Crosslinked sulfonated polyacrylamide (Cross-PAA-SO_3H) tethered to nano-Fe_3O_4 as a superior catalyst for the synthesis of 1,3-thiazoles

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Abstract
Crosslinked sulfonated polyacrylamide (Cross-PAA-SO_3H) attached to nano-Fe_3O_4 as a superior catalyst has been used for the synthesis of 3-alkyl-4-phenyl-1,3-thiazole-2(3H)-thione derivatives through a three-component reactions of phenacyl bromide or 4-methoxyphenacyl bromide, carbon disulfide and primary amine under reflux condition in ethanol. A proper, atom-economic, straightforward one-pot multicomponent synthetic route for the synthesis of 1,3-thiazoles in good yields has been devised using crosslinked sulfonated polyacrylamide (Cross-PAA-SO_3H) tethered to nano-Fe_3O_4. The catalyst has been characterized by Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), dynamic light scattering (DLS), X-ray powder diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA) and vibrating-sample magnetometer (VSM).

Keywords: Polyacrylamide, Thiazole, Nanocatalyst, Nano-Fe_3O_4

Introduction
1,3-thiazoles show anticancer [1], antimicrobial [2], anti-inflammatory [3], and anti-candida properties [4]. The synthesis of 1,3-thiazole derivatives have been developed in the presence of different catalysts including DBU [5], HClO_4-SiO_2 [6], Bi(SCH_2COOH)_3 [7], [Et_3NH][HSO_4] [8], Ytterbium(III) Triflate [9] 2-pyridinecarboxaldehyde oxime [10] and potassium iodide [11]. The synthetic strategies of 1,3-thiazole derivatives were recently reviewed [12]. Despite the use of these ways, there remains a need for further new procedures for the preparation of 1,3-thiazoles. The modifying crosslinked polyacrylamides make them attractive objects in chemistry and polymer science [13–15]. Sulfonated polyacrylamides have unique characteristics such as high strength, hydrophilicity, and proton conductivity [16, 17]. Recently, magnetic nanoparticles (MNPs) have been successfully utilized to immobilize enzymes, polymers, transition metal catalysts and organocatalysts [18, 19]. Different stabilizers-electrostatic (surfactants), [20] or steric (polymers) [21–23] have been proposed to overcome the aggregation of magnetite (Fe_3O_4). In the current study, we investigated an easy and rapid method for the synthesis of thiazole-2(3H)-thione through three-component reactions of phenacyl bromide or 4-methoxyphenacyl bromide, carbon disulfide and primary amine using crosslinked sulfonated polyacrylamide (Cross-PAA-SO_3H) attached to nano-Fe_3O_4, as an efficient catalyst under reflux condition in ethanol (Scheme 1). A schematic representation of the catalyst is provided in Scheme 2.

Results and discussion
Characterization of the nanocatalyst
In this study, we synthesized the crosslinked sulfonated polyacrylamide (Cross-PAA-SO_3H) with simultaneous radical co-polymerization in presence of initiator and crosslinking agent. The FT-IR absorbance spectra of the dried crosslinked sulfonated polyacrylamide (poly AAM-co-AAMPS), Fe_3O_4 and Cross-PAA-SO_3H@nano-Fe_3O_4...
are shown in Fig. 1 (AAM is abbreviation acrylamide; AAMPS is abbreviation 2-acryl amido-2-methylpropane-sulfonic acid).

The peaks at 3100–3500 cm$^{-1}$ are related to O–H (sulfonic acid group) and N–H (amide groups) in AAM and AAMPS. The strong band in the 1654 cm$^{-1}$ can be ascribed to the stretching vibrations of carbonyl groups in both AAM and AAMPS. The sharp peak at 1040 cm$^{-1}$ is related to sulfonic acid (–SO$_3$H) group. The bands at 700–800 cm$^{-1}$ and 1540 cm$^{-1}$ are related to the bending vibration of the N–H bond (primary and secondary amide respectively). Table 1 gives the main characteristic peak assignment of the FT-IR spectra. Meanwhile, a schematic illustration of the reaction is presented in the Scheme 3. The results in Fig. 1c suggest the integration of Fe$_3$O$_4$ NPs and Cross-PAA-SO$_3$H. The carbon nuclear magnetic resonance ($^{13}$C NMR) of Cross-PAA-SO$_3$H is displayed in Fig. 2. The peaks at 63.16 (CH$_2$SO$_3$H), 46.83 (CHCONH$_2$), 37.36 (CNHMe$_2$), 34.23 (–CCH$_2$CO), 29.15 (CH$_3$), 22.91, 22.16 ppm (2 CH$_3$), 18.14 (CH$_2$CHCONH$_2$) are shown in Fig. 2. The $^{13}$C NMR spectrum of the Cross-PAA-SO$_3$H in DMSO-$d_6$ displayed two peaks at 176.36 and 173.89 ppm due to amide groups.

The morphology of Cross-PAA-SO$_3$H@nano-Fe$_3$O$_4$ was determined by Scanning Electronic Microscopy (SEM). It is observed that the particles are strongly aggregated and glued with very large and continuous aggregates (Fig. 3). In order to investigate the size distribution of nanocatalysts [24, 25], dynamic light scattering (DLS) measurements of the nanoparticles were showed in Fig. 4. The size distribution is centered at a value of 52.4 nm. The dispersion for DLS analysis (2.5 g
nanocatalyst at 50 mL ethanol) was prepared using an ultrasonic bath (60 W) for 30 min.

XRD patterns of Cross-PAA-SO₃H, Fe₃O₄ and Cross-PAA-SO₃H@nano-Fe₃O₄ are shown in Fig. 5. The patterns for Cross-PAA-SO₃H indicate a peak at 2θ = 28° which is the most intense peak height (Fig. 5a). All the strong peaks appeared at 2θ = 30.08°, 35.40°, 43.17°, 53.59°, 57.20°, 62.86°, and 74.02° can be easily indexed to nano-Fe₃O₄ (Fig. 5b). The pattern agrees well with the reported pattern for Fe₃O₄ (JCPDS No. 75-1609). The particle size diameter (D) of the nanoparticles has been calculated by the Debye–Scherrer equation ($D = K\lambda/\beta \cos \theta$), where $\beta$ FWHM (full-width at half-maximum or half-width) is in radian and $\theta$ is the position of the maximum of the diffraction peak. $K$ is the so-called shape factor, which usually takes a value of about 0.9, and $\lambda$ is the X-ray wavelength (1.5406 Å for CuKa). The crystallite size of Cross-PAA-SO₃H@nano-Fe₃O₄ was calculated by the Debye–Scherer equation is about 48–52 nm. The weaker diffraction lines of Cross-PAA-SO₃H@nano-Fe₃O₄ (Fig. 5c) compared with Fe₃O₄ nanoparticles indicate that the Fe₃O₄ nanoparticles were covered by amorphous polymer.

An EDS (energy dispersive X-ray) spectrum of Cross-PAA-SO₃H@nano-Fe₃O₄ (Fig. 6) exhibits that the elemental compositions are carbon, oxygen, sulfur, iron and nitrogen.

The magnetic attributes of nano-Fe₃O₄ and Cross-PAA-SO₃H@nano-Fe₃O₄ were given with the help of a vibrating sample magnetometer (VSM) (Fig. 7). The amount of saturation-magnetization for nano-Fe₃O₄ and Cross-PAA-SO₃H@nano-Fe₃O₄ is 47.2 emu/g and 26.8 emu/g.

Thermogravimetric analysis (TGA) evaluates the thermal stability of the Cross-PAA-SO₃H and Cross-PAA-SO₃H@nano-Fe₃O₄. The curve displays a weight loss about 37.5% for Cross-PAA-SO₃H@nano-Fe₃O₄ from 240 to 550 °C, resulting from the destruction of organic spacer attaching to the nanoparticles. Hence; the nanocatalyst was stable up to 240 °C, confirming that it could be stably utilized in organic reactions at temperatures between the ranges of 80–160 °C (Fig. 8).

Catalytic behaviors of Cross-PAA-SO₃H@nano-Fe₃O₄ for the synthesis of 1,3-thiazoles

Initially, we had optimized conditions for the synthesis of 3-alkyl-4-phenyl-1,3-thiazole-2(3H)-thione derivatives by the reaction of phenacyl bromide, carbon disulfide and benzyl amine as a model reaction. The model reactions were performed by CAN, NaHSO₄, InCl₃, ZrO₂, p-TSA, nano-Fe₃O₄, Cross-PAA-SO₃H and Cross-PAA-SO₃H@nano-Fe₃O₄. The reactions were tested using diverse solvents including ethanol, acetonitrile, water or dimethylformamide. The best results were gained in EtOH and we found that the reaction gave convincing results in the presence of cross-PAA-SO₃H@nano-Fe₃O₄ (7 mg) under reflux conditions (Tables 2). However, the activity of catalysts is determined by the acid–base properties, surface area, the distribution of sites and the polarity of the surface sites [26, 27]. We studied the feasibility of the reaction by selecting some representative substrates (Table 3). To investigate the extent this catalytic process, phenacyl bromide or 4-methoxyphenacyl bromide, carbon disulfide and primary amine were elected as substrates. Seeking of the reaction scope demonstrated that various primary amines can be utilized in this method (Table 3).

Scheme 4 displays a proposed mechanism for this reaction in the presence of cross-PAA-SO₃H@nano-Fe₃O₄ as catalyst. Initially, the nucleophilic attack by amines on the carbon disulfide generates intermediate (I). The next step involves nucleophilic attack of intermediate (I) on the methylene carbon of phenacyl bromide, leading to intermediate (II), and then ring closure by intramolecular attack of nitrogen at the carbonyl carbon to afford the 3-alkyl-4-phenyl-1,3-thiazole-2(3H)-thione derivatives 4. In this mechanism the surface atoms of cross-PAA-SO₃H@nano-Fe₃O₄ activate the C=S and C=O groups for better reaction with nucleophiles.
The reusability of Cross-PAA-SO$_3$H@nano-Fe$_3$O$_4$ was studied for the reaction of phenacyl bromide, carbon disulfide and benzyl amine and it was found that product yields reduced to a small extent on each reuse (run 1, 94%; run 2, 94%; run 3, 93%; run 4, 93%; run 5, 92%; run 6, 92%). After completion of the reaction, the
The catalyst was washed four times with ethanol and dried at room temperature for 18 h. The possibility of recycling of the catalyst is an important process from different aspects such as environmental concerns, and commercial applicable processes.

To study the applicability of this method in larger scale synthesis, we performed selected reactions at 10 mmol scale. As can be seen, the reactions at large scale gave the product with a gradual decreasing of reaction yield (Table 4).

To compare the efficiency of Nano Fe₃O₄@PAA-SO₃H with the reported catalysts for the synthesis of 1,3-thiazoles, we have tabulated the results in Table 5. As Table 5 indicates, nano Fe₃O₄@PAA-SO₃H is superior with respect to the reported catalysts in terms of reaction time, yield and conditions. As expected, the increased surface area due to small particle size increased reactivity of catalyst. This factor is responsible for the accessibility of the substrate molecules on the catalyst surface.

nanocatalyst was separated by an external magnet. The catalyst was washed four times with ethanol and dried at room temperature for 18 h. The possibility of recycling of the catalyst is an important process from
Conclusions
In conclusion, we have reported an efficient way for the synthesis of 3-alkyl-4-phenyl-1,3-thiazole-2(3H)-thione derivatives using cross-PAA-SO$_3$H@nano-Fe$_3$O$_4$ under reflux condition in ethanol. The method offers several advantages including easy availability, high yields, shorter reaction times, reusability of the catalyst and low catalyst loading. The present catalytic procedure is extensible to a wide diversity of substrates for the synthesis of a variety-oriented library of thiazoles.

Experimental section
Chemicals and apparatus
NMR spectra were obtained on a Bruker spectrometer with CDCl$_3$ as solvent and TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) are given in Hz. FT-IR spectra were recorded with KBr pellets by a Magna-IR, spectrometer 550 Nicolet. CHN compositions were measured by Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X’pert Company with monochromatized Cu Kα radiation (λ = 1.5406 Å). Microscopic morphology of products was visualized by SEM (MIRA3). The thermogravimetric analysis (TGA) curves are recorded using a V5.1A DUPONT 2000. The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of
70 eV. The magnetic property of magnetite nanoparticle has been measured with a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co.; Kashan Kavir; Iran) at room temperature.

**Preparation of crosslinked sulfonated polyacrylamide (Cross-PAA-SO<sub>3</sub>H)**

In a round-bottom flask (200 mL) equipped with magnetic stirrer and condenser, 5 g of acrylamide (AAM) (70 mmol) and 5.17 g of 2-acrylamido-2-methylpropanesulfonic acid (25 mmol) (AAMPS), [approximately AAM/AAMMPS (3/1)] and 0.77 g of N,N-methylene-bis-acrylamide (NMMBA) (5 mmol) as crosslinking agent and benzoyl peroxide as initiator were added to 80 mL EtOH under reflux condition for 5 h. After completion of reaction, the white precipitate was formed, filtered, washed and dried in vacuum oven in 70 °C for 12 h. The weight of polymer was 10.1 gr with the yield of 91.8%. Cross-PAA-SO<sub>3</sub>H was characterized with infrared spectroscopy and back titration acid–base to confirm sulfonation and determine accurate sulfonation levels. Acidic capacity of this catalyst was estimated 1.1 mmol/g.

**Preparation of crosslinked sulfonated polyacrylamide@nano-Fe<sub>3</sub>O<sub>4</sub>**

1 gr of synthesized polymers were poured in 100 mL round bottom flask under stirring at room-temperature, then 50 mL HCl (0.4 M) was added to it. Our target molecules was synthesized by magnetic nanocatalyst with mass ratio polymer/nano-Fe<sub>3</sub>O<sub>4</sub> = 2/1. So, 0.43 g (2.1 mol) FeCl<sub>2</sub>·4H<sub>2</sub>O and 1.17 g (2 × 2.1) FeCl<sub>3</sub>·6 H<sub>2</sub>O were added and the mixture was stirred until dissolved completely (flask1). In another 500 ml round-bottom flask no 2, 400 mL aqueous solution of NH<sub>3</sub> (0.7 M) was poured under argon gas. Then flask 1 was added to flask 2 immediately. Nanocatalyst was filtered and washed with water (2 × 25 mL) and dried in oven on 50 °C.

**General procedure for the synthesis of 1,3-thiazoles**

A mixture of primary amine (1.0 mmol) and carbon disulfide (1 mmol) in ethanol (8 mL) was stirred for 5 min and then phenacyl bromide or 4-methoxyphenacyl bromide (1.0 mmol) and Cross-PAA-SO<sub>3</sub>H attached to nano-Fe<sub>3</sub>O<sub>4</sub> (7 mg) were added, and the mixture was stirred for the appropriate times. The reaction was monitored by TLC (n-hexane/ethyl acetate 8:2). After completion of the reaction, the nanocatalyst was easily separated using an external magnet. The solvent was evaporated and the solid obtained washed with EtOH to get pure product. The characterization data of the compounds are given below and in Additional file 1.

**Table 2 Optimization of reaction conditions**

| Entry | Solvent (reflux) | Catalyst | Time (min) | Yield (%)<sup>a</sup> |
|-------|------------------|----------|------------|-----------------------|
| 1     | EOH              | –        | 500        | 39                    |
| 2     | EOH              | CAN (7 mol%) | 250        | 53                    |
| 3     | EOH              | NaH<sub>2</sub>SO<sub>4</sub> (5 mol%) | 300        | 45                    |
| 4     | EOH              | InCl<sub>3</sub> (4 mol%) | 200        | 56                    |
| 5     | EOH              | ZrO<sub>2</sub> (6 mol%) | 250        | 60                    |
| 6     | EOH              | p-TSA (3 mol%) | 200        | 64                    |
| 7     | EOH              | Nano-Fe<sub>3</sub>O<sub>4</sub> (10 mg) | 200        | 52                    |
| 8     | EOH              | Cross-PAA-SO<sub>3</sub>H (10 mg) | 150        | 56                    |
| 9     | EOH              | nano-Fe<sub>3</sub>O<sub>4</sub> (5 mg) + Cross-PAA-SO<sub>3</sub>H (5 mg) | 150        | 60                    |
| 10    | H<sub>2</sub>O   | Cross-PAA-SO<sub>3</sub>H@nano-Fe<sub>3</sub>O<sub>4</sub> (7 mg) | 150        | 77                    |
| 11    | DMF              | Cross-PAA-SO<sub>3</sub>H@nano-Fe<sub>3</sub>O<sub>4</sub> (7 mg) | 150        | 82                    |
| 12    | CH<sub>3</sub>CN | Cross-PAA-SO<sub>3</sub>H@nano-Fe<sub>3</sub>O<sub>4</sub> (7 mg) | 150        | 89                    |
| 13    | EOH              | Cross-PAA-SO<sub>3</sub>H@nano-Fe<sub>3</sub>O<sub>4</sub> (5 mg) | 150        | 92                    |
| 14    | EOH              | Cross-PAA-SO<sub>3</sub>H@nano-Fe<sub>3</sub>O<sub>4</sub> (7 mg) | 150        | 94                    |
| 15    | EOH              | Cross-PAA-SO<sub>3</sub>H@nano-Fe<sub>3</sub>O<sub>4</sub> (9 mg) | 150        | 94                    |

<sup>a</sup> Isolated yield

Phenacyl bromide (1 mmol), carbon disulfide (1 mmol) and benzyl amine (1 mmol)
47.24, 98.85, 127.06, 128.52, 128.55, 129.08, 133.32, 137.45, 154.85, 178.37, 197.18. MS (EI, 70 eV): m/z (%) = 283 (5), 267 (68), 181 (7), 91 (100), 77 (4), 65 (12), 45 (4). Anal. Calcd. for C16H13NS2 (283): C, 67.81; H, 4.62; N, 4.94. Found: C, 67.70; H, 4.52; N, 4.73%.

3-(3,4-dichlorobenzyl)-4-phenyl-1,3-thiazole-2(3H)-thione (4b) Colorless viscous oil; FT-IR (KBr): $\bar{\nu} = 3152, 3004, 1628, 1603, 1477, 1302, 1104$ cm$^{-1}$. $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 4.83 (s, 2H, CH$_2$), 6.05 (CH of alkene), 6.75–7.97 (m, 8H, CH of ArH). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 46.07, 99.25, 126.72, 128.65, 128.74, 129.35, 129.66, 133.54, 130.50, 135.38, 136.62, 137.21, 172.70, 194.15. Anal. Calcd. for C$_{16}$H$_{12}$Cl$_2$NS$_2$ (350): C, 54.55; H, 3.15; N, 3.98. Found: C, 54.36; H, 3.05; N, 3.84%.

Table 3 Synthesis of thiazoles using Cross-PAA-SO$_3$H@nano-Fe$_3$O$_4$

| Entry | Amine (R-NH$_2$) | ArCOCH$_2$Br | Product | Time (min) | Yield (%)$^a$ |
|-------|-----------------|--------------|---------|------------|--------------|
| 1     | NH$_2$O         | 4b           | 160     | 87         |
| 2     | NH$_2$Cl        | 4b           | 160     | 86         |
| 3     | NH$_2$O         | 4c           | 160     | 86         |
| 4     | O             | 4d           | 155     | 92         |
| 5     | O             | 4e           | 180     | 90         |
| 6     | O             | 4f           | 150     | 94         |
| 7     | O             | 4g           | 185     | 89         |
| 8     | O             | 4h           | 190     | 84         |
| 9     | O             | 4i           | 190     | 82         |
| 10    | O             | 4j           | 180     | 88         |

$^a$ Isolated yield

Table 4 The large-scale synthesis of some 1,3-thiazoles using cross-PAA-SO$_3$H@nano-Fe$_3$O$_4$

| Entry | Product | Time (min) | Yield (%)$^a$ |
|-------|---------|------------|--------------|
| 1     | 4a      | 200        | 90           |
| 2     | 4e      | 200        | 84           |
| 3     | 4g      | 250        | 82           |
| 4     | 4i      | 250        | 75           |
| 5     | 4j      | 250        | 78           |

$^a$ Isolated yield

3-(3,4-dichlorobenzyl)-4-phenyl-1,3-thiazole-2(3H)-thione (4b)

3-(2-Naphthyl methyl)-4-phenyl-1,3-thiazole-2(3H)-thione (4c)

3-(2-Furyl methyl)-4-phenyl-1,3-thiazole-2(3H)-thione (4d)
### Table 5 Comparison of catalytic activity of nano Fe$_3$O$_4$@ PAA-SO$_3$H with other reported catalysts for the synthesis of 1,3-thiazoles

| Entry | Catalyst (condition) | Time (min) | Yield*, % | [Ref] |
|-------|----------------------|------------|-----------|-------|
| 1     | Bi(SCH$_2$COOH)$_3$ (15 mol%, 70 °C) | 180        | 80        | [7]   |
| 2     | Yb(OTf)$_3$ (15 mol%) | 240        | 60        | [9]   |
| 2     | 2- pyridinecarboxaldehyde oxime (20 mol%, DMF) | 400        | 85        | [10]  |
| 3     | potassium iodide (10 mol%, CH$_3$OH) | 400        | 80        | [11]  |
| 4     | Nano Fe$_3$O$_4$@ PAA-SO$_3$H (7 mg, EtOH (under reflux condition)) | 150        | 94        | This work |

* Isolated yield

CDCl$_3$): δ 4.84 (s, 2H, CH$_2$), 6.10 (s, 1H, CH of alkene), 6.22 (1H, CH of furan), 7.25–8.05 (m, 7H, CH of ArH and CH of furan). $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 44.25, 98.32, 109.52, 110.83, 128.76, 129.58, 142.12, 144.54, 147.92, 155.44, 192.18. Anal. Calcd. for C$_{17}$H$_{15}$NOS$_2$ (313): C, 65.14; H, 4.82; N, 4.47. Found: C, 65.03; H, 4.74; N, 4.35%.

3-(2-Methoxybenzyl)-4-phenyl-1,3-thiazole-2(3H)-thione (4h) Colorless viscous oil; FT-IR (KBr): ν = 3157, 3012, 1645, 1616, 1478, 1209, 1107 cm$^{-1}$. $^{1}$H NMR (250 MHz, CDCl$_3$): δ 3.89 (s, 3H, OCH$_3$), 5.25 (s, 2H, CH$_2$), 6.28 (s, 1H, CH of alkene), 6.85–7.39 (m, 9H, CH of ArH). $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 48.50, 55.37, 99.86, 110.55, 114.54, 122.54, 128.38, 129.54, 132.86, 137.54, 145.68, 160.85, 185.36. MS (EI, 70 eV): m/z (%) = 313 (M). Anal. Calcd. for C$_{17}$H$_{13}$NO$_2$S$_2$ (313): C, 65.14; H, 4.82; N, 4.47. Found: C, 65.02; H, 4.56; N, 4.34; %.

3-(2-Methylbenzyl)-4-(4-methoxyphenyl)-1,3-thiazole-2(3H)-thione (4i) Colorless viscous oil; FT-IR (KBr): ν = 3144, 3012, 1665, 1618, 1478, 1209, 1112 cm$^{-1}$. $^{1}$H NMR (250 MHz, CDCl$_3$): δ 3.88 (s, 2H, CH$_2$), 4.82 (s, 2H, CH$_2$), 5.98 (2H, CH of furan), 6.20 (s, 1H, CH of alkene), 6.75–7.42 (m, 5H, CH of furan and CH of ArH). $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 41.35, 55.34, 98.36, 108.35, 110.35, 118.35, 122.54, 130.22, 138.54, 142.53, 150.65, 161.25, 178.25. Anal. Calcd. for C$_{18}$H$_{17}$NO$_2$S$_2$ (303): C, 59.38; H, 4.32; N, 4.62; Found: C, 59.15; H, 4.14; N, 4.42; %.

3-(2-Methoxybenzyl)-4-(4-methoxyphenyl)-1,3-thiazole-2(3H)-thione (4j) Colorless viscous oil; FT-IR (KBr): ν = 3142, 3010, 1654, 1583, 1209, 1102 cm$^{-1}$. $^{1}$H NMR (250 MHz, CDCl$_3$): δ 2.23 (s, 3H, CH$_3$), 3.86 (s, 3H, OCH$_3$), 4.95 (s, 2H, CH$_2$), 5.98 (s, 1H, CH of alkene), 6.82–7.35 (m, 8H, CH of ArH). $^{13}$C NMR (62.5 MHz, CDCl$_3$): δ 21.35, 48.54, 55.95, 98.68, 115.38, 123.42, 125.64, 130.65, 131.25, 139.25, 160.20, 174.25, 183.56. Anal. Calcd. for C$_{18}$H$_{17}$NO$_2$S$_2$ (327): C, 66.02; H, 5.23; N, 4.28; Found: C, 65.90; H, 5.14; N, 4.12%.

### Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s13065-019-0637-0.

Additional file 1. The spectral data of products are described in the additional file 1.
Abbraviations
Cross-PAA-SO₃H: crosslinked sulfonated polyacrylamide; FT-IR: Fourier-transform infrared spectroscopy; SEM: scanning electron microscope; XRD: X-ray powder diffraction; EDS: energy-dispersive X-ray spectroscopy; TGA: thermogravimetric analysis; VSM: vibrating-sample magnetometer; AAM: acrylamide; AAMPS: 2-acrylamido-2-methylpropanesulfonic acid; DLS: dynamic light scattering.

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Associated content
Copies of ¹H-NMR and ¹³C-NMR spectra of all compounds are provided in Additional file 1.

Authors' contributions
HSHA has designed the study, participated in discussing results and revised the manuscript. MT, JSG and GHM have designed, carried out the literature study, performed the assay, conducted the optimization, purification of compounds and prepared the manuscript. All authors read and approved the final manuscript.

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All data generated or analysed during this study are included in this published article [and its additional information files].

Competing interests
The authors declare that they have no competing interests.

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