared to the precursor polymer P1 obtained via 24 h polymerization of M1 and M2, the SEC trace of P2 polymer was almost the same as that of P1 (Figure S4). After the treatment of P2 solution with DTP, no UV absorption of pyridine-2-thione was observed (Figure S3), verifying the absence of the thiol terminal in P2.

After the P2 solution was purified by dialysis, the dried polymer was characterized by SEC and $^1$H NMR. SEC analysis showed that P2 had a weight-average molecular weight ($M_w$) of 16,000 g/mol and a dispersity ($Đ$) of 1.44 (Figure 1b). Next, polymer P2 was treated with excess tributyl phosphine ($Bu_3P$) in DMF for 12 h. The SEC curve of $Bu_3P$-treated P2 was almost the same as that of the initial P2 polymer, eliminating the presence of disulfide linkage in P2. If P2 had contained disulfide bonds, treatment with $Bu_3P$ would have resulted in the production of lower molecular weight species due to the cleavage of disulfide bonds by $Bu_3P$. The SEC results indicate that P2 was generated by coupling M1 with M2, with structure units bonded covalently through stable pyridinyl thioether linkages. The formation of pyridinyl thioether linkages was also confirmed by $^1$H NMR characterization. Figure 2 shows the $^1$H NMR spectrum of polymer P2. The signal of methylene protons on the sulfur atom ($SCH_2$) appeared at $\delta$ 2.98 ppm (peak p). The proton signals of the pyridinyl moieties adjacent to thioethers were present at $\delta$ 8.80–8.86 (peak a′) and 7.25–7.40 ppm (peak b′), along with the signals for the terminal phenylsulfone and pyridine ring at $\delta$ 7.61–7.81 (peak d, e), 7.95–8.03 (peak c), and 8.91(peak a) ppm. The SEC and $^1$H NMR results verified the successful

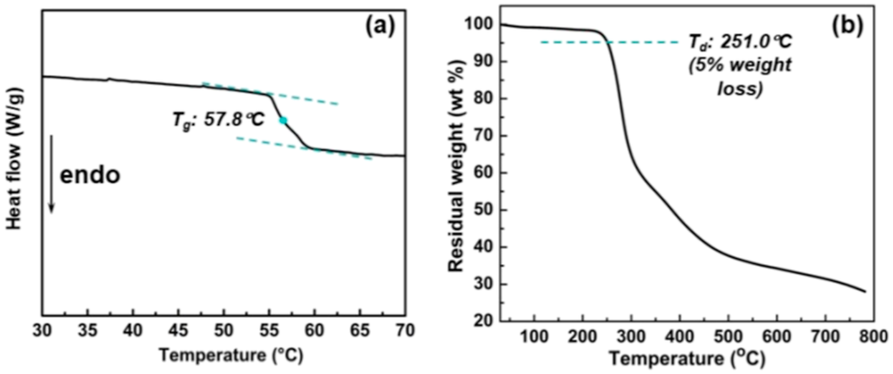


**Figure 3.** DSC (a) and TGA (b) curves of polymer P2.

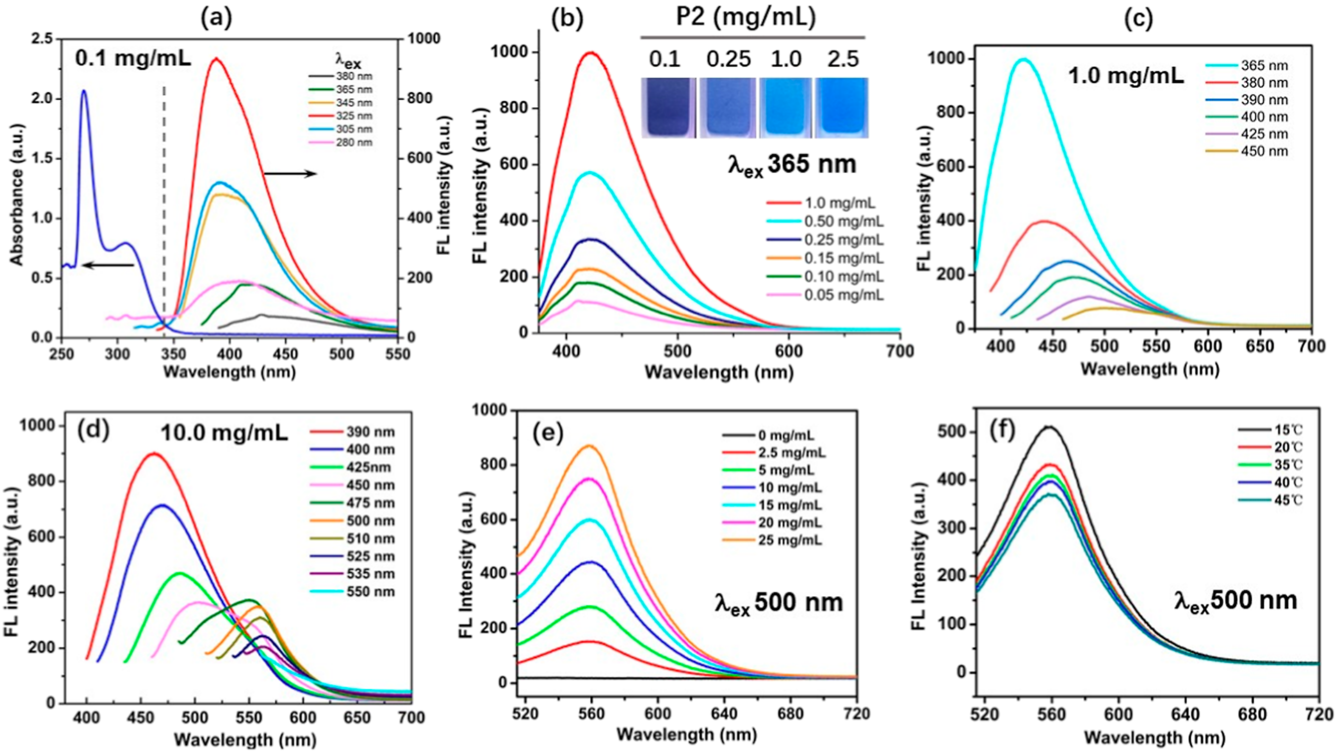


**Figure 4.** (a) Absorption spectrum of P2/DMF solution (0.1 mg/mL) and emission spectra of P2/DMF solution (0.1 mg/mL) with different excitation wavelengths at room temperature. (b) Emission spectra of P2/DMF solutions with various concentrations excited at $\lambda_{ex}$ 365 nm (inset: photographs of P2/DMF solutions with various concentrations under a UV transilluminator of $\lambda$365 nm). (c) Emission spectra of 1.0 mg/mL P2/DMF solution excited at different wavelengths. (d) Emission spectra of 10.0 mg/mL P2/DMF solution excited at different wavelengths. (e) Emission spectra of P2/DMF solutions with various concentrations excited at $\lambda_{ex}$ 500 nm. (f) Influence of temperature on emission spectra of 10 mg/mL P2/DMF solution excited at $\lambda_{ex}$ 500 nm (excitation slit 5 nm, emission slit 3 nm).

generation of pyridinyl polythioether P2 through the click step-growth polymerization of M1 and the in situ produced M2.

A polymer material intended for practical applications must exhibit dimensional stability at elevated temperatures during device fabrication. The thermal property of the P2 polymer was assessed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC result shows that P2 is amorphous and has a glass-transition temperature ($T_g$) of 57.8 °C (Figure 3). The decomposition temperature ($T_d$) of P2, representing the temperature at which a 5% weight loss occurs under nitrogen, is determined to be 251 °C, indicating that the P2 polymer is thermally stable.

**Photophysical Properties of P2.** The electron-rich moieties containing heteroatoms (N, O, S, and P), such as amine, amide, phosphate, ester and sulfone, are attractive building blocks for fluorescent materials with CTE effects.[56] According to the CTE mechanism, the clustering of electron-rich moieties causes overlap of their n and $\pi$ electrons, which enhances extended electron delocalization and rigidified conformations, thereby creating extended conjugation and facilitating the photoluminescence excitation and consequent emission.[57] Although the P2 polymer lacks conjugated structures with an extended $\pi$-system, it is still expected to be luminescent due to pyridinyl, thioether, amide, and ester moieties in repeating units of P2.

In the first step, the UV−vis absorbance spectrum of the P2/DMF solution was recorded at a concentration of 0.10 mg/mL. Two absorption peaks were observed at $\lambda$ 280 and 305 nm (Figure 4). Based on the UV−vis result, fluorescence emission spectra of the P2/DMF solution (0.10 mg/mL) were

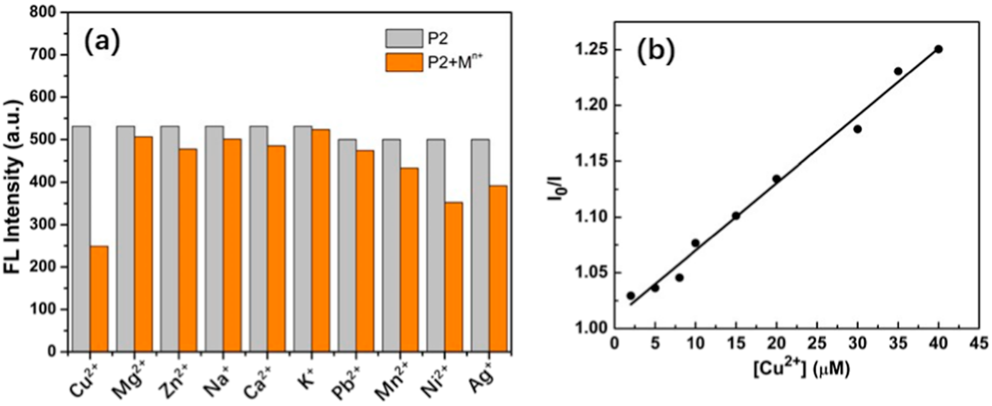


**Figure 5.** (a) Effect of different metal ions on the fluorescence intensity ($\lambda_{em}$ 560 nm) of P2 in DMF/$H_2O$ (v/v = 30:1) excited at $\lambda_{ex}$ 510 nm (excitation slit 5 nm, emission slit 5 nm). (b) Plot of $I_0/I$ as a function of the $Cu^{2+}$ concentration ($I_0$ and $I$ are the fluorescence intensities of the P2 at $\lambda_{em}$ 560 nm without and with $Cu^{2+}$, respectively).

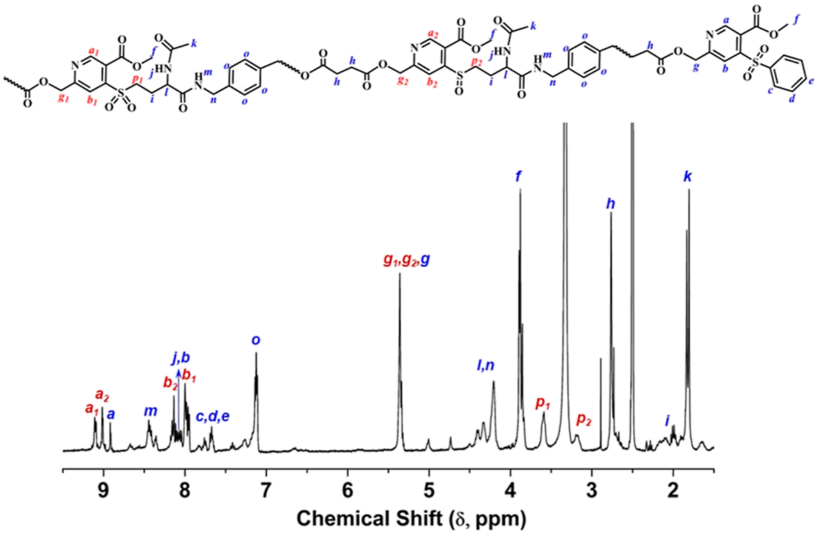
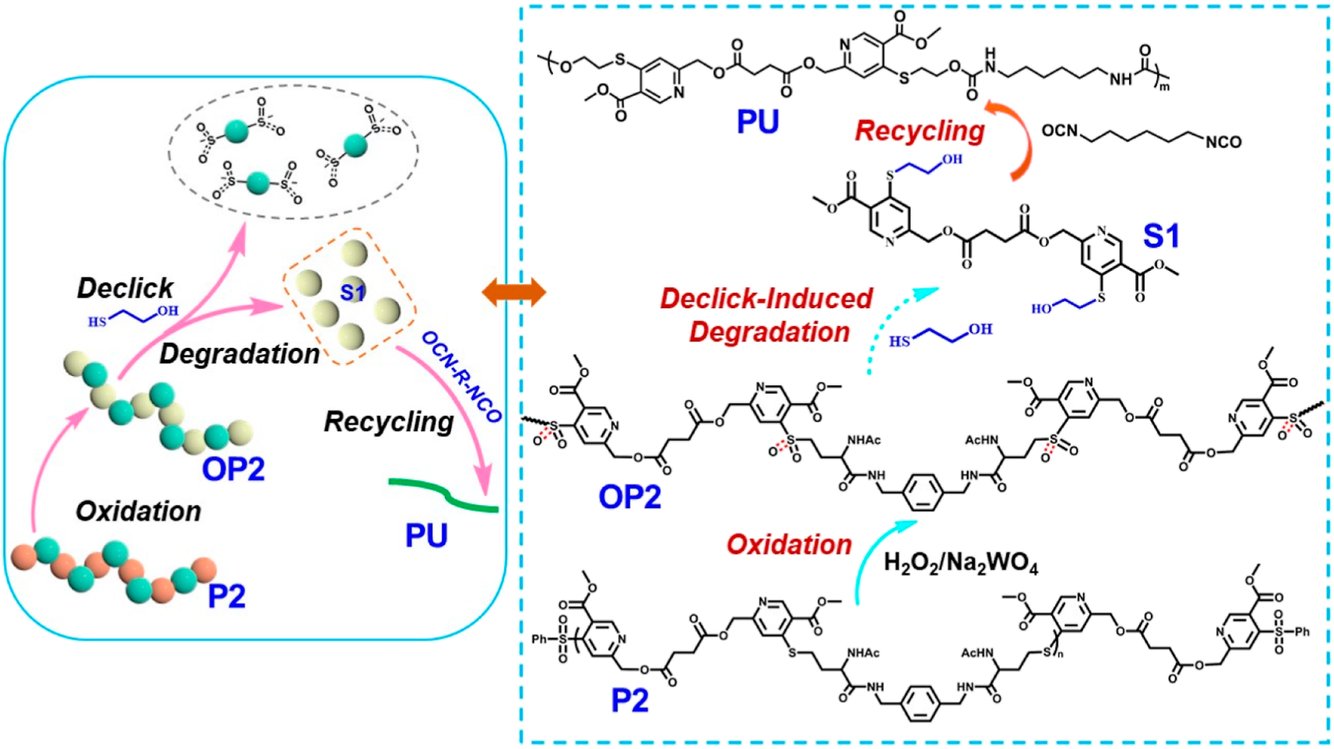


**Figure 6.** $^1$H NMR spectrum of OP2-40 in DMSO-$d_6$.

measured, varying the excitation wavelength from $\lambda_{ex}$ 280 to 380 nm. When the solution was excited at $\lambda_{ex}$ = 325 nm, a strong emission with a maximum of $\lambda_{em}$ = 375 nm was observed. Under the excitation of $\lambda_{ex}$ 365 nm, the 0.10 mg/mL P2/DMF solution displayed a weak fluorescence emission. However, as the P2 concentration was increased from 0.1 to 1 mg/mL, a concentration-enhanced emission phenomenon was observed, and the FL intensity was significantly boosted with a maximum emission wavelength of $\lambda_{em}$ 425 nm ($\lambda_{ex}$ 365 nm). Also, under UV light (365 nm) irradiation, the P2/DMF solution gradually exhibited blue-white emission as its solution became concentrated. Moreover, the P2/DMF solution exhibited excitation-dependent fluorescence, one of the characteristics of nonconjugated luminescent polymers.[58−60] For the P2/DMF solution of 1 mg/mL, the emission peaks showed a red shift from $\lambda_{em}$ 425 to 500 nm as the excitation wavelength changed from $\lambda_{ex}$ 365 to 450 nm. In a more concentrated 10 mg/mL solution, the emission peaks continually red-shifted to $\lambda_{em}$ 562 nm when the excitation wavelength increased to $\lambda_{ex}$ 535 nm. The concentration-enhanced emission phenomenon was also observed in the visible region. When excited at $\lambda_{ex}$ 500 nm, the FL intensity progressively intensified with a maximum emission wavelength at $\lambda_{em}$ 560 nm as the concentration increased from 2.5 to 25 mg/mL. The enhanced emission can be ascribed to the collapse of P2 polymer chains in concentrated solutions, inducing the clustering of pyridinyl, ester, amide, and thioether moieties. The clustering results in the overlap of n and π electrons within these moieties, leading to the buildup of the chromophores and consequent fluorescence emission of P2 polymer. The DLS result verified the aggregation of P2 polymer chains at the concentration of 10 mg/mL in DMF (Figure S5). The emission spectra of the P2/DMF solution varied with different excitation wavelengths, implying the presence of multiple emission centers. The effect of temperature on fluorescence emission was investigated at the excitation wavelength of $\lambda_{ex}$ 500 nm. The results showed that the FL intensity decreased as the temperature rose from 15 to 45 °C, another typical characteristic of CTE materials. The reduced FL intensity can be ascribed to the dissociation of the emission clusters and more activated nonradiative channels, triggered by the increase in the movement of polymer chains, molecular vibration, and internal loss at higher temperatures.[58]

**Fluorescence Detection of $Cu^{2+}$ Ions.** As the P2 polymer contains N, O, and S heteroatoms, metal ions can theoretically coordinate with P2 to affect its intrinsic fluorescence property. We investigated the fluorescence response of P2/DMF solution to some metal ions, including $Na^+$, $Mg^{2+}$, $K^+$, $Ca^{2+}$,

**Scheme 3. Illustration of P2 Oxidation, Polymer Degradation Induced by a Declick Reaction with 2-ME, and Recycling of the Degradation Product**



$Mn^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Ag^{+}$, and $Pb^{2+}$. The P2/DMF solution at a concentration of 2.5 mg/mL was chosen for complexation with metal ions. Taking advantage of the FL behavior of P2, the emission spectra were measured with an excitation wavelength in the visible region. After adding the aqueous solution of different metal ions (20 $\mu$L, 200 $\mu$M) into 0.6 mL P2/DMF solution, the emission spectra were recorded at $\lambda_{ex}$ 510 nm. When excited at 510 nm, the blank P2 solution showed a strong emission at $\lambda_{em}$ = 560 nm (Figure S6). As shown in Figure 5a, introducing $Cu^{2+}$ ions significantly quenched the fluorescence emission of P2, while other metal ions have minimal or no effect on its emission. This result indicates that P2 can selectively detect $Cu^{2+}$ ions. The quenched fluorescence is induced by electron or charge transfer due to the coordination of $Cu^{2+}$ ions with the electron-rich moieties (including carbonyl, N in amide and pyridinyl, and S) in the P2 polymer.

Next, an aqueous solution of $Cu^{2+}$ with different concentrations, ranging from 2 to 40 $\mu$M, was added to determine the limit of detection (LOD) of P2 to $Cu^{2+}$ ions. The emission spectra were recorded after each addition. With the increase in $Cu^{2+}$ concentration, the FL intensity of the P2 solution gradually decreased. Additionally, the FL intensity at $\lambda_{em}$ 560 nm shows a good linear correlation with the $Cu^{2+}$ concentration ($R^2$ = 0.99) (Figure 5b). Based on the equation LOD = $3\sigma/K$ (where $\sigma$ represents the standard deviation of the blank measurement and $K$ represents the slope of the calibration curve), the LOD of P2 for $Cu^{2+}$ detection was calculated to be about 0.67 $\mu$M. This value was much lower than the maximum level (~20 $\mu$M) of $Cu^{2+}$ in drinking water defined by the U.S. Environmental Protection Agency. Additionally, the LOD of P2 for $Cu^{2+}$ detection was lower than that of several recently reported fluorescent probes for $Cu^{2+}$, as shown in Table S1. The quantitative analysis result suggests that P2 can be used as a potential fluorescent polymeric probe to detect $Cu^{2+}$ ions in the visible region.

**Thiol-Induced Polymer Degradation by the Declick Reaction.** Thioethers can be transformed into sulfoxides or sulfones under oxidative condition. Using $H_2O_2/Na_2WO_4$ as the oxidant, the oxidation of P2 was conducted in DMF at 30 and 40 °C, respectively. Figure 6 shows the $^1$H NMR spectrum of the oxidized polymer OP2-40 obtained at 40 °C. After 24 h of oxidation at 40 °C, the signals of methylene ($\delta$ 2.98 ppm) adjacent to the sulfur atom completely disappeared, and new signals representing methylene adjacent to sulfone and sulfoxide were observed at $\delta$ 3.59 (peak $p_1$) and 3.19 (peak $p_2$) ppm, respectively. Additionally, the proton signals corresponding to the pyridinyl ring shifted downfield to $\delta$ 8.0−8.14 (peak $b_1$, $b_2$) and 9.02−9.09 (peak $a_1$, $a_2$) ppm, caused by the transformation of S to sulfone and sulfoxide.[47] These results confirm the formation of oxidized sulfur species, and the OP2-40 polymer contains both sulfoxide and sulfone moieties (Scheme 3). For the oxidized polymer OP2-30 obtained at 30 °C, the $^1$H NMR spectrum still displayed weak proton signals at $\delta$ 2.98 ppm (Figure S7), implying that some thioether moieties in OP2-30 remained unoxidized.

Our previous work confirmed that pyridinyl sulfoxide and sulfone were able to undergo nucleophilic substitution with a thiol group.[47] Next, we investigated the reactions of oxidized polymers (OP2-30 and OP2-40) and 2-ME at 35 °C. SEC was used to monitor the molecular weight change (Figure 7). After a 24 h reaction with 2-ME, SEC curves revealed that the molecular weight of these two polymers significantly decreased compared to the initial P2 polymer, indicating that both OP2-30 and OP2-40 degraded in the presence of 2-ME. Although OP2-30 still contained some thioether moieties in its backbone, it demonstrated a degradation behavior as OP2-40. In addition, the oxidized P2 polymer was reacted with

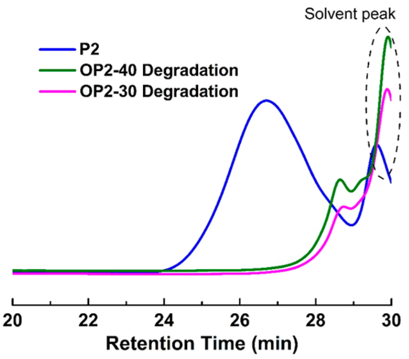


**Figure 7.** SEC curves of the OP2 polymers after 24 h incubation with 2-ME and the P2 polymer.

methyl thioglycolate and *N*-acetyl-L-cysteine methyl ester. In both cases, the decrease of molecular weight showed a similar profile to the degradation in the presence of 2-ME (Figure S8). These results indicate that a monothiol-containing compound can trigger degradation of the oxidation-treated pyridinyl polythioether via a declick reaction. Therefore, incorporating pyridinyl thioether into the polymer backbone enables the development of an on-demand degradable polymer through a click-declick strategy based on thioether oxidation and the thiol-click reaction.

Next, the degradation product after the reaction of OP2 and 2-ME was dispersed in $CH_2Cl_2$. The light-yellow solid (S1) obtained from the supernatant was analyzed by $^1$H NMR and HRMS. The $^1$H NMR spectrum showed the thioether ($SCH_2$) signal at $\delta$ 3.17 ppm (peak m), the signals of protons on pyridinyl rings at $\delta$ 7.33 (peak b) and 8.96 ppm (peak a), and the signal of methylene ($CH_2OH$) (peak n) adjacent to the hydroxy group (Figure 8A). The $^1$H NMR spectrum with the peak integrals is shown in Figure S9. $^1$H NMR analysis indicates that S1 is the product of the nucleophilic substitution of OP2 by 2-mercaptoethanol (Scheme 3). HRMS analysis showed that the molecular mass of $[C_{24}H_{28}N_2O_{10}S_2 + H]^+$ was 569.1255 (Figure S10), which agreed well with the calculated mass of $[S1 + H]^+$ (569.1264). $^1$H NMR and HRMS results demonstrate that the degradation of OP2 is induced through the thiol-triggered breakage of the covalent bond between pyridinyl and sulfoxide/sulfone via thiol-pyridinyl sulfoxide/sulfone nucleophilic substitution. To explore the recyclability of compound S1, S1 was polymerized with hexamethylene diisocyanate to prepare PU. After 24 h polymerization at 50 °C, a polymer with a peak molecular weight of 5,600 g/mol was obtained (Figure 8B). The structure of the resulting polymer was analyzed by $^1$H NMR. The proton signals corresponding to methylene groups adjacent to urethane moieties were observed at $\delta$ 4.16 ppm ($-NHCOOCH_2-$) and $\delta$ 2.93 ppm ($-CH_2NHCOO-$) (Figure S11), respectively. The signal corresponding to urethane appeared at $\delta$ 7.18 ppm ($-NHCOO-$). The GPC and $^1$H NMR results confirm the successful production of PU through the polymerization of S1 and hexamethylene diisocyanate. Therefore, S1 can be recycled as a diol monomer to make new polymers.

## ■ CONCLUSIONS

We developed an on-demand degradable polymer by incorporating pyridinyl thioether moieties into the polymer backbone. The resulting pyridinyl polythioether can undergo degradation through a click-declick strategy based on thioether oxidation and the thiol-click reaction. The pyridinyl polythioether was prepared through NHTL ring-opening and subsequent thiol-phenylsulfone click polymerization via a one-pot approach. The obtained pyridinyl polythioether P2 demonstrates CTE behavior and exhibits an excitation-dependent fluorescence. The emission peak showed a red shift from $\lambda_{em}$ 425 to 562 nm with an increase of the excitation wavelength from $\lambda_{ex}$ 365 to 535 nm. The P2 polymer can be used as a fluorescent probe to detect $Cu^{2+}$ ions in the visible region. Upon oxidation with $H_2O_2/Na_2WO_4$, the thioether moieties in the P2 backbone are transformed into sulfoxide and sulfone moieties. Consequently, when exposed to a monothiol-containing molecule, the pyridinyl sulfoxides/sulfones facilitate polymer degradation through a declick reaction. Additionally, we explored the chemical recycling of the pyridinyl thioether-containing diol compound separated from the degradation product after the reaction of oxidized P2 polymer and 2-ME. The obtained diol compound can be used as a monomer to prepare PU by polymerization with hexamethylene diisocyanate. The synthesized pyridinyl polythioether represents a promising candidate for applications as a new type of degradable material.

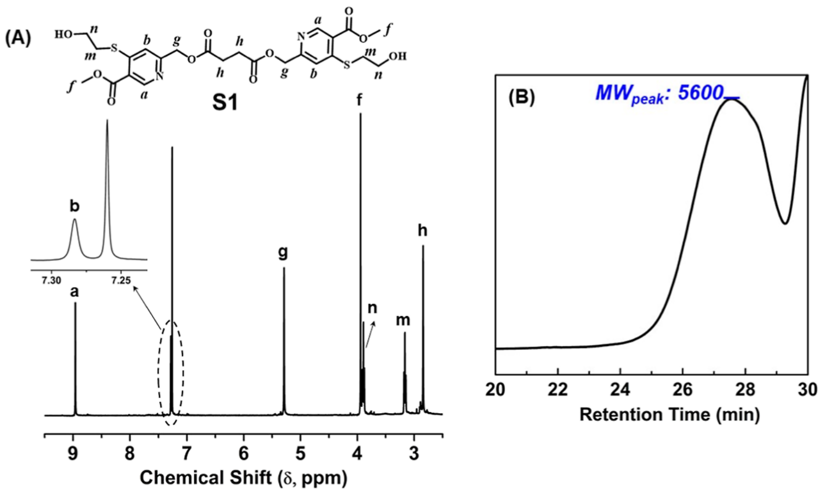


**Figure 8.** (A) $^1$H NMR spectrum of S1 in $CDCl_3$. (B) SEC curve of PU obtained by polymerization of S1 and hexamethylene diisocyanate.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02963.

Materials and characterizations and additional NMR, HRMS, UV−vis, fluorescence, SEC, and DLS data (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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