Colorimetric Naked-Eye Recognizable Anion Sensors Synthesized via RAFT Polymerization

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Received 30 September 2009; accepted 4 January 2010 DOI: 10.1002/pola.23922 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A polymeric sensor (PTH) containing naphthalimide signal moiety and thiourea recognition moiety for the detection of anions was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization, which can guarantee controllable molecular weight, narrow molecular weight distribution, and precise polymer structure. Both PTH and its corresponding monomer (TH) showed naked-eye recognizable yellow-to-orange changes upon addition of fluoride (F⁻), acetate (AcO⁻), and dihydrogen phosphate ($H_2PO_4^-$) of low concentration. However, only F⁻ can result in orange-to-purple change when the aforementioned anions were added at high concentration.

tions, which was attributed to the deprotonation of the thiourea N—H groups and the mechanism was supported by the UV-Vis absorption spectra and ¹H NMR titration. The effect of these anions on thin PTH films was also investigated, and the addition of F⁻ led to obvious spectra change. It was found that other halide anions (Cl⁻, Br⁻, and l⁻) could hardly induce any variation of absorption spectra. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1551–1556, 2010

KEYWORDS: anion; colorimetric; fluorescence; living radical polymerization (LRP); RAFT polymerization; sensors

INTRODUCTION It is widely known that some biologically important anions, such as fluoride (F⁻), acetate (AcO⁻), and dihydrogen phosphate (H₂PO₄⁻), have attracted great attention in the recent decades, because of their importance on human health, environmental protection,^{1,2} and other fields.^{3,4} Accordingly, quite a few chemosensors, monomeric and polymeric, have been successfully created, developed, and studied these years.⁵⁻⁷ Most of the interactions between analytes and sensors are achieved by noncovalent binding.⁸ Thiourea moiety is widely used on chemosensors because there are two N-H groups serving as recognition sites.^{9,10} However, most thiourea sensors are small molecules,^{11,12} polymer sensors with thiourea moiety are rarely reported. What is more, since most of the polymers were synthesized by traditional polymerization, the degree of polymerization and polydispersity of previously reported anion polymer sensors can hardly be controlled.^{13–15}

To avoid or to reduce the aforementioned shortcomings, monomer TH with thiourea moiety and the corresponding polymer PTH (Scheme 1) were prepared. As an innovative on colorimetric sensors, PTH was synthesized by reversible addition-fragmentation chain transfer polymerization (RAFT), which was one of the most promising controlled/living radical polymerization methods that can control the molecular weight and distribution with the usage of chain transfer agent, such as esters disulfide compounds.^{16–21} The use of RAFT can not only control the degree of polymerization, but also keep the polymer active, which can guarantee further modification to improve polymer's properties, such as solubility, functionality, and so on.^{22–24} It was reported that for some polymeric chemosensors, the degree of polymerization of the polymer has effect of on the sensing ability. Therefore we used RAFT method to control the degree of polymerization herein. The RAFT method on fluorescent sensors synthesis was reported in our recent research.²⁵

During this research, different anions, such as F^- , AcO⁻, and $H_2PO_4^-$, were used as analytes. A yellow-to-orange change happened upon the addition of these anions, which was due to the intramolecular charge transfer (ICT) occurring on the *N*—H site near the 4-amino-1,8-naphthalimide.^{26–28} Moreover, an orange-to-purple change was observed at high F^- concentrations, which was due to the sufficient basicity of F^- to deprotonate the naphthalimide *N*—H. Similar deprotonation effect was also reported by Gunnlaugsson and coworkers^{29,30} and Fabbrizzi and coworkers.^{31,32} To confirm the above proposed mechanism, UV-Vis absorption spectra and the ¹H NMR titration were conducted. In addition, the sensing properties of PTH thin film on the aforementioned anions were also investigated. Detailed discuss was processed in the following text.

EXPERIMENTAL

Characterization

¹H NMR and ¹³C NMR measurements were conducted on a Bruker AV-500 spectrometer with deuterated dimethyl

Additional Supporting Information may be found in the online version of this article. Correspondence to: P. Zhao (E-mail: pzhao@ecust.edu.cn) Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 1551–1556 (2010) © 2010 Wiley Periodicals, Inc.



SCHEME 1 Synthetic scheme of TH and PTH.

sulfoxide (DMSO-d₆) as solvent using tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) measurements were carried out on ESI mass spectroscopy. The number-average molecular weight (M_n) and polydispersity indices (PDIs) of the polymers were determined with a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector and calibrated with polystyrene (PSt) standard samples. Dimethylformamide (DMF) was used as the eluent with a flow rate of 1.00 mL/min at 30 °C. UV-Vis absorption spectra were performed on a Varian Cray 500 spectrophotometer.

Materials

All anions, in the form of tetrabutylammonium salts, were purchased from J&K Chemical Company, stored in a desiccator under vacuum containing self-indicating silica (desiccant), and used without any further purification. 1-Methyl-2-pyrrolidinone (NMP) was used immediately after it was distilled under vacuum. Dimethyl sulfoxide (DMSO) was distilled over calcium hydride. Azobisisobutyronitrile (AIBN, 97%) was recrystallized from ethanol twice, dried at room temperature under vacuum, and stored at -10 °C in the fridge. Compound **1** (Scheme 1) was obtained according to our previous research.²⁵ Cumyl dithiobenzoate (CDB) was synthesized according to the method described previously,³³ with purity above 99%. All other reagents were of analytical purity and used without further treatment.

Preparation of TH

Benzoyl isothiocyanate (2.77 g, 17.00 mmol) was added to the acetone solution (160 mL) of compound **1** (1.74 g, 5.37 mmol). After stirring for 4 h at 50 °C, some yellow suspension appeared. Remove about half of the acetone under vacuum, add ethanol (80 mL) to the yellow residue, and then filter to get the rude yellow solid product. Monomer TH was obtained as a red brownish product after purification by column chromatography on silica gel with dichloromethaneethyl acetate (9:1, v/v) as the eluent.

Yield: 39.40% (1.03 g). ¹H NMR (500 MHz, DMSO-d₆, ppm): δ 1.78 (s, 3H), 4.42 (dd, 4H), 5.60 (s, 1H), 5.94 (s, 1H), 7.59 (t, J = 7.81 Hz, 2H), 7.70 (t, J = 7.41 Hz, 1H), 7.96 (t, J =

7.64 Hz,1H), 8.06 (d, J = 7.37 Hz, 2H), 8.27 (d, J = 7.89 Hz, 1H), 8.49 (t, J = 8.37 Hz 1H), 8.56 (dd, 2H), 11.96 (s, 1H), 12.95 (s, 1H). ¹³C NMR (125 MHz, DMSO-d₆, ppm): δ 17.9, 61.5, 120.4, 122.4, 125.1, 125.8, 127.0, 127.6, 128.2, 128.4, 128.8, 129.2, 130.7, 131.1, 132.0, 133.3, 135.7, 140.7, 163.0, 163.4, 166.5, 168.4, 181.4. MS (m/z): calcd for C₂₆H₂₁N₃O₅S, 487.1; found, 510.1 [M+Na]⁺.

Polymerization of TH

TH (249.6 mg, 0.51 mmol), AIBN (0.3 mg, 0.0025 mmol), CDB (1.36 mg, 0.005 mmol), and distilled NMP (3.0 mL) were placed in a dry Schlenk tube. The tube was sealed and immerged in liquid nitrogen for 5 min to make the solvents frozen, evacuated to eliminate the small amount of residual oxygen, and then recharged with argon. Repeat this procedure three times to remove the oxygen thoroughly. Then, the Schlenk tube was placed in a constant-temperature oil bath of 70–75 °C. The polymerization was terminated after 38 h by immersion of the reactor in liquid nitrogen. The polymer (PTH) was purified by precipitating twice from THF solution to diethyl ester, and once from NMP solution to a mixture of diethyl ether/methanol (1:1, v/v). Yellow polymer was obtained after filtration and then dried at 50 °C under vacuum overnight.

RESULTS AND DISCUSSION

RAFT Polymerization

The polymer PTH was prepared via RAFT polymerization using CDB (Scheme 1) as chain transfer agent (CTA), AIBN as initiator, and NMP as solvent at about 70 °C. The main advantage of RAFT polymerization was the controllability of molecular weight and low polydispersity index.^{19,34–37} The number average molecular weight of the resulted polymer is 49,700 g/mol, with narrow polydispersity of 1.17, determined by GPC. This GPC result reveals that the RAFT polymerization is successfully realized in this system.

Colorimetric Properties

The interactions of TH and PTH with anions (F⁻, AcO⁻, $H_2PO_4^-$, Cl^- , Br^- and I^-) were investigated in DMSO at 25 °C. The concentration of TH was 10^{-5} mol/L and the naphthalimide segment of PTH was equivalent to 10^{-5} mol/L, too. Standard solutions of tetrabutylammonium anions (5 \times 10⁻³ and 0.1 mol/L) were added stepwise to these solutions. On addition of F^- , AcO⁻, and $H_2PO_4^-$ at the concentration of 2 mmol/L (modulated by the standard anion solutions), the light yellow solutions of TH and PTH turned to orange, as shown in the graphic abstract and Figure S2, which were very obvious and naked-eve recognizable. While continuing modulating the solution to higher concentrations of 6 mmol/L, only F^- can lead to the orange-to-purple change, AcO⁻ and H₂PO₄⁻ can hardly result in any further color change. This can be explained by the deprotonation of the thiourea N—H by the F⁻ with sufficient basicity and can be supported by the UV-Vis absorption spectra and ¹H NMR titration.

The effect of the anions on the UV-Vis absorption spectra was examined by adding a few μ mol of the anions stock to a



FIGURE 1 Absorption spectra of PTH in DMSO on addition of AcO^- of various concentrations (0–8.0 mmol/L).

known volume of the sensor solution (3 mL). As can be seen from the spectra, upon the addition of AcO^{-} (Fig. 1) and $H_2PO_4^-$ (Fig. S3) to the PTH solution, both from 0-8.0 mmol/L, there was slight change centered at 450 nm, this was due to the ICT mechanism upon recognition at the receptor site. Similar behavior was also observed after the addition of AcO^- (Fig. 2) and $H_2PO_4^-$ (Fig. S4) into the TH solution. In the case of F^- for both TH and PTH, as shown in Figures 3 and 4 at lower concentrations, mainly from 0-4.0 mmol/L, the absorption spectra were as similar as those under the addition of AcO^- and $H_2PO_4^-$. With respect to Cl^- , Br⁻, and I⁻, there was hardly any change as displayed in Figures S5-S10. However, different behavior happened after the addition of F⁻ at higher concentrations to the TH solution, mainly from 4.0-8.0 mmol/L, the band at 450 nm decreases progressively, while new bands with two peaks at 342 nm and 560 nm form and develop, with two isosbestic points at



FIGURE 2 Absorption spectra of TH in DMSO on addition of AcO^- of various concentrations (0–8.0 mmol/L).



FIGURE 3 Absorption spectra of TH in DMSO on addition of F^- of various concentrations (0–8.0 mmol/L).

387 and 493 nm. As for PTH solution, the spectra were somewhat different after the addition of equal quantities of F⁻, mainly from 4.0–8.0 mmol/L. The appearance of band at 513 nm was not as obvious as that of the TH solution, which was probably due to the mutual influence of the sensing moiety on the polymer bone. These results were in agreement with the naked-eye recognizable phenomena, with the assumption of deprotonation of *N*—H and the formation of HF₂⁻. To confirm this assumption, ¹H NMR titrations of TH were carried out upon addition of F⁻, AcO⁻, and H₂PO₄⁻ (Figs. 5–7).

The binding of TH to F⁻, AcO⁻, and $H_2PO_4^-$ was investigated by monitoring the changes in the ¹H NMR spectra with DMSO-d₆ as solvent. Upon addition of different concentrations of F⁻, the two thiourea *N*—H signals became obviously broadened after the addition of only small quantities of 0.05 eq. (Fig. 5) and nearly disappeared after the addition of 1.0



FIGURE 4 Absorption spectra of PTH in DMSO on addition of F^- of various concentrations (0–8.0 mmol/L).



FIGURE 5 Plot of ¹H NMR spectra in DMSO-d₆ after the addition of various quantities of F⁻ (0–5 eq.). \triangle indicates the appearance of HF₂⁻.

eq. Furthermore, after the addition of 4.0–5.0 eq. of F^- , a new triplet appeared at about 16.1 ppm, which was assigned to the formation of bifluoride [FHF]⁻ anion.²⁴ Both the striking color change and the detection of bifluoride can well support the deprotonation of thiourea *N*—H.

On the other hand, successive addition of AcO^- (0–5 eq.; Fig. 6) and $H_2PO_4^-$ (0–3 eq.; Fig. 7) resulted in significant



FIGURE 6 Plot of ¹H NMR spectra in DMSO-d₆ after the addition of various quantities of AcO⁻ (0–5 eq.).



FIGURE 7 Plot of ¹H NMR spectra in DMSO-d₆ after the addition of various quantities of $H_2PO_4^-$ (0–3 eq.).

changes in the chemical shifts of thiourea N—H, but no bifluofide peak was observed. This indicated that the basicity of AcO⁻ and H₂PO₄⁻ were not strong enough to deprotonate the thiourea N—H, which was consistent with the color change and the UV-Vis absorption spectra.

The effect of F⁻, AcO⁻, and $H_2PO_4^-$ on absorption spectra of thin polymer films was also investigated. The polymer films were immersed in anion solution of 5×10^{-3} mol/L, and after drying for 20 min the absorption spectra were monitored. The band at 408 nm decreased dramatically for F⁻, while slightly for AcO⁻ and $H_2PO_4^-$, as can be seen in Figures 8, 9, and S11. On the basis of the present investigation, it can be assumed that the polymer sensors can be made and applied as convenient detecting apparatus for environmental researchers for selective detection of biologically important anions, such as F⁻.



FIGURE 8 Absorbance spectra of PTH processed on polymer films after the addition of F^- .



FIGURE 9 Absorbance spectra of PTH processed on polymer films after the addition of AcO^{-} .

The desirable selectivity of TH and PTH was better demonstrated by the previous experiments. The sensors had obvious response signals for F^- due to its sufficient basicity. In the case of AcO⁻ and H₂PO₄⁻, similar spectra plot was observed, but not as obvious as that for F^- . While the addition of Cl⁻, Br⁻, and I⁻ did not lead to any significant changes in the spectra possibly due to their large size and low charge density. This reveals that both TH and PTH have good selectivity to the halide anions.

CONCLUSIONS

A new polymeric colorimetric sensor (PTH) for biologically important anions (F⁻, AcO⁻, and $H_2PO_4^-$) was synthesized by RAFT polymerization. The polymer and the corresponding monomer showed yellow-to-orange change at low anion concentrations and only F⁻ resulted in further orange-to-purple change at higher anion concentrations, which was attributed to the protonation of the thiourea *N*—H. UV-Vis spectra and ¹H NMR titration was operated to successfully support the mechanism. Thin PTH films were also capable of sensing F⁻, AcO⁻, and H₂PO₄⁻. The addition of the anions (Cl⁻, Br⁻, and I⁻) presented undesirable sensing performance in neither the solution nor solid state. The results reveal that both TH and PTH have good selectivity to the halide anions.

This work was financially supported by NSFC/China (50673025), National Basic Research 973 Program (2006CB806200), Scientific Committee of Shanghai, and ECUST Funds for Excellent Youth Faculties (YJ0157116).

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