



Synthesis, Characterization, and Chemosensing Application of Poly(Methyl Methacrylate-co-Hydroxyethyl Methacrylate) with Dansyl Side Group

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Abstract: A novel dansyl side-functional polymer (**P2**) was prepared and employed as the metal cation sensing chemical probe. The synthesis of **P2** was performed via consecutive free radical polymerization and esterification reactions. **P2** showed characteristic UV-Vis and fluorescence emission bands for the dansyl unit. The fluorescence emission intensity of **P2** gradually decreased as the concentrations of the added metal ions were increased. The highest quenching efficiencies (QE) were observed for Pb²⁺ (84.56%) and Co²⁺ (83.69%). Besides, the responses of **P2** to the addition of Pb²⁺ cation were quite linear up to 50 equivalent. The presence of Cd²⁺, Hg²⁺, Mn²⁺, and Zn²⁺ cations did not pose significant interferences. Thus, **P2** is a potential candidate for the fluorescence chemical sensor for Pb²⁺ cation.

Keywords: Dansyl group; metal ion sensor; methyl methacrylate; 2-hydroxyethyl methacrylate; twisted intramolecular charge transfer.

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INTRODUCTION

Heavy metal pollution in natural water or soil environments has attracted a worldwide attention because of their severe effects to human health and the environment [1, 2]. While certain heavy metals, including iron, copper, manganese, and zinc, are essential nutrients in small quantities to have a healthy life, some others (Hg^{2+} , Pb^{2+} , As^{3+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , and Cr^{3+}) are highly toxic and carcinogenic for human health [3-6]. Recently, accumulation of heavy metals in rivers, lakes, and seas due to increasing industrial, agricultural, mining, and transportation activities resulted in serious environmental pollution and threatened biolife, particularly in developing countries [7-9]. Contrary to organic contaminants, since they are not biodegradable; they recirculate and accumulate in the environment [7, 10]. Besides, heavy metal ions have great tendencies to produce complexes with nitrogen, sulfur, or oxygen containing biologically important ligands. Consequently, molecular structures of proteins change, hydrogen bonds break, or enzymes are inhibited [3, 11]. The toxic heavy metals affect various tissues and organs, including central nervous system, kidneys, liver, skin, bones, and teeth [4-6]. Therefore, maximum contamination levels for various metal cations in drinking water have been set by different organizations [3, 12]. World Health Organization (WHO) defined the maximum acceptable contamination level for Hg^{2+} , Pb^{2+} , and other toxic metal ions as $10 \mu\text{g L}^{-1}$ [13].

There is urgent requirement for simple, sensitive, selective, and inexpensive determination of metal cations for various applications, including environmental monitoring, industrial process management, food quality control, and chemical threat detection [13, 14]. In this respect, fluorescence spectroscopy is a robust method with its simplicity, low detection limit, sensitivity, selectivity, and fast response among the others [15-17]. Dansyl group, consisting of dimethylamino and naphthalene sulfonyl as donor and acceptor parts, respectively, is one of the most attractive fluorophores and has been extensively used in a wide variety of optical sensing applications since it has intense fluorescence emissions in the visible region with high quantum yields and it can be easily attached to various structures in a covalent way [18-20]. Additionally, being one of the smallest available fluorophores, its emission spectrum is sensitive to chemical environment, such as pH and polarity [21]. Thus, dansyl-containing small molecular compounds, dendrimers, or polymers were used as fluorescent probes against metal cations, anions, biological materials, and nitro aromatic compounds [19, 20, 22-25]. Zhou *et al.* synthesized a dansyl-based fluorescence probe for selective determination of Hg^{2+} in complicated environment samples [26]. Jisha *et al.* repaired dansyl-naphthalimide dyads for fluorescence ratiometric selective recognition of Cu^{2+} ions [27].

Liu *et al.* synthesized calix[4]arene compounds having two dansyl units and employed them in enantioselective sensing of amino acid anions [28]. Yin *et al.* produced thermo-responsive microgels, based on dansyl-containing poly(N-isopropylacrylamide) (PNIPAM), for the selective fluorescent detection of Cu^{2+} cations [29]. Murariu and Buruiana prepared dansyl-labelled poly(acrylamide/methacrylurea-co-vinyl acetate) copolymers for the fluorescent sensing studies towards some organic acids (1-S-camphorsulfonic acid and p-toluenesulfonic acid) and cations (H^+ , Cu^{2+} , Hg^{2+} , and Fe^{2+}) [30]. Recently, we have synthesized dansyl end-functional phosphazene-cored poly(ϵ -caprolactone) star polymer and employed as a selective fluorescent probe for the detection of Pb^{2+} [1].

With this background information in mind, we are reporting herein the synthesis and characterization of novel poly(methyl methacrylate)-co-poly(2-hydroxyethyl methacrylate) copolymer with dansyl side groups ((poly(MMA-co-HEMA-DNS), **P2**). To the best of our knowledge, this is the first report on the synthesis and optical chemosensing application of dansyl-functional PMMA-co-PHEMA copolymer which were obtained via free radical polymerization (FRP) of MMA and HEMA monomers and esterification. Dansyl group was selected as a fluorophore for the preparation of the polymeric chemosensing agent due to its intense emissions, sensitivity to its microenvironments, and strong absorption in the near UV and structural flexibility for derivatization [31-33]. The structural characterizations of **P1** and **P2** polymers were performed using by FT-IR and ^1H NMR spectroscopies. The thermal properties of the obtained polymers were confirmed via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Then, the sensing capacity of the polymers was investigated by fluorescence spectroscopy with quenching studies using Pb^{2+} , Hg^{2+} , Co^{2+} , Cd^{2+} , Mn^{2+} , and Zn^{2+} metal ions in the analytic media.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, Alfa Aesar, 99%) and 2-hydroxyethyl methacrylate (HEMA, Aldrich, 98%) were passed through a column of alumina for the removal of stabilizers and then stored under argon. Triethylamine (TEA, Fluka, $\geq 99.5\%$) was dried over CaH_2 and stored over 3 Å molecular sieves. Benzoyl peroxide (BPO, Aldrich, 98%) was recrystallized from methanol and dried before use. Tetrahydrofuran (THF, Merck, 99.8%) was freshly dried over Na/benzophenone ketyl and freshly distilled under argon atmosphere before use. Dansyl chloride (Alfa Aesar, $97\geq\%$), methylene chloride (DCM, Sigma-Aldrich, $98\geq\%$), diethyl ether (Aldrich, $\geq 99\%$), n-hexane (Sigma-Aldrich, $\geq 95\%$), cadmium chloride (Alfa Aesar, 99.0%), lead(II) nitrate (Alfa Aesar, 99%), manganese(II)

chloride (Alfa Aesar, 97%), cobalt(II) chloride hexahydrate (Alfa Aesar, 98%), zinc chloride (Aldrich, 98%), and mercury(II) chloride (Alfa Aesar, 98%) were used as received.

Instrumentation

^1H NMR spectra were measured in CDCl_3 solutions on a Varian UNITY INOVA 500 MHz spectrometer using solvent residue as the internal reference (7.26 ppm for chloroform) at 25°C. FT-IR spectra were obtained via the attenuated total reflectance (ATR) method on a Perkin-Elmer Paragon 1000 spectrometer equipped with PIKE MIRacle™ diamond ATR attachment at wavenumbers ranging from 600 to 4500 cm^{-1} . Gel permeation chromatography (GPC) measurements were recorded on an Agilent GPC instrument (Model 1100) having a Waters Styragel column (HR 5E), a refractive index detector, and a pump. THF was used as the eluent at a flow rate of 0.3 mL min^{-1} at 24 °C. Average molecular weights and molecular weight distributions were estimated based on a calibration curve drawn using linear polystyrene (PS) polymers as monodisperse standards. Differential scanning calorimetry (DSC) experiments were performed on a DSC 4000 (PerkinElmer) under a protective nitrogen flow (10 mL min^{-1}) from 25 to 220 °C to determine glass transition temperatures (T_g) of the polymers. Thermal stabilities of the obtained polymers were investigated using a Mettler Toledo TGA/SDTA 851 thermogravimetric analyzer from room temperature to 700 °C at a heating rate of 10 °C min^{-1} under a nitrogen flow. UV-Vis spectroscopy measurements of the samples were recorded at room temperature on a Shimadzu UV-2600 spectrophotometer and fluorescence emission spectra of the samples were obtained on an Agilent Cary Eclipse spectrophotometer. Quartz cuvettes (1 cm path length) were used both UV-Vis and fluorescence spectra.

Synthesis of methyl methacrylate-co-2-hydroxyethyl methacrylate copolymer, poly(MMA-co-HEMA) (P1)

Poly(MMA-co-HEMA) (**P1**) was synthesized according to the literature method with minor modifications [42]. HEMA (0.97 g, 7.431 mmol), MMA (4.46 g, 44.586 mmol), and BPO (0.03 g, 0.124 mmol) were added to a 25-mL one-necked round-bottomed flask equipped with a magnetic stirrer under argon atmosphere. The mixture was deoxygenated by purging gently with argon and the reaction was carried out at 80°C for 2 h. The reaction was quenched by dipping the flask into a salt-ice mixture, the crude product was dissolved in 10 mL DCM, and precipitated into cold hexane. The precipitation procedure was performed once more, **P1** was isolated by filtration, and dried at room temperature *in vacuo* until a constant weight was obtained.

Yield: 4.07 g (75%). $M_{n,GPC}$: 57100 g mol⁻¹; M_w/M_n : 1.84. FT-IR (cm⁻¹): 3515 (broad, OH); 2997 and 2951 (C-H); 1720 (C=O) 1476 (C-H); 1248 ((C=O)-O). ¹H NMR (500 MHz, CDCl₃, d, ppm): 0.8-1.13 (6H, s, backbone -CCH₃); 1.84 (4H, t, backbone -CH₂-); 3.59 (3H, s, -COOCH₃ of MMA); 3.84 (2H, t, -CH₂CH₂OH of HEMA); 4.11 (2H, t, -CH₂CH₂OH of HEMA).

Synthesis of dansyl side-functional poly(MMA-co-HEMA) copolymer (poly(MMA-co-HEMA-DNS), P2)

P1 (0.5 g, contains 0.724 mmol OH units) was dissolved in dry THF (12 mL) under dry nitrogen atmosphere. After addition of TEA (0.220 g, 2.171 mmol), the reaction mixture was cooled to -15°C by an ice-salt mixture and dansyl chloride (0.976 g, 3.619 mmol) in dry THF (8 mL) was added drop-wise into the mixture via dropping funnel over 25 min. Subsequently, the cooling bath was removed and the solution was stirred for 60 h at room temperature. The salts were filtered off, the filtrate was concentrated using a rotary evaporator, and then precipitated into a cold diethyl ether twice. **P2** was isolated by filtration and dried at room temperature *in vacuo*.

Yield: 0.599 g (86.2%). $M_{n,NMR}$: 71464 g/mol; $M_{n,GPC}$: 76300 g/mol; M_w/M_n : 1.93. FTIR (cm⁻¹): 2997 (C-H), 2951 (C-H); 1720 (C=O); 1476 (C-H); 1248 ((C=O)-O). ¹H NMR (CDCl₃, δ, ppm): 0.8-1.13 (6H, s, backbone -CCH₃); 1.84 (4H, t, backbone -CH₂-); 2.88 (s, -N(CH₃)₂, in dansyl moiety); 3.59 (3H, s, -COOCH₃ of MMA); 3.84 (2H, t, -CH₂CH₂OH of HEMA); 4.11 (2H, t, -CH₂CH₂OH of HEMA); 8.60 ppm (1H, d, -CH- of dansyl moiety); 8.25 ppm (2H, d, -CH- of dansyl moiety); 7.56 ppm (2H, q, -CH- of dansyl moiety); 7.24 ppm (1H, d, -CH- of dansyl moiety).

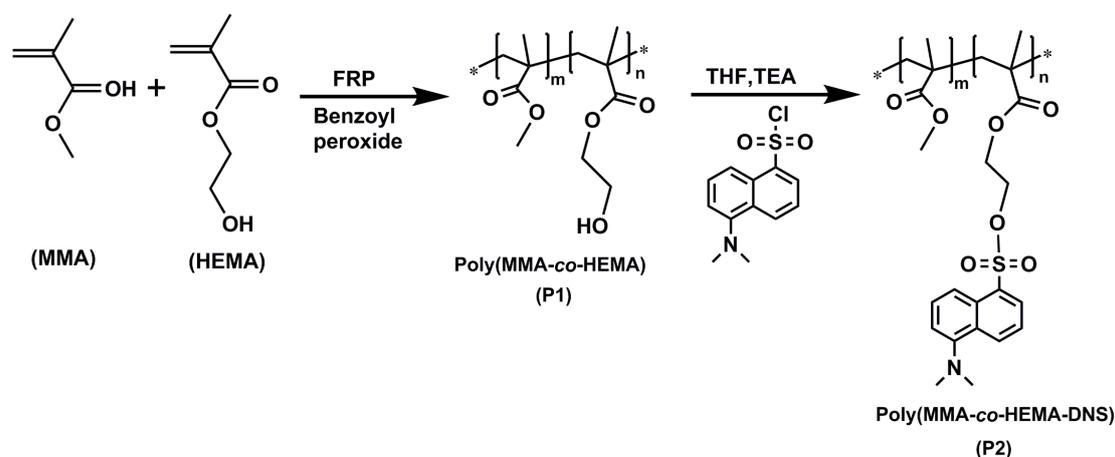
Fluorescence sensing application of P2 against metal cations

A definite amount of poly(MMA-co-HEMA-DNS) copolymer (**P2**) was dissolved in ACN:water (6:4, v/v) solvent mixture to provide the concentration of DNS group to be 2.7 10⁻⁵ M. Then, **P2** was titrated with prescribed amount of Cd²⁺, Co²⁺, Hg²⁺, Pb²⁺, Mn²⁺, and Zn²⁺ cations and the fluorescent responses of **P2** were measured by fluorescence spectroscopy at room temperature.

RESULTS AND DISCUSSION

The poly(MMA-co-HEMA-DNS) (**P2**) copolymer was prepared via a combination of free radical polymerization (FRP) and esterification reactions (Scheme 1). Firstly, poly(MMA-co-HEMA) copolymer with the hydroxyl side groups (**P1**) was synthesized by FRP using MMA and hydroxyl functional HEMA monomers in the presence benzoyl peroxide as

initiator. In the final step, dansyl groups were successfully attached as side groups by esterification between dansyl chloride and hydroxyl-functional groups of **P1**, yielding **P2**.



Scheme 1. General procedure for the synthesis of dansyl functional poly(MMA-co-HEMA-DNS) (**P2**).

^1H NMR and FT-IR spectroscopic methods were employed to characterize the structures of **P1** and **P2** polymers with hydroxyl and dansyl side group, respectively. The FT-IR spectra of the polymers are shown in Figure 1. In these spectra, the observation of strong and sharp peak at 1720 cm^{-1} was ascribed to the carbonyl groups in HEMA and MMA repeating units of both polymers. The signals between 2950 and 3000 cm^{-1} was due to asymmetric and symmetric CH stretching vibrations of the obtained polymers, respectively. In the FT-IR spectrum of **P1**, the intense broad band around 3515 cm^{-1} corresponds to the OH stretching frequencies of HEMA units. After esterification of **P1** with dansyl chloride, these signals completely disappeared in the FT-IR spectrum of **P2**, indicating the success of the reaction.

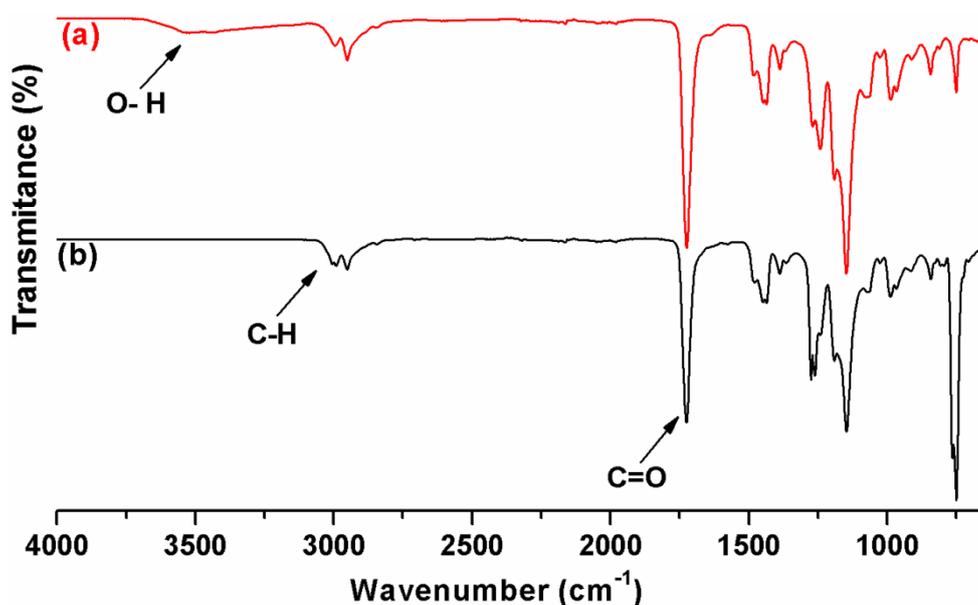


Figure 1. FTIR spectra of (a)**P1** and (b)**P2**.

The ¹H NMR spectra of **P1** and **P2** were given in Figure 2. The peaks between 0.8 and 1.14 ppm were attributed to the protons of H_a methyl groups in the polymer chain of **P1** and **P2**. The signals of the H_b methylene protons of the polymer skeleton were seen around 0.8 and 1.13 ppm. The peak at 3.59 ppm were assigned to H_c methyl protons in the MMA repeating units of both polymers while H_e and H_d methylene protons in the HEMA repeating units of **P1** resonated at 3.84 and 4.11 ppm, respectively [43]. The ratio of MMA and HEMA repeating units (m/n, see Scheme 1) in **P1** was calculated as 5.6 using the integration ratio between the H_c methyl protons of MMA and H_d methylene protons of HEMA repeating units. Upon esterification of **P1** with dansyl chloride, the signal of the methylene protons (H_e) next to the hydroxyl group in **P1** (Figure 2a) moved to lower magnetic fields and overlapped by H_d methylene proton signals (adjacent to the ester group in HEMA repeating unit) in the ¹H NMR spectrum of **P2** (Figure 2b). Besides, some new peaks also appeared in the spectrum (Figure 2b) related to the aromatic CH (δ = 8.60, 8.25, 7.56, and 7.24 ppm) and H_f methyl protons (δ = 2.88 ppm) in the DNS moiety. Overall, these data clearly showed the successful synthesis of the polymers.

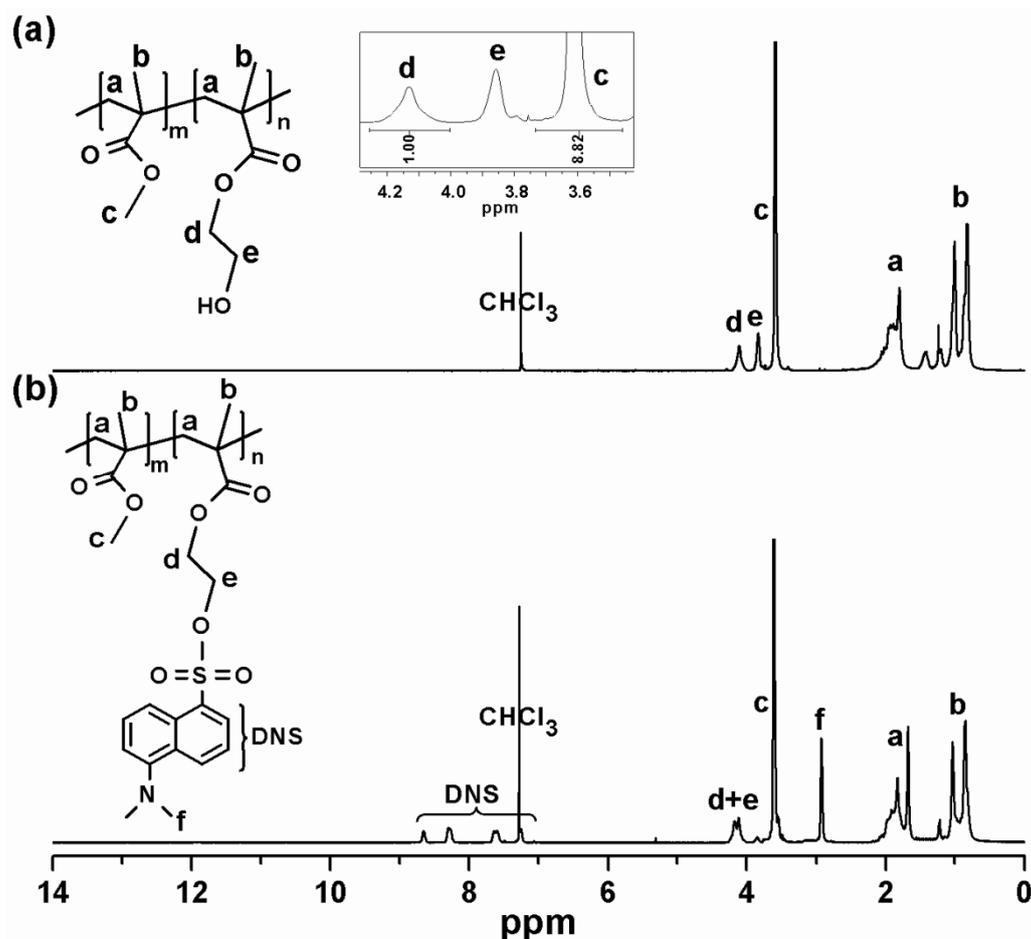
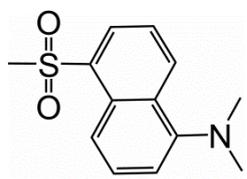


Figure 2. ^1H NMR spectra of (a) **P1** and (b) **P2** in CDCl_3 at room temperature.

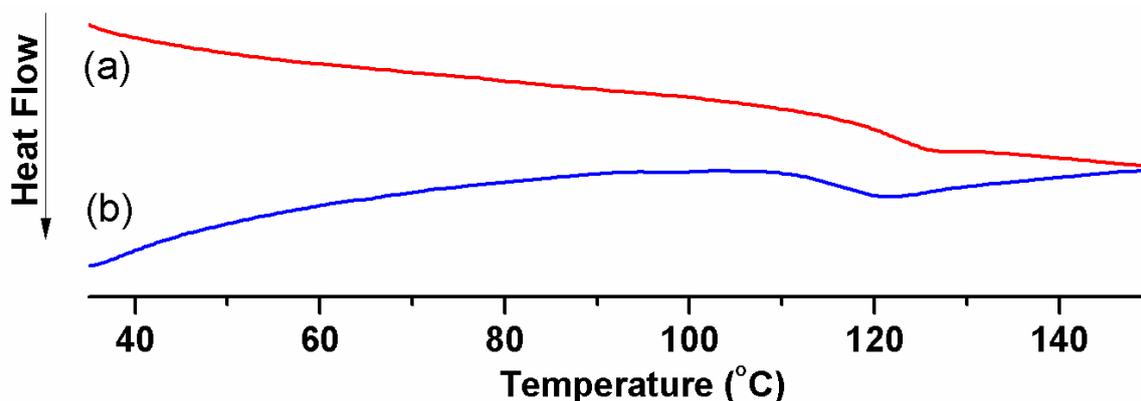
The average molecular masses of the copolymers (**P1** and **P2**) were estimated by gel permeation chromatography (GPC) based on linear polystyrene calibration standards. Related data are given in Table 1 and GPC chromatograms are presented in Figure S1 and S2 in the Supporting Information. The polymers showed symmetrical and unimodal elution peaks in these chromatograms with polydispersity values in the range of 1.84–1.93, indicating that the purified polymerization products contained only the targeted polymers. Since the hydrodynamic volumes of the obtained polymers (**P1** and **P2**) and polystyrene calibration standards are different, the average molecular weights of the polymers obtained from GPC measurements are regarded to be less reliable than those calculated from ^1H NMR data. In the ^1H NMR spectra of the polymers, initiator residue signals could not be observed due to dilution of the terminal units in the polymer chains [34]. On the other hand, the molar weights of the polymer fragment containing single OH (**P1**) or DNS (**P2**) units were calculated from the equation $(m/n) \times \text{MW of MMA} + \text{MW of OH or DNS functional unit}$.

Table 1. Molecular weight analysis of the MMA-co-HEMA copolymers with different side groups.

Polymers	$M_{n, GPC}^a$	$M_{w, GPC}^a$	M_w/M_n^a	Side Group
P1	57100	105100	1.84	-OH
P2	76300	147300	1.93	

^aDetermined by GPC with linear polystyrene standards. THF was used as eluent (RI detector)

Since PMMA and PHEMA are amorphous in nature [44, 45], glass transition temperature (T_g) of the polymers with different side-functional groups were investigated by differential scanning calorimetry (DSC) experiments. The related thermograms of polymers in the second heating runs were presented in Figure 3 and the data were briefly given in Table 2. In these thermograms, T_g of **P1** and **P2** were observed at 121 and 117 °C, respectively. The slight decrease in the T_g values of the polymers can be attributed to the presence of bulky DNS side groups, decreasing molecular packing in **P2**.

**Figure 3.** DSC curves of (a)**P1** and (b)**P2** in the second heating runs.

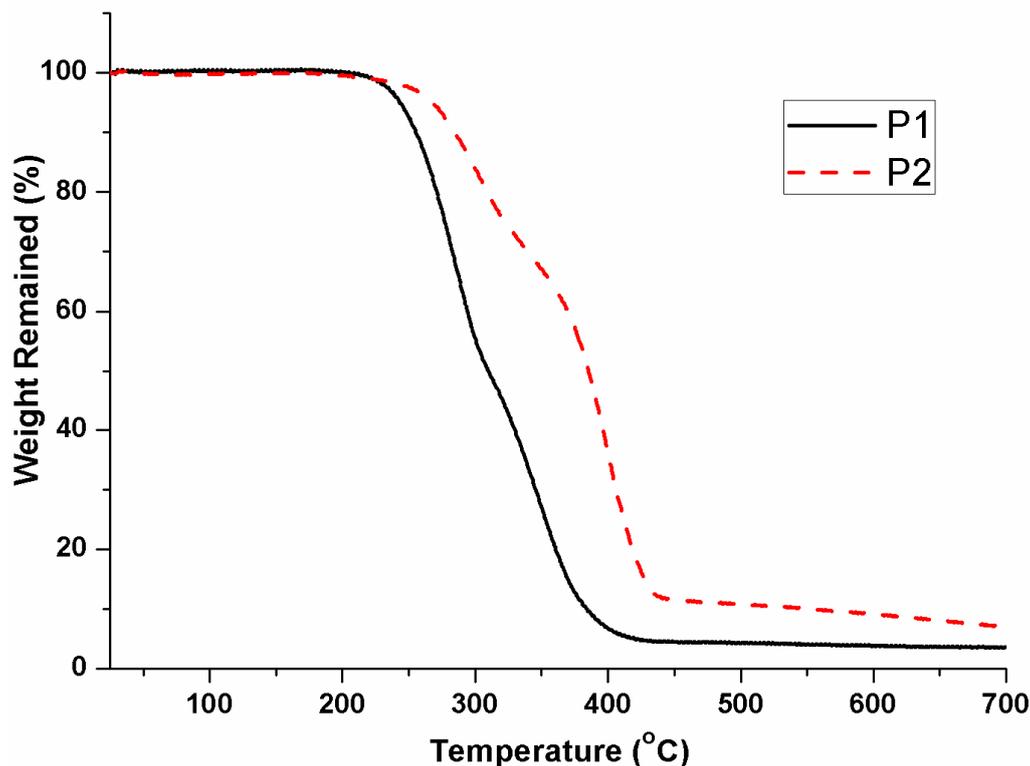
Thermal stabilities of the hydroxyl (**P1**) and dansyl (**P2**) side-functional polymers were determined by thermogravimetric analysis (TGA) experiments under nitrogen flow with a heating rate of 10 °C min⁻¹ from room temperature to 700 °C. Figure 4 demonstrates the percent remaining weight versus temperature curves of the polymers whereas data related to $T_{d, onset}$, $T_{d, max}$, and char yield are summarized in Table 2. Hydroxyl functional groups are known to be thermally labile [35]. Upon esterification of hydroxyl side-functional polymer (**P1**) with dansyl chloride, there observed a significant increase in $T_{d, onset}$, $T_{d, max}$, percent char yield values of the obtained DNS-functional polymer (**P2**).

Table 2. Thermal properties of the polymers.

Entry	T_g (°C) ^a	$T_{d, onset}$ (°C) ^b	$T_{d, max}$ (°C) ^c	Char Yield(%) ^d
P1	121	243	315	3.49
P2	117	268	387	6.87

^a T_g is the glass transition temperature determined by DSC experiments in the second heating run.

^b $T_{d, onset}$, ^c $T_{d, max}$, and ^dChar yield were determined by TGA experiments at 700 °C under a argon atmosphere. ^b $T_{d, onset}$, ^c $T_{d, max}$, and ^dChar yield are the onset decomposition temperature of the polymers, the temperature corresponding to the maximum rate of weight loss, and the percent of mass remaining in TGA experiments, respectively.

**Figure 4.** TGA curves of **P1** and **P2**.

The presence of DNS side-groups in the chemical structure of **P2** was further proved by absorbance and fluorescence emission spectra. In the UV-Vis spectrum of **P2** (containing $2.7 \cdot 10^{-5}$ M DNS) taken in ACN:water (6:4) solvent system at room temperature, there was seen a very strong absorption around 200 nm, a shoulder peak at 254 nm, and comparatively weak band with a maximum of 344 nm (Figure 5). The position of band maxima and the relative peak strengths are in accordance with the literature [1, 36]. The fluorescence emission spectrum of **P2** was taken in the same experimental conditions and depicts a broad band with a maximum at 530 nm (Figure 5). This band is called as Band A and ascribed to twisted intramolecular charge transfer (TICT) emission due to charge transfer between dimethyl amino donor and naphthalene sulfonyl acceptor groups of the dansyl fluorophore [37].

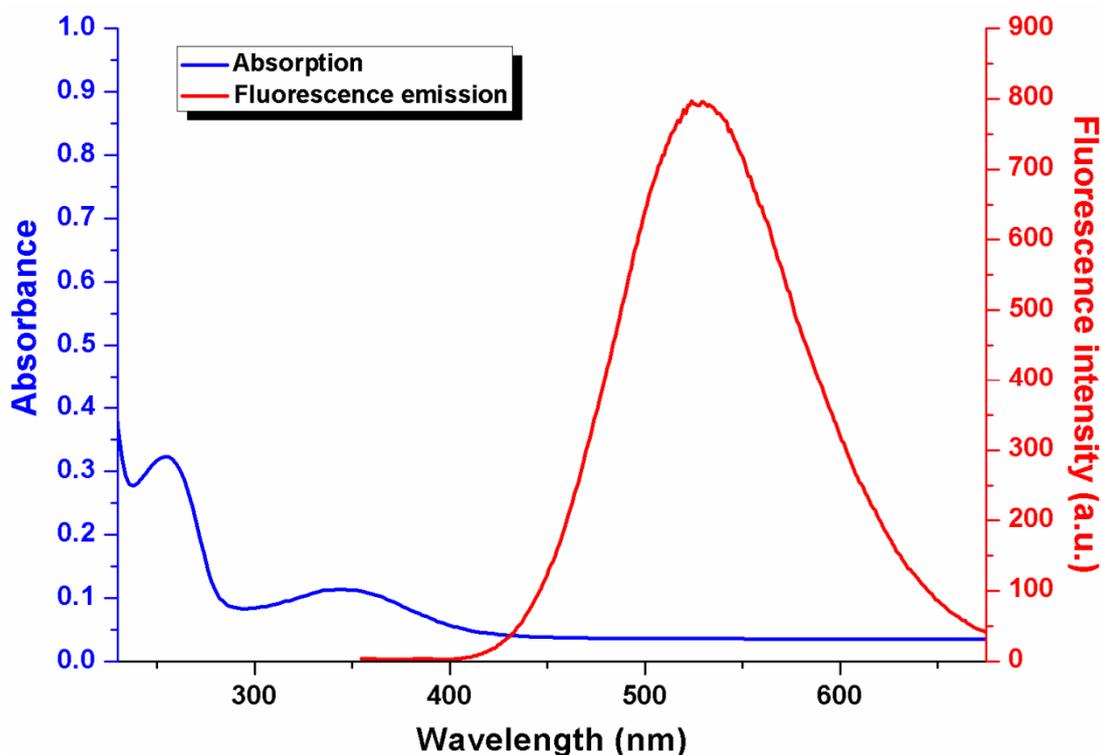


Figure 5. Absorbance and fluorescence emission spectra ($\lambda_{\text{ex}} = 344 \text{ nm}$) of **P2** in ACN:water (6:4). The concentration of DNS units was $2.7 \cdot 10^{-5} \text{ M}$.

The binding and recognition behavior of the dansyl side-functional polymer (**P2**) towards different metal cations were investigated via fluorescence measurements. Metal cation sensing experiments were conducted in ACN:water (6:4) solvent system at 344 nm excitation wavelength at room temperature and the obtained spectra were given in Figure 6. In these spectra, dansyl fluorophore of **P2** gave a very strong emission spectrum in the absence of any metal cations due to intramolecular charge transfer (ICT) from nitrogen atom of the dimethylamino group to naphthalene moiety [37]. When **P2** was titrated with 100 equivalents of Cd^{2+} , Co^{2+} , Hg^{2+} , Pb^{2+} , Mn^{2+} , and Zn^{2+} cations, ICT emission of **P2** was quenched remarkably with slight blue-shifting of the band maxima. The quenching of the emission intensity of **P2** was attributed to electron transfer from the excited DNS to nearby metal cations. Quenching efficiency ratios (QE) of the metal cations were calculated from the equation: $\text{QE} = ((I_0 - I) / I_0) \times 100$. The obtained results were demonstrated in Figure 7. The highest QEs among the studied metal cations were observed for Pb^{2+} (84.56%) and Co^{2+} (83.69%). As seen from Figure 8, the interferences resulting from other cations are not significant. Besides, dansyl fluorophore of **P2** gave very linear responses to the addition of Pb^{2+} cation up to 50 eq with R^2 value of 0.99 (Figure 9). These results indicate that **P2** could be employed as Pb^{2+} sensing fluorescence chemical probe.

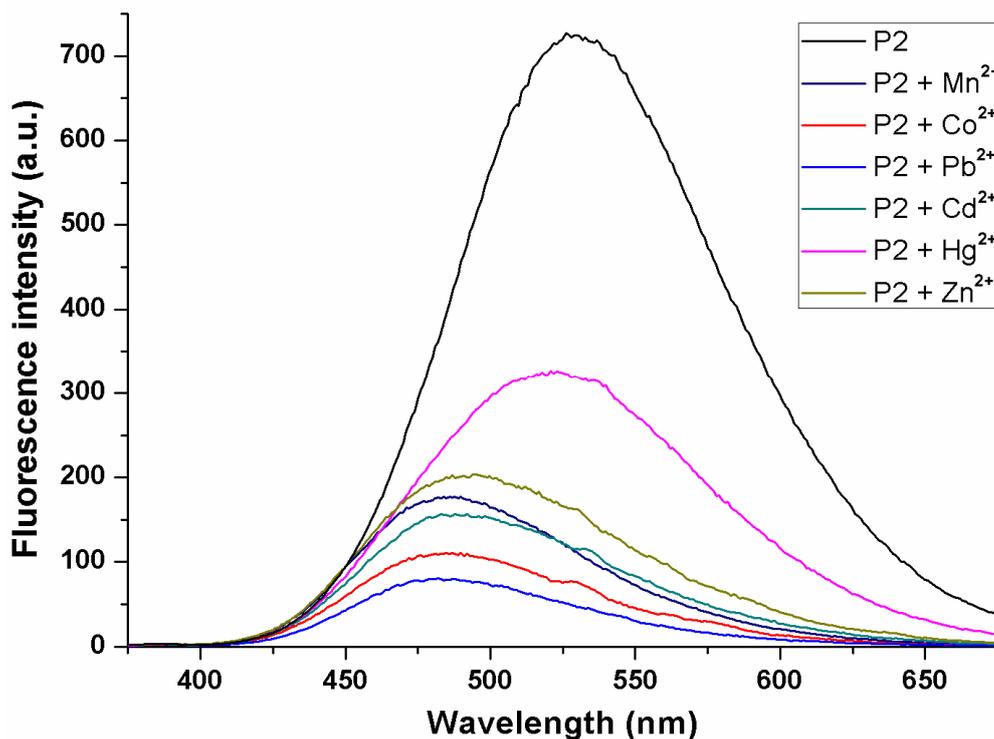


Figure 6. Fluorescence spectral response of **P2** solution (containing 2.7 10⁻⁵ M DNS) in ACN:water (6 : 4, v/v) upon addition of 100 eq. of Cd²⁺, Co²⁺, Hg²⁺, Pb²⁺, Mn²⁺, and Zn²⁺ cations.

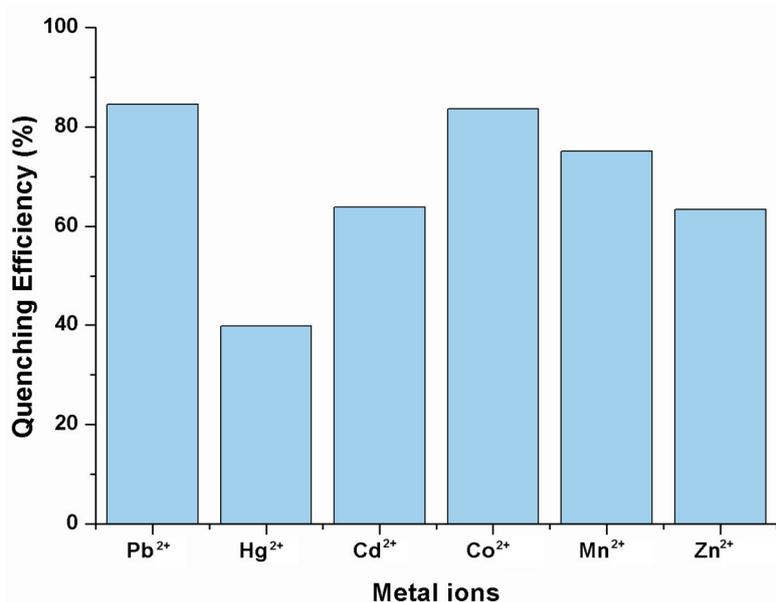


Figure 7. Responses of the dansyl-modified polymer (**P2**) upon addition of 100 eq. targeted metal ions.

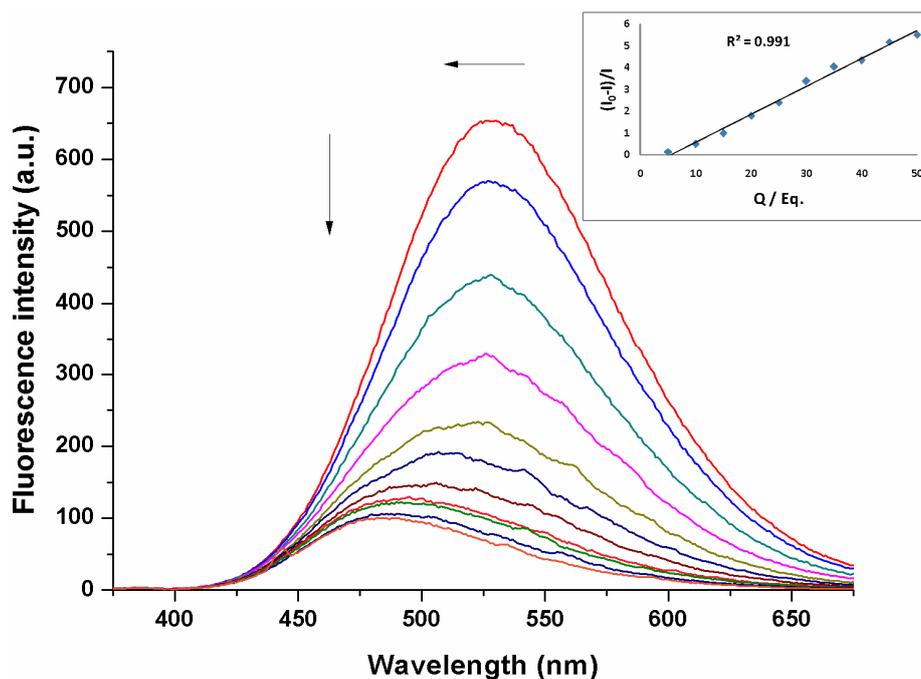


Figure 8. Fluorescence emission spectra of **P2** ($2.7 \cdot 10^{-5}$ M) in ACN :water (6:4) in the presence of Pb^{2+} cation at 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 equivalent ratios.

CONCLUSION

The dansyl side-functional polymer (**P2**) was synthesized via free radical polymerization of MMA and HEMA monomers and esterification of the obtained polymer (**P1**) with dansyl chloride. The FT-IR, ¹H NMR, UV-Vis, and fluorescence spectral data confirm the successful synthesis of the polymers. Then, **P2** was employed as fluorescence sensor probe for various metal cations. Fluorescence emissions of **P2** were effectively quenched upon addition of metal cations. The highest QEs were observed for Pb^{2+} (84.56%) and Co^{2+} (83.69%). Besides, **P2** gave highly linear response to the addition of Pb^{2+} up to 50 equivalent. Interferences resulting from the presence of Cd^{2+} , Hg^{2+} , Mn^{2+} , and Zn^{2+} cations are not significant. Therefore, **P2** has the potential to be used as a fluorescent-active chemical probe for the determination of Pb^{2+} cation.

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Türkçe Öz ve Anahtar Kelimeler

Dansil Yan Grubuna Sahip Poli(Metil Metakrilat-ko-Hidroksietil Metakrilat) Polimerinin Sentezi, Karakterizasyonu ve Kemo-hissetme Uygulaması

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Öz: Yeni bir dansil yan grubuna sahip polimer (**P2**) hazırlanmış ve metal katyon hissedici kimyasal prob olarak kullanılmıştır. **P2**'nin sentezi art arda gelen serbest radikal polimerizasyonu ve esterleştirme ile gerçekleştirilmiştir. **P2**, dansil grubuna ait karakteristik UV-Vis ve floresans emisyon bantları göstermektedir. **P2**'nin floresans emisyon şiddeti, ilave edilen metal iyonlarının derişimi artırıldıkça azalmaktadır. En yüksek söndürme etkinliği (QE) Pb^{2+} için (%84,56) ve Co^{2+} için (%83,69) elde edilmiştir. Bunun yanında, **P2**'nin Pb^{2+} ilavesine verdiği cevaplar 50 eşdeğere kadar oldukça doğrusal bir şekilde gitmektedir. Cd^{2+} , Hg^{2+} , Mn^{2+} ve Zn^{2+} katyonlarının varlığı belirgin bir girişim etkisine neden olmamaktadır. Bu sebeple, **P2**'nin Pb^{2+} katyonu için potansiyel bir floresans kimyasal sensör olarak kullanılabileceği anlaşılmaktadır.

Anahtar kelimeler: Dansil grubu; metal iyon sensörü; metil metakrilat; 2-hidroksietil metakrilat; bütülmüş molekül içi yük iletimi.

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