Synthesis of Magnetite-Based Polymers as Mercury and Anion Sensors Using Single Electron Transfer-Living Radical Polymerization

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ABSTRACT: In this work, hydrophilic polymers modified with iron oxide nanoparticles, such as iron oxide–poly(2-dimethylaminoethyl methacrylate) [P(DMAEMA)] magnetite-based and iron oxide–poly(acrylamide) [P(AAm)] magnetite-based polymers, were prepared via a single electron transfer-living radical polymerization approach. Bile acid and 2-bromo-2-methylpropionic acid were covalently attached onto the surface of Fe3O4 nanoparticles, and these immobilized magnetite nanoparticles were used as an initiator for the polymerization. The binding capabilities of different ions, such as Hg2+, CN−, Cl−, F−, and NO3−, were tested using these polymeric sensors monitored by UV−vis spectroscopy. Magnetite-based P(DMAEMA) showed enhanced binding capability due to the presence of tertiary amine groups. In addition, it was possible to easily separate the bound ions from aqueous media using an external magnetic field.

1. INTRODUCTION

Most modern farming requires a large number of fertilizers and soil amendments for efficient plant growth. All such fertilizers as well as paints, detergents, and batteries are composed of significant quantities of metal ions. In spite of the important contributions of these ions, they can also cause severe environmental problems. Environmental pollution, especially from hazardous heavy metals (Cu, Cr, Ni, and Hg), is a global problem due to their high toxicity and non-biodegradable properties. Removal of heavy metal ions from water resources has become a crucial issue owing to their tendency to accumulate in living organisms and to provide prompt harmful effects to natural resources. Therefore, there is a requirement for newer and effective methods for selective removal of metal ions, which are also cost-effective, to build a sustainable society. Heavy metal ions could be detected by several traditional methods, including chemical precipitation, reverse osmosis, electrochemical treatment techniques, ion exchange, membrane filtration, coagulation, extraction, irradiation, and adsorption. Adsorption technology has been considered to be one of the most promising methods to trace heavy metal ions in recent years. Various materials, including activated carbons, clay minerals, chelating ligands, cross-linked materials, and natural zeolites, have been successfully used to adsorb metal ions from waste under treatment. Even though traditional sorbents could remove heavy metal ions from wastewater, it may suffer from low binding capacities, recovery, and reuse. Therefore, the rapid development of nanotechnology has been proved to show remarkable potential for solutions to environmental problems. Compared with traditional materials, nanomaterial-based adsorbents have exhibited much improved efficiency, eco-friendliness, and ease of handling in water treatment.

The nanomaterial-based adsorbents provide more advantages due to their large surface-to-volume ratio. The affinity of activated carbon, carbon nanotubes, and carbon-encapsulated magnetic nanoparticles on binding metal ions, such as Co2+ and Cu2+, has been studied by Pyrzynska and Bystrzejewski. They found that carbon nanomaterials have significantly higher sorption efficiency compared with activated carbons. A series of anions, including F−, Cl−, Br−, I−, CN−, SCN−, HCO3−, SO42−, PO43−, and NO3−, were tested with a family of polymeric sensory materials containing pyridyl cations, which gave a general response to basic anions and, particularly, a selective chromogenic response to hydrogen carbonate in pure water. However, in a dissimilar way, polymers have a
huge amount of polyfunctional groups, which can effectively bind heavy metal ions, but it may suffer from low specific area and adsorption rate. Therefore, scientists and researchers pay more attention to develop new sorbents with both polyfunctional groups and high surface area, which open new opportunities for the field of tracing toxic ions. Polymers hold polyfunctional groups in their backbone, which might act as a platform capable of arranging a large number of receptors along the backbone for enhanced anion recognition. Thus, as a platform capable of arranging a large number of receptors hold polyfunctional groups in their backbone, which might act as adsorbents, prepared via the process of controlled radical polymerization (CRP), namely, single electron transfer-living radical polymerization (SET-LRP). This SET-LRP method was reported by Percec and co-workers, which has gained more and more attention in recent years and is considered to be a convenient tool for rapid polymerization with low polydispersity index (PDI) values and more efficient for surface modifications. The SET-LRP method is less vulnerable to side reactions and radical termination because some tools of the process occur via outer-sphere electron transfer in comparison to the normal polymerization methods. Recently, several articles have been published on utilizing the principles developed in SET-LRP toward synthesizing well-defined polymers, including sensing materials with controlled compositions, thereby advancing the controlled radical polymerization methodology. Two different controlled amphiphilic polymer sensors are successfully prepared in this study by SET-LRP and compared for their binding efficiency. The bound ions can be easily separated from aqueous media using an external magnet, which is very useful for practical applications. Weller and co-workers reported cross-linked polystyrene shells grown on iron oxide nanoparticles via surface-grafted activator generated by electron transfer—atom transfer radical polymerization (AGET−ATRP) in a microemulsion, which, in turn, were conjugated with biomolecules to enable a broad variety of bioanalytical and biomedical applications. Illes and co-workers reported multifunctional poly(ethylene glycol) (PEG)-carboxylate copolymer-coated superparamagnetic iron oxide nanoparticles for biomedical application with the utilization of atom transfer radical polymerization. Queimener and co-workers investigated the magnetoresponsive behavior of mixed matrix membranes under a magnetic field of different strengths by reversible addition fragmentation chain transfer (RAFT) polymerization. A detailed review about the utilization of controlled radical polymerization for molecularly imprinted polymers and polymer brushes with the combination of various nanomaterials was also reported.

2. EXPERIMENTAL SECTION

2.1. Materials. The monomers, dimethylaminoethyl methacrylate (DMAEMA) and acrylamide (AAM), were purchased from Aldrich and used as received. Methylene tetrahydrofuran (THF), dimethylformamide (DMF), and hexane were dried and distilled as per standard protocols before use.

2.2. Synthesis of Initiator-Immobilized Magnetite Nanoparticles. Magnetite nanoparticles were synthesized according to a literature report by adding an aqueous solution of Fe^{2+}/Fe^{3+} at a ratio of 1:2, maintained in an inert atmosphere at a basic pH, which was obtained by the addition of ammonium hydroxide at ambient temperature. In brief, 1.76 g of ferrous sulfate (6.22 mmol) and 2.04 g of anhydrous ferric chloride (12.44 mmol) were mixed in 50 mL of water and sonicated for 1 h at room temperature. Then, 200 mL of aqueous ammonia was slowly added to the above mixture by stirring to precipitate magnetite nanoparticles. Then, the precipitate was separated by centrifugation at 10,000 rpm and dried under vacuum at 50 °C overnight.

Initially, bile acid was reacted with iron oxide to form Fe_{3}O_{4}−CA in THF at 50 °C followed by the addition of 2-bromo-2-methylpropionic acid in a one-pot synthesis to give the corresponding initiator-immobilized magnetite nanoparticles (Fe_{3}O_{4}−CA−Br), which were suitably characterized by Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and other instrumental methods. The results were used to immobilize the polymerization of DMAEMA and acrylamide at a moderate temperature in the presence of a Cu/PMDETA complex under SET-LRP conditions.

2.3. Synthesis of Initiator-Immobilized Magnetite Nanoparticles (Fe_{3}O_{4}−CA−Br). Typically, 0.5 g of magnetite nanoparticles was mixed with 10 mmol bile acid dissolved in 10 mL of methanol. The mixture was sonicated for 2 h and heated at 45−55 °C for 12 h. The magnetite nanoparticles capped with bile acid [Fe_{3}O_{4}−CA] were separated using a bar magnet, treated with 2-bromo-2-methylpropionic acid (5 mmol) in methanol under sonication for 2 h, and further allowed to stir for 12 h at room temperature. The reaction mixture was centrifuged and then rinsed with ethanol several times and finally with chloroform. Then, it was dried under vacuum to get initiator-immobilized magnetite nanoparticles (Fe_{3}O_{4}−CA−Br).

2.4. Surface-Initiated SET-LRP Polymerization of DMAEMA and Acrylamide from the Magnetite Surface. The polymerization was carried out by adding about 10 mg of initiator-immobilized magnetite nanoparticles (Fe_{3}O_{4}−CA−Br) in 5 mL of DMSO and 7.15 mg (0.049 mmol) of copper into a well-dried 50 mL Schlenk flask with a magnetic stirrer and rubber septum. It was then degassed and refilled with nitrogen gas and the process was repeated three times. This was followed by the addition of the degassed monomer (DMAEMA and acrylamide) of interest (1.0 mL, 27.86 mmol) via a syringe, and the reaction mixture was degassed by four freeze−thaw pump cycles. Finally, 8.63 mg (0.049 mmol) of PMDETA was added to the mixture and sealed under an argon atmosphere, which was stirred in an oil bath maintained at 45 °C. After the desired time, the polymerization was terminated by exposing to air and diluting the reaction mixture with THF, followed by precipitation in 200 mL of methanol/hexane. Then, the material was dispersed in 5 mL of THF and centrifuged to remove the unreacted monomer and the
Cu(II)/PMDETA complex. The obtained magnetite polymers (magnetite-based P(DMAEMA) and magnetite-based P(AAm)) were characterized by various instrumental methods, such as FTIR spectroscopy, TGA, XRD, NMR spectroscopy, dynamic light scattering (DLS), UV–vis spectroscopy, X-ray photoelectron spectroscopy (XPS), and gel permeation chromatography (GPC) analyses.

2.5. Methods. FTIR spectra were recorded on a DIGILAB–FTS-3500 Fourier transform infrared spectrometer in the region of 4000–500 cm⁻¹ by attenuated total reflection (ATR) with a wave number accuracy of 4 cm⁻¹ and 64 scans collected. Before the analysis, all samples were dried at least for 12 h to remove absorbed water. The morphology of the iron oxide initiator and the polymer was observed on a JEOL JSM-6700F field emission scanning electron microscope at an accelerating voltage of 3 kV, whereas the TEM image of the same was recorded on a JEOL JEM 2010 model with an acceleration voltage of 120.0 kV. All of the samples were cut into 5 × 5 mm² coupons and coated on a copper grid before use. The thermal properties of the samples were examined using thermogravimetric analysis (TGA 2950). The sample was placed into an alumina crucible for TGA and heated from room temperature to 800 °C with an increasing temperature rate of 10 °C min⁻¹ under flowing argon gas at 20 cm³ min⁻¹. The ²H and ¹³C NMR spectra were recorded using a Varian Unity INOVA 600 NMR (600 MHz for ¹H and 100 MHz for ¹³C). Spectra were recorded in D₂O and methanol-d₄ at room temperature whichever is applicable. The X-ray diffraction pattern was obtained on an X-ray diffractometer (type HZG41 B-PC) using Cu Kα radiation (λ = 1.5406 Å) at a scanning rate of 0.075° (2θ) min⁻¹. The acceleration voltage and the applied currents were 40 kV and 80 mA, respectively. UV–vis absorption spectra were measured on a Shimadzu UV–vis 2550 spectrophotometer in the wavelength range of 200–800 nm. The molecular weight data were recorded on a WATERS GPC equipped with three columns of average pore size 10⁵, 10⁴, and 10³ Å (particle size 5 nm) and connected in series. DMF was used as the eluent at a flow rate of 1 mL min⁻¹. Detection was performed using a refractive index detector (WATERS 2410). Narrow molecular weight polystyrene (PS) standards were used for calibration.

3. RESULTS AND DISCUSSION

To explore the possibility of ion binding studies, magnetite-based water-soluble polymers were synthesized via SET-LRP. The polymerization was carried out successfully without the addition of a sacrificial initiator. The structure of the magnetite initiator and the process of polymerization are shown in Scheme 1.

3.1. FTIR Analysis. The introduction of the bromide moiety on the iron oxide surface and the polymer formation was verified by FTIR spectroscopy. The FTIR spectra of the iron oxide and its related polymers are shown in Figure 1. The FTIR spectra of the initiator-immobilized magnetite nanoparticles (Fe₃O₄–CA–Br) and magnetite polymers (magnetite-based P(DMAEMA) (A, C) and magnetite-based P(AAm) (B, D)).

Figure 1. FTIR spectra of the initiator-immobilized magnetite nanoparticles (Fe₃O₄–CA–Br) and magnetite polymers (magnetite-based P(DMAEMA) (A, C) and magnetite-based P(AAm) (B, D)).
N–H stretching of the amide group. The absence of an absorption peak around 2000 cm\(^{-1}\) for C==C is the proof that polymerization has occurred. In addition, the presence of peaks around 1100 and 543 cm\(^{-1}\) corresponds to the characteristic pattern of the iron oxide. The spectra of magnetite-based P(DMAEMA) are shown in Figure 1D. The intense bands at 1723 and 1144 cm\(^{-1}\) are attributed to the presence of carbonyl and C–N stretching of the polymer. In addition, the peaks at 2941, 1454, 2819, and 2767 cm\(^{-1}\) are assigned to the C–H stretching, C–H bending, and –N(CH\(_3\))\(_2\)\(\cdot\) Likewise, in P(AAm), the absence of peak around 2000 cm\(^{-1}\) confirms the complete formation of P(DMAEMA).

### 3.2. Thermal Analysis

Thermogravimetric analysis (TGA) of the magnetic nanoparticles, initiator-immobilized magnetite nanoparticles (Fe\(_3\)O\(_4\)--CA--Br), and magnetite polymers (magnetite-based P(DMAEMA) and magnetite-based P(AAm)) was carried out from room temperature to 650 °C, and the results are presented in Figure 2. Through TGA measurements, it was able to determine the amount of polymer on the surface of the iron oxide. In Figure 2a, the curve for iron oxide shows a 6% weight loss around 160 °C, which is due to the loss of adsorbed water. The bromine end-functionalized magnetite initiator (Fe\(_3\)O\(_4\)--CA--Br) exhibits a total weight loss of 25%, which may be attributed to the loss of adsorbed water and the monolayer of bile acid and bromide molecules adsorbed on the surface of the nanoparticle (Figure 2b).

The curve for the P(AAm)-grafted magnetic nanoparticles exhibits two main weight loss regions and one minor region (Figure 2c). The first minor weight loss region around 160 °C can be assigned to the loss of adsorbed water, atmospheric CO\(_2\), and the residual monomer, whereas the major weight loss around 260 °C can be attributed to the decomposition of the initiator moiety on the surface of magnetite. The significant weight reduction in the third region is observed around 355 °C, which is mainly attributed to the sharp decomposition of polymer chains in magnetic P(AAm), producing a total weight loss of 70%. After 500 °C, it does not show any weight loss, which directly confirms the thermal stability of the magnetite-encapsulated P(AAm). P(DMAEMA) appears to have two major and one minor degradation stages, as shown in Figure 2d. This polymer shows a minor degradation near 130 °C that continues to 188 °C, which may be due to the loss of adsorbed water, atmospheric CO\(_2\), and the residual monomer. The bromine functionality from the initiator also decomposes in this temperature region, resulting in a weight loss of 20%. The second major degradation step between 245 and 310 °C with a weight loss of 35% is attributed to the loss of the dimethylaminoethyl groups from P(DMAEMA), while the weight loss around 372–423 °C is associated with the third major degradation stage leading to a weight loss of 25% due to the elimination of CO\(_2\) and CO groups and to the carbonization processes. In the absence of polymer encapsulation, the weight loss is less than 30% (Figure 2d), which is attributed to the desorption of the initiator from the surface. The weight loss from polymer-stabilized particles is much more substantial, ranging from 70%, depending on the polymer molecular weights and the nanoparticle sizes. It is possible to correlate the weight loss with the number of chains per particle and thus determine the grafting density.\(^{48,49}\)

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grafting\ density = \frac{W_{60–650^\circ C} - W_{650} – 60^\circ C}{100 - W_{650–660^\circ C}} \times 100 - \frac{W_{magnetite}}{M \times S \times 100} \times 10^6 [\text{mol m}^{-2}] \tag{1}\]

Here, \(W_{60–650^\circ C}\) is the weight loss between 60 and 650 °C, corresponding to the decomposition of immobilized molecules on magnetic nanoparticles (MNs), \(W_{magnetite}\) is the weight loss of MNs before grafting, \(M\) is the molar mass of the immobilized molecules on magnetite, and \(S\) is the surface area of MNs as measured using the Brunauer–Emmett–Teller (BET) adsorption.\(^{50}\) The grafting density, \(d\), of the immobilized initiator molecules on the iron oxide surface was calculated using eq 1 from the thermogravimetric analysis. It was found to be 1.91 molecules nm\(^{-2}\). The grafting density as calculated from the TGA data was found to be a nearly constant value of 0.86 molecules nm\(^{-2}\). Such a constant grafting density was observed for repeated polymerization processes and it correlates well with other literature reports, e.g., the polymerization of methyl methacrylate from silica nanoparticles at 70 °C.\(^{51}\) The grafting density is nearly 2:1, as expected from the initiator graft density, which might be due to the insufficient dispersion of the particles, resulting in nonparticipation of some of the magnetite in the polymerization. It may also be due to the fact that more radical–radical coupling followed by subsequent termination is likely to occur under surface polymerization conditions, which might be due to the proximity of the propagating chain ends to each other.

### 3.3. NMR Measurement for the Polymers

The \(^1\)H and \(^13\)C NMR spectra of all of the polymer samples were recorded in methanol-d\(_4\) and D\(_2\)O, as shown in Figure 3. The spectrum (Figure 3b) for P(DMEMA) shows five prominent \(^1\)H NMR peaks at 0.8, 1.9, 4.1, 2.3, and 2.5 ppm, which were expected as a result of the repeating monomer integrating to three and two protons, respectively. These peaks correspond to (1) the protons from the methyl group of the polymer backbone in dimethylaminoethyl methacrylate; (2) the methylene protons that are a part of the backbone in the polymers; (3) the ethoxy protons next to the carboxyl group of the dimethylaminoethyl methacrylate; and (4) the methyl and methylene protons attached directly to the nitrogen of the amine group. Similarly, in the case of P(AAm) (Figure 3a), the spectra show three prominent peaks at 1.5 and 2.2 ppm, which are expected as a result of the repeating monomer integrating to two and one protons, respectively. These peaks correspond to (1) the protons from the methylene group that is a part of the backbone in the polymers, (2) the methine group proton of the polymer backbone in acrylamide, and (3) the protons from...
the primary amine directly attached to the carbonyl group of the amide, which are usually exchangeable protons and are not counted. Assignments of the ethoxy, methylene, and methyl protons on the backbone were made easier by comparing the spectra of the monomers and the polymers. In comparison to monomers, all polymer chemical shifts were slightly shifted upfield regardless of the NMR solvent. The shifts are associated with the relative expected values for the different types of protons. The vinyl proton signals disappeared in the corresponding polymer, due to its conversion to the methylene types of protons. The vinyl proton signals disappeared in the monomers in a controlled manner.

3.4. XRD Measurements. The XRD patterns of initiator-immobilized magnetite nanoparticles (Fe₃O₄–CA–Br) and magnetite polymers (magnetite-based P(DMAEMA) and magnetite-based P(AAm)) are depicted in Figure 4. The figure exhibits six characteristic peaks at 2θ values of 30.16, 35.52, 43.14, 53.56, 57.10, and 62.66 caused by the (220), (311), (400), (422), (511), and (440) phases (JCPDS No. 89-3854), indicating the face-centered cubic structure of iron oxide. This also indicates that Fe₃O₄ is coated with organic polymers and the bile-acid-based bromide initiator, without destroying its spinal structure. Furthermore, new peaks at 2θ < 26 in magnetite polymers, which display high intensity, are possibly due to the amorphous organic polymers.

3.5. Surface-Initiated SET-LR Polymerization of Hydrophilic Monomers. To explore the efficacy of the magnetite initiator and the possibility of controlled grafting of P(DMAEMA) and P(AAm) on the surface of iron oxide, mediated by SET-LRP, an iron oxide–CA–bromide-functionalized initiator was utilized without any free initiators. The detailed synthetic procedure regarding the polymerization is described in the Experimental Section. SET-LRP offers a unique method for the rapid synthesis of well-defined controlled polymers under very mild conditions. This polymerization proceeds by an outer-sphere SET mechanism, in which Cu(0) species act as electron donors, whereas the dormant initiator and propagating R–X species act as electron acceptors. The Cu(I) species generated during the formation of radicals spontaneously disproportionate into extremely reactive nascent atomic Cu(0) and Cu(II)X₂/L species that mediate the initiation and the reversible termination.

The optimization for the polymerization of DMAEMA and AAm was investigated through SET-LRP, as shown in Table 1, which was performed under solution conditions at ambient and moderate temperatures. The initiator-immobilized magnetite nanoparticle (Fe₃O₄–CA–Br) undergoes dispersion in solution without the use of any free initiator, and hence, it mediates the polymerization at a moderate rate as evidenced by the experimental data with a narrow polydispersity index. The obtained results demonstrate that the initiator offers a unique and reasonably controlled way to synthesize the magnetite polymer nanocomposite without the use of a free initiator. Under the SET-LRP conditions, the polymerization of hydrophilic monomers using initiator-immobilized magnetite nanoparticles (Fe₃O₄–CA–Br) results in moderate conversion in the presence of a Cu(0)/PMDETA catalyst.
system. The monomer DMAEMA undergoes 67.0% conversion in 4 h at ambient temperature for a lower degree of polymerization producing a polymer with a PDI value of 1.3 (entry 2). The same polymerization when performed in the presence of tris-(2-aminoethyl)amine (TREN) or Me₆TREN produces different results. In the presence of TREN, it produces lower conversion with a higher PDI even at a higher temperature (entry 4). However, in the case of Me₆TREN, it produces higher conversion with a lower PDI even at a higher Dp (entry 1). Among the ligands, Me₆TREN produces a faster rate of polymerization in comparison with PMDETA due to the higher catalytic activity of the Cu(I)-Me₆TREN complex. However, the agreement between the theoretical and expected molecular weight is poorer in Me₆TREN compared to that in PMDETA. Similarly, in the case of AAm, it undergoes 85% conversion in 60 min at ambient temperature (entry 6). Both Me₆TREN and PMDETA work better for the polymerization producing a polymer with a PDI value of 1.33.

| sl. no. | monomer | Dp  | Cu(0)/Lig | ligand | DMSO (mL) | time (h) | temp. | % conv. | \(M_n\) (GPC) | \(M_n\) (GPC) | PDI |
|--------|---------|-----|-----------|--------|-----------|----------|-------|---------|--------------|--------------|-----|
| 1      | DMAEMA  | 500 | 1:1       | Me₆TREN| 0.5       | 4        | 45    | 46.0    | 36 100      | 42 000       | 1.31|
| 2      | DMAEMA  | 100 | 0.5:0.5   | PMDETA | 0.5       | 4        | 27    | 67.0    | 10 500      | 14 000       | 1.3 |
| 3      | DMAEMA  | 200 | 1:1       | PMDETA | 0.5       | 5        | 27    | 46.0    | 14 400      | 19 500       | 1.34|
| 4      | DMAEMA  | 300 | 0.5:0.5   | TREN   | 1.0       | 2        | 70    | 18.0    | 84 000      | 16 000       | 1.6 |
| 5      | AAm     | 500 | 0.5:0.5   | PMDETA | 0.5       | 4        | 27    | 22.0    | 17 300      | 19 000       | 1.4 |
| 6      | AAm     | 200 | 0.5:0.5   | PMDETA | 0.5       | 1        | 45    | 85.0    | 12 000      | 18 000       | 1.42|
| 7      | AAm     | 200 | 0.5:0.5   | Me₆TREN| 0.5       | 1.5      | 27    | 63.0    | 89 000      | 12 000       | 1.33|
| 8      | AAm     | 100 | 0.5:0.5   | PMDETA | 0.5       | 1        | 27    | 64.6    | 46 000      | 85 000       | 1.4 |
| 9      | AAm     | 200 | 1:1       | PMDETA | 1.5       | 2        | 27    | 62.0    | 88 000      | 11 500       | 1.3 |

Figure 5. Molecular weight vs % conversion and PDI for magnetite-based polymers [magnetite-based P(AAm) (A, C) and magnetite-based P(DMAEMA) (B, D)].
tetrabutylammonium fluoride, tetrabutylammonium chloride, and mercuric chloride, as shown in Figures 8 and 9. The binding interaction shows similar absorption bands but with a shift in absorption regions, and also there is an increase or decrease in peak positions. In the case of P(AAm), binding interactions of all ions show a similar pattern with regard to the polymer, except for mercury, which shows a shift to the blue region due to binding interactions. While monitoring the binding interactions, a hyperchromism effect is observed for most of the ions, especially for nitrate and mercury, which shows the increase in the intensity of absorption compared to the bare polymer moiety. Similarly, in the case of P(DMAEMA), binding interactions with chloride, fluoride, and cyanide show a similar pattern to that of the polymer, but
with nitrate and mercury, the shift is different. In the case of nitrate, a red shift is observed, whereas in the case of mercury, it shows a blue shift with regard to the polymer. In both polymers, enhanced binding efficiency is observed for the mercury ion. However, the interaction with P(DMAEMA) is more significant, implying that the tertiary amine has a more pronounced tendency to interact with mercury compared to the primary amine.

4. CONCLUSIONS

A magnetite-based initiator was successfully synthesized by reacting with iron oxide, bile acid, and 2-bromo-2-methylpropionic acid in a one-pot synthesis under mild conditions, and it was conveniently used as an initiator for SET-LRP to synthesize hydrophilic polymers, namely, magnetite-based P(DMAEMA) and magnetite-based P(AAm). The living nature of the grafted polymer was monitored by means of kinetic measurements with the plot of molecular weight vs. monomer conversion. Both the polymers produce lower and almost constant PDI values, which may be attributed to a less competitive termination. However, at higher conversion, PDI values around 1.4 were due to the increased steric hindrance of the polymers on the surface of magnetic particles, but the polymers still possessed living nature with minimal termination. The grafting density, as calculated from the TGA data, was found to be a nearly constant value of 0.86 molecules/nm². The advantages of Fe₃O₄ grafted with polymer chains may be potentially used to detect metal ions and anions present in wastewater. The absorption measurement studies reveal an enhanced binding efficiency for mercury ions, especially in magnetite-based P(DMAEMA), which implies that the tertiary amine present in P(DMAEMA) has a more pronounced tendency to interact with mercury compared to the primary amine present in P(AAm).

Figure 9. UV−Vis measurements for the interactions of poly(AAm) [10⁻⁴ M] in water with different ions at a concentration of 10⁻⁵ mol L⁻¹ [(A) cyanide, (B) chloride, (C) mercury, (D) fluoride, and (E) nitrate].

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Notes
The authors declare no competing financial interest.

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