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Epoxy-based polymeric probe bearing trifluoroacetyl azobenzene units: Selective colorimetric sensing of aliphatic primary amines

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ABSTRACT

A simple epoxy-based polymer 1 bearing trifluoroacetyl azobenzene reporter groups is shown to be colorimetric probe for the sensitive and selective discrimination of amine analytes. The titled polymer 1 displayed selectivity for unbranched aliphatic primary amine such as *n*-propylamine over other amines examined. The color of 1 changes from red-orange to yellow on addition of *n*-propylamine in THF solution, which can be detected by the naked eye. © 2015 Trade Science Inc. - INDIA

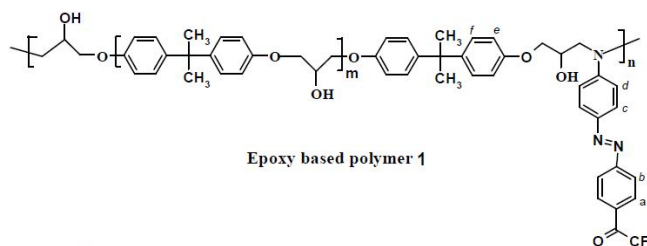
KEYWORDS

Epoxy based polymer;
Colorimetric probe;
Trifluoroacetyl azobenzene;
Amine sensing.

INTRODUCTION

Volatile amines arise from rapidly growing cells and organic decomposition. Some amines have established role as quality indicators of foodstuffs and biomarkers in metabolic diseases^[1]. Heavy exposure to biogenic amines can cause pathogenic reactions in the human body and lead to serious problems for human health. Therefore, the design and synthesis of efficient chemosensors for amine analytes is of realistic significance^[2-5]. However, compared to the large number of small molecular probes, the development of macromolecular probes^[6,7] for amines faces tremendous challenges. In this context, the particular attraction of epoxy-based polymers stems from their easy preparation and processibility, good chemical resistance and dimensional stability and potentiality for reuse. In addition, the epoxy resins contain the reactive epoxy groups capable of doing easy reaction with a

variety of functional groups like $-\text{COOH}$, $-\text{NH}_2$ etc. and thus they can be used as excellent precursors for the synthesis of functionalized polymers. Furthermore, trifluoroacetyl azobenzene unit is a promising amine-binding motif for preparing a variety of probes for the recognition and sensing of amines^[6b,7]. Therefore, in continuing research on the application of epoxy-based polymer as colorimetric probe for sensing amine analytes, we present here a new example of an epoxy-based polymer 1, which contains trifluoroacetyl azobenzene as reporter groups. Our design, in particular, is interesting because it avoids migration or leaching and crystallization of trifluoroacetyl azobenzene moi-



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ety due to covalent linkage to the polymer matrix. The designed probe was found to be an efficient sensor for amines by the change in UV-vis and naked-eye observation.

EXPERIMENTAL

Materials and characterizations

Chemicals were purchased and used without purification. NMR spectra were recorded on a Bruker NMR spectrometer. IR spectra were recorded on Perkin Elmer spectrophotometer using KBr discs. Molecular weights and molecular weight distribution of polymer 1a were determined by Waters gel permeation chromatography (GPC) instrument. THF was used as eluent (flow rate 0.8 mL/min, polystyrene was used as standard, RI detector and UV-2487 dual λ absorbance detector were used to record the signal. Elemental analyses were performed on 2400 Series II CHN analyser (Perkin Elmer) using helium as driving gas and oxygen as combustion gas. TGA/DTG and DSC analyses were conducted with Perkin Elmer Diamond TG/DTA and Perkin Elmer Diamond DSC instruments, respectively under nitrogen atmosphere. UV-vis spectra were recorded on Shimadzu UV-1800 spectrophotometer.

Synthesis of polymer 1a

Epoxy-based precursor polymer 1a was obtained from the reaction between diglycidyl ether of bisphenol-A and aniline according to the literature^[7,8] at 95-100 °C for 48h. GPC (polystyrene, THF): $M_w = 65,000$, PDI = 2.21.

Synthesis of polymer 1

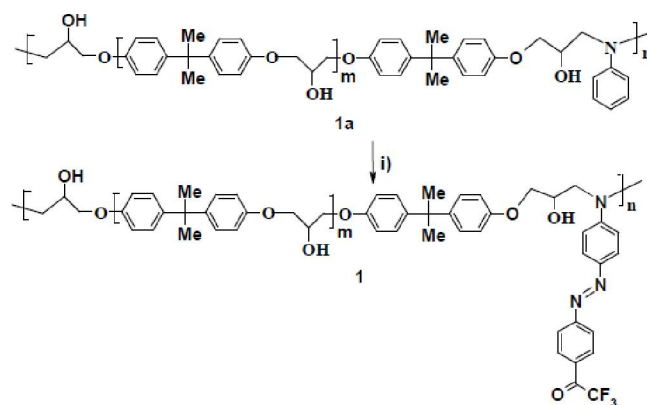
Precursor polymer 1a (0.36g, 0.39 mmol) was dissolved in a mixture of DMF (8ml) and water (0.4 ml) at 0°C. A diazonium salt of 4-trifluoroacetylaniline was prepared by adding an aqueous solution of NaNO_2 (52 mg in 0.25 ml water) into a solution of 4-trifluoroacetylaniline (0.12g, 0.65 mmol in a mixture of 0.25ml water and 0.40 ml sulphuric acid). The mixture was stirred at 0°C for 2 min and then added dropwise into the solution of 1a. The yellow color gradually turned into red. The solution was stirred at 0°C for 3h and then precipi-

tated with addition of water into the reaction mixture. Precipitate was collected and kept in fresh water for 24h. The product was collected, washed with 5% NaHCO_3 solution for two times and then washed with water several times, collected and vacuum dried at 50 – 55°C for 24h. FT-IR (KBr): $\nu_{\text{max}} = 3493, 2966, 2844, 1644, 1468, 1364, 1188, 1059, 896 \text{ cm}^{-1}$; $^1\text{H NMR}$ (DMSO-d_6 , 400 MHz) δ : 8.15 (d, 2H, H_a , $J = 4 \text{ Hz}$), 7.92 (m, 2H, H_b), 7.74 (m, 2H, H_c), 7.61 (s, 2H, H_d), 7.07 (s, H_e), 6.91 (d, $J = 4\text{Hz}$, $\text{H}_{\text{aniline moiety}}$), 6.83 (m, H_f), 4.11 (br s, -OH), 3.88 (bm, -OH), 3.92 (s, polymer chain $-\text{CH}_2-$, $-\text{CH}-$), 1.54 (s, $-\text{CH}_3$); $^{13}\text{C NMR}$ (DMSO-d_6 , 100 MHz) δ : 172.0, 156.2, 151.9, 150.4, 145.4, 142.8, 137.5, 135.0, 130.3, 127.4, 123.0, 121.0, 114.0, 111.3, 70.0, 67.1, 61.0, 56.0, 52.5, 47.0, 41.8, 31.0; Anal. Calcd for $(\text{C}_{53}\text{H}_{53}\text{N}_3\text{O}_8\text{F}_3)_n$: C, 69.43; H, 5.78; N, 4.58%. Found: C, 69.0; H, 5.70; N, 4.48%.

RESULTS AND DISCUSSION

Synthesis and characterization

Epoxy-based polymer matrix is potentially useful as supporting material, whilst retaining the ability of trifluoroacetyl azobenzene reporter group to sense amines. To the best of our knowledge, linear, unbranched aliphatic amine selective epoxy-based macromolecular probe bearing trifluoroacetyl azobenzene units has not been reported yet. The designed polymer 1 was synthesized by applying post azo coupling reaction of 1a with aromatic diazonium salt derived from 4-trifluoroacetylaniline as outlined in Scheme 1 and



Scheme 1 : Synthesis of polymer 1: i) Diazonium chloride of 4-trifluoroacetylaniline, DMF/water, 0-5°C, 3h

unambiguously characterized by FT-IR, UV-vis and NMR (^1H & ^{13}C), elemental and thermal (TG, DSC) analyses. Polymer 1 is soluble in common organic solvents such as THF, 1,4-dioxane, DMF and DMSO. Epoxy-based precursor polymer 1a was obtained according to the literature procedure^{8,9} by carrying out the reaction between diglycidyl ether of bisphenol-A and aniline.

^1H NMR spectrum of 1 indicated the appearance of signals due to trifluoroacetyl azobenzene moiety at 8.15-7.92 ppm along with the dramatic decrease of the resonance at 6.54 ppm corresponding to the proton in *p*-position of anilinic moiety confirming azo-coupling reaction (Figure 1). In addition to this, the resonance attributed to protons *ortho* and *meta* to the aniline moieties showed significant downfield shift due to the presence of electron-withdrawing trifluoroacetyl group.

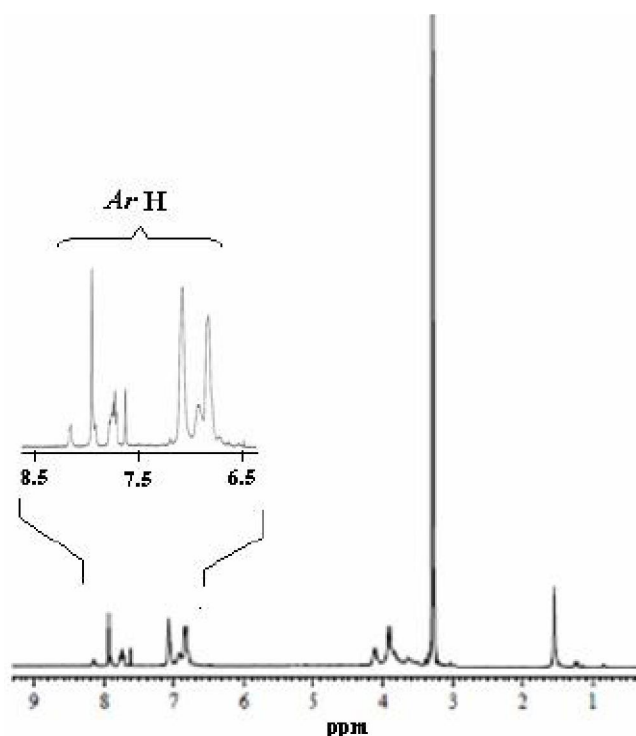


Figure 1 : ^1H NMR spectrum of 1

The percentage of trifluoroacetyl azobenzene moiety in the polymer was estimated to be about 61% which was calculated from ^1H -NMR by comparing the integrations of the signals of the substituted anilinic protons (H_c) with methyl protons of bisphenol-A moiety. The azo coupling reaction was also monitored using ^{13}C NMR spectroscopy where

the trifluoroacetyl signal at 172 ppm was well separated from the remaining carbon signals. Thermal properties of 1a and 1 were investigated by DSC and TGA/DTG. The results are summarized in TABLE 1. It is evident from DSC thermograms that both the polymers are amorphous. However, increased dipole moment due to azo functionalization might be responsible for higher T_g value of 1 than that of 1a. Thermogravimetric analysis (TGA) shows that the polymer has a high thermal stability without loss of weight below 230 °C (TABLE 1). Therefore, the resulting polymer can provide a desirable thermal property for the practical application as a colorimetric sensor.

TABLE 1: Thermal properties of 1a and 1

| Polymer | DSC ^a [T _g (°C)] | TG/DTG ^b | | | | | |
|---------|---|----------------------------------|-------|---------------------|-----------------------|------------------|-------------------------------------|
| | | T _d ⁵ (°C) | Stage | Temp. range (°C) | T _{max} (°C) | Weight loss % | Y _c at 600°C (wt%) |
| 1a | 99.8 | 315 | 1 | 315-441.6 | 378.8 | 76.3 | 12 |
| 1 | 140 | 230 | 2 | 230-272 272-440 | 273.1 346 | 10 42 | 30 |

^aSamples were first heated from -50°C to 200°C at a heating rate of 10°C/min under a nitrogen atmosphere, followed by cooling to -50°C at a rate of 10°C/min after stopping at 200°C for 2 min, and finally heating to 200°C at a rate of 10°C/min. T_g = Glass transition temperature. ^bTGA analysis was performed at a heating rate of 10°C/min under nitrogen flow (100ml/min); T_d^5 = Temperature at which 5% weight loss occurred; T_{max} = maximum rate of weight loss; Y_c = char yield.

Chemosensing behavior

The UV-vis absorption spectrum of 1 in THF ($[1] = 1.33 \times 10^{-4}$ g/ml; $\sim 1.45 \times 10^{-4}$ (M) with respect to repeat unit) exhibited the broad absorption bands peaked at $\lambda_{max} = 417$ nm and 507 nm. The peak at 507 nm is assigned to the charge transfer between donor and acceptor part (*D-π-A*) of trifluoroacetyl azobenzene unit due to *push-pull* effect. The absorption maximum at 417 nm is ascribed to the formation of hemiacetal moieties derived from trifluoroacetyl groups and more exposed hydroxyl groups of polymer chain. Typical Uv-vis absorption spectral features of related (Trifluoroacetyl) azobenzene dyes^[10], developed by Mohr and co-workers, strongly support our observation. Although the absorption band at 507 nm is weak, the designed polymer 1 permits safely the selective

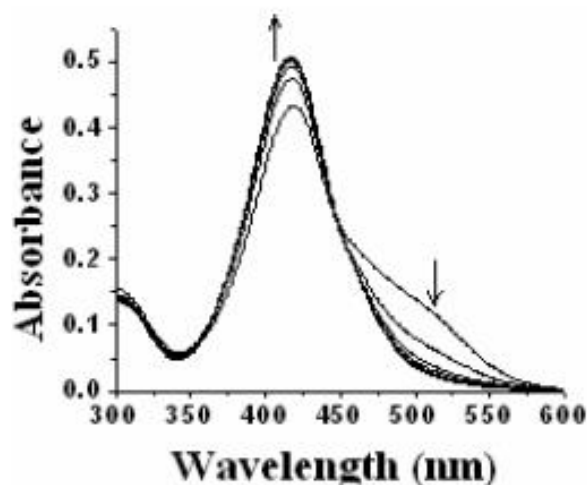


Figure 2 : UV-vis spectral response of 1 (1.45×10^{-4} M) upon addition of *n*-propylamine (up to 17×10^{-3} M) in THF

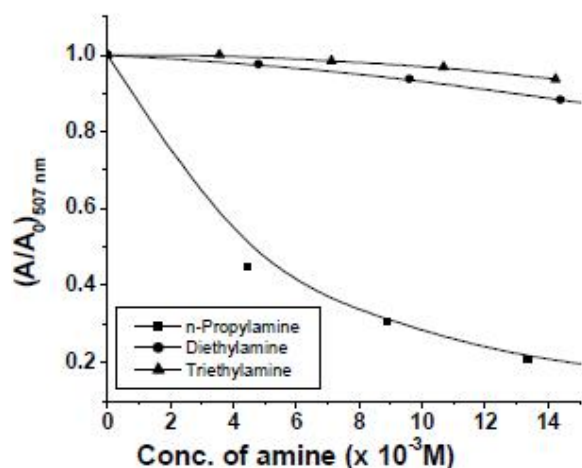


Figure 4 : In absorption spectra $(A/A_0)_{507\text{nm}}$ as a function of primary, secondary and tertiary amines ($[1] = 1.45 \times 10^{-4}$ M) in THF

recognition of primary amine, for instance *n*-propylamine over secondary and tertiary amines such as diethylamine and triethylamine, respectively in THF is evidenced from UV-vis titration experiment (Figure 2).

Remarkably, only *n*-propylamine induced a gradual decrease in absorption intensity at 507 nm accompanied by an increase in absorption intensity at 417 nm. Two clear isobestic points at 355 nm and 448 nm were observed, indicating the formation of a new species upon treatment of 1 with *n*-propylamine. Interestingly, upon the addition of *n*-propylamine, polymer 1 resulted in immediate color change from red-orange to yellow. No significant changes in absorbance as well as color were ob-

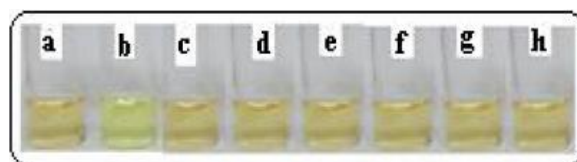


Figure 3 : Visual response of 1 (1.45×10^{-4} M) in THF upon addition of amines: a) 1 only, b) 1+*n*-propylamine, c) 1+diethylamine, d) 1+triethylamine, e) 1+isopropylamine, f) 1+*tert*-butylamine, g) 1+cyclohexylamine, h) 1+aniline

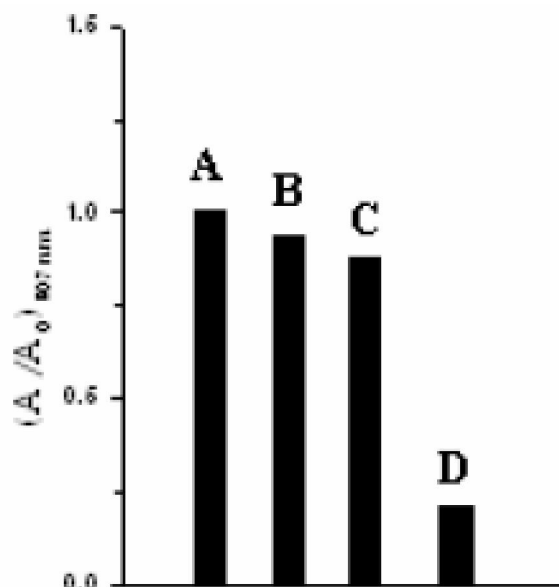


Figure 5 : Bar graph of UV-vis spectral changes of 1 in the presence of various amines: (A) 1 only; (B) 1+ Triethylamine (14×10^{-3} M); (C) 1+ Diethylamine (14×10^{-3} M); (D) 1+ *n*-Propylamine (13×10^{-3} M)

served on adding other representative amines to the red-orange colored solution of 1 (Figure 3). The absorption intensity $(A/A_0)_{507\text{nm}}$, decreases with the gradual increase in concentration of *n*-propylamine (Figure 4). This corroborates a potential application of 1 as colorimetric sensor for the primary amine. However, in comparison, UV-vis spectral changes of 1 in the presence of secondary and tertiary amines such as diethylamine, triethylamine, respectively, were small as shown in Figures 4 and 5.

Next, we evaluated the absorption behavior of 1 toward other primary amines such as isopropylamine, *tert*-butylamine, cyclohexylamine and aniline, the results of which are summarized in Figures 6 and 7. Upon the addition of this series of primary amines, only *n*-propylamine showed perceptible spectral

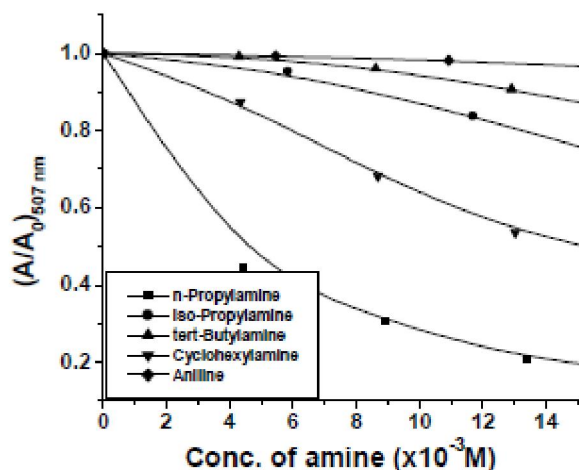


Figure 6 : Plot of $(A/A_0)_{507 \text{ nm}}$ as a function of different primary amines ($[1] = 1.45 \times 10^{-4} \text{ M}$ in THF)

changes with the effect of changing color of the solution instantly from red-orange to yellow (Figure 3). Furthermore, no noticeable changes in color and absorption spectra were observed in the presence of aniline, representative of aromatic primary amine. This result also demonstrates that the epoxy-based polymer approach to sensing aliphatic primary amine can provide excellent selectivity over aromatic primary amine.

The colorimetric change of trifluoroacetyl azobenzene forming carbinolamine upon addition of primary amine has been observed in a number of studies^[6b,7,11]. The electron withdrawing CF_3 substituent makes the carbonyl group more electron deficient and hence, a better amine receptor. Thus, the binding of 1 with *n*-propylamine converts trifluoroacetyl azobenzene group into tetrahedral carbinolamine, which modulates the degree of electronic delocalization and results in a drastic spectral/colorimetric transitions. The marked selectivity of 1 for *n*-propylamine may be due to the nu-

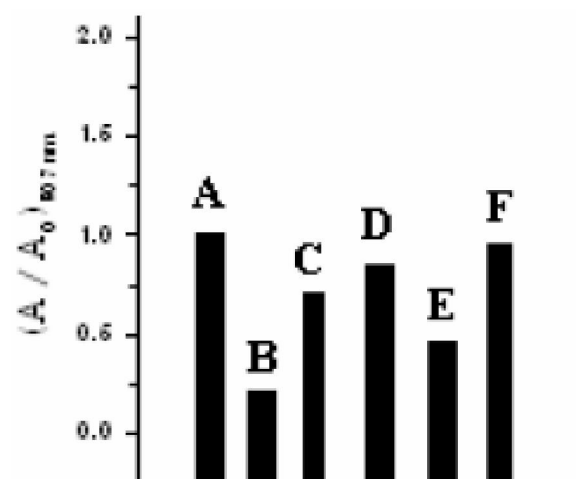
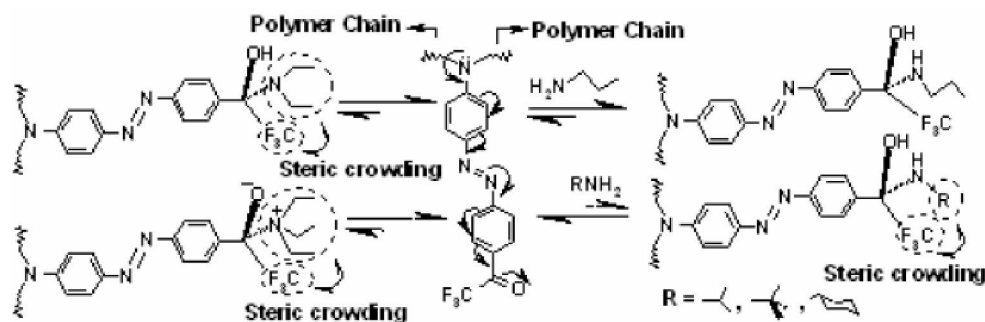


Figure 7 : Bar graph of UV-vis spectral changes of 1 in the presence of various amines: (A) 1 only; (B) 1+ *n*-Propylamine ($13 \times 10^{-3} \text{ M}$); (C) 1+ iso-Propylamine; (D) 1+ *tert*-Butylamine (E) 1+ Cyclohexylamine (F) 1+ Aniline (Conc. of other amines: $\sim 17 \times 10^{-3} \text{ M}$)

cleophilicity of nitrogen atom that adds to the carbonyl group forming favorable tetrahedral carbinolamine. In case of diethylamine and triethylamine the free rotating ethyl groups remain folded towards, and partly covering the lone pair of electrons leading to the sharp decrease in nucleophilicity of amino group towards trifluoroacetyl group. In addition, tetrahedral carbinolamine formation becomes sterically restrictive for secondary and tertiary amines as shown in Scheme 2.

On the other hand, it is quite unhappy to move from sp^2 to sp^3 hybridization of $-\text{COCF}_3$ group with increasing the bulk of the alkyl group of primary amines because there is significant increase in steric crowding between the groups as the bond angle changes from 120° to 109° . In case of cyclohexylamine the large steric bulk of cabinolamine at the equatorial position is particularly noteworthy.



Scheme 2 : Suggested sensing mechanism of 1 in the presence of amines

CONCLUSION

In summary, we have developed a quick, convenient, and inexpensive way to prepare epoxy-based polymer 1 with trifluoroacetyl azobenzene reporter groups. The designed polymer 1 displays excellent selectivity and sensitivity toward linear, unbranched aliphatic primary amine such as n-propylamine which induces a fast color change from red-orange to yellow and a dramatic ratiometric change in UV-vis spectra. The greater processing ability and modular nature of polymer (i.e., into particles, films, etc.) might be exploited in the preparation of handy sensory materials compared to that of small molecules. To our opinion, colorimetric macromolecule of this type would be of great importance to a new generation of chemosensory materials for amines. Further study is under progress in our laboratory.

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