Magnetite-Containing Sulfonated Polyacrylamide as a Nanocatalyst for the Preparation of Biscoumarins

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Abstract

Magnetite-containing sulfonated polyacrylamide was easily prepared through polymerization of the corresponding monomers followed by the reaction with Fe3O4 nanoparticles. The characterization of the obtained catalyst was performed by Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and vibrating sample magnetometer (VSM). The acidic SO3H moiety was found to be 1.1 mmol per gram of the obtained polymer. The catalytic activity of the polymer was examined for the synthesis of biscoumarin derivatives by two-component one-pot domino Knoevenagel-type condensation/Michael reaction between aldehydes and 4-hydroxycoumarin. Biscoumarins were obtained in high to excellent yields in short time. The work-up procedure of this reaction was very simple. The catalyst is stable (as a bench top catalyst) with easy-handling and it can be used again.

Keywords: Nanoparticles; Radical polymerization; Magnetism and magnetic properties; Catalysts; Biscoumarins

1. Introduction

Due to the unique characteristics of magnetite Fe3O4 nanoparticles, they have attracted great attention in the field of biology, medicine, electronics, and catalytic processes.1 However, Fe3O4 nanoparticles respond to external stimuli such as the pH value and temperature, due to the pH- and temperature-sensitive properties. Also, they are unstable in the presence of oxygen at light and coagulation of nanoparticles is usually unavoidable during their use. Therefore, there has been a considerable research effort to stabilize Fe3O4 nanoparticles through coating the surface of such nanoparticles with carbon, precious metals, silica, and polymers. In this regard, the use of polymers containing a functional group that binds strongly to the nanoparticles through covalent or electrostatic interactions has been the subject of great interest to researchers.2 For this purpose, a variety of polymeric materials, such as poly(glycerol monoacrylate), polyaniline, polyacrylamide, poly(N-vinyl-2-pyrrolidone), poly(para-phenylene-diamine), poly(vinylalcohol), poly(ether-amide), polypyrrole, and chitosan as well as polymers containing polar pendant groups, such as carboxylate, phosphate, or sulfate groups have been used.3–6

Recently, magnetic nanomaterials have emerged as a promising catalysts for various organic and inorganic reactions because of their large surface-to-volume ratio relative to bulk materials and hence the large ratio of atoms available at the surface.2 These types of catalysts can be easily separated using an external magnet and their catalytic activity remains high even after several reaction cycles. Magnetite catalysts were used as efficient catalytic systems in many chemical transformations including asymmetric hydrogenation of aromatic ketones,7 the desymmetrization of racemic 1,2-diols through asymmetric benzylation,8 synthesis of 14-aryl- or alkyl-14H-dibenz[a,j]xanthenes and 1,8-dioxo-octahydroxanthene derivatives,9,10 Sonogashira cross-coupling reaction,11 synthesis of tetrahydrobenzo[a]xanth-11-ones,12 C–N bond formation via aza-Michael addition,6 and preparation of functionalized tricarboxamides derivatives.13
Coumarin and its derivatives are important as anti-HIV, antibiotic, antifungal, antibacterial, antioxidant, anticancer, and anticoagulant agents. Among various derivatives of coumarin, biscoumarins have aroused considerable interest. These important compounds were usually prepared from the reaction of aldehydes with 4-hydroxycoumarin. Several types of catalysts were introduced previously for this reaction, such as piperidine, tetrabutyamine, potassium fluoride, sodium dodecyl sulfate, and sodium glutamate. However, many of these methods have some drawbacks, such as a requirement for either a long reaction time or harsh reaction conditions, provide low yields, include laborious work-up procedures, inefficiency of method when aliphatic aldehydes are used in the reaction, and the use of unrecyclable, hazardous or difficult to handle catalysts.

In continuation of our research on the synthesis and applications of polymer-supported catalysts and nanocomposites, we now wish to introduce poly(2-acrylamido-2-methyl propane sulphonic acid-co-acrylamide) containing Fe3O4 nanoparticles (poly(AMPS-co-AA)@Fe3O4) as a heterogeneous catalyst for the synthesis of biscoumarin derivatives. Poly(AMPS-co-AA)@Fe3O4 was prepared by benzoyl peroxide (Bz2O2) initiated polymerization of 2-acrylamido-2-methyl propane sulphonic acid (AMPS) with acrylamide (AA) followed by reaction with Fe3O4 nanoparticles.

2. Experimental

2.1. Materials and Methods

All chemicals were either prepared in our laboratory or were purchased from Merck and Fluka. Reaction monitoring and purity determination of the products were accomplished by GLC or TLC on silica-gel polygram SILG/UV254 plates. Gas chromatography was carried out on a Shimadzu GC 14-A. IR spectra were obtained by a Shimadzu model 8300 FT-IR spectrophotometer. 1H NMR spectra were recorded on 400 MHz spectrometer in CDCl3. TGA was carried out on a Stanton Redcroft STA–780 with a 20 °C/min heating rate. Melting points were determined on a Fisher–Jones melting-point apparatus. XRD patterns were recorded by a Phillips X-ray diffractometer using graphite monochromatized Cu Kα radiation. A morphological study of the synthesized products was carried out directly by a Hitachi S4160 field emission scanning electron microscope (FESEM).

2.2. Preparation of Fe3O4 Nanoparticles

To a solution of ferrous chloride (FeCl2, 1 M), NaOH (4 M) was added dropwise with vigorous stirring to produce a black solid product (magnetite Fe3O4 nanoparticles) when the reaction media reaches pH 12. The resulting nanoparticles were carefully decanted and washed repeatedly with doubly distilled water and absolute ethanol and then dried under vacuum at room temperature.

2.3. Synthesis of (Poly(AMPS-co-AA)@Fe3O4)

First, in a round bottomed flask (50 mL) equipped with a reflux condenser, 0.051 g (0.214 mmol) of Bz2O2 was added to a solution of acrylamide (15 mmol, 1.066 g), AMPS (6.42 mmol, 1.330 g), and ethanol (25 mL) and the mixture was refluxed for 5 h. Afterwards, Fe3O4 nanoparticles (12 mmol, 2.78 g) were added to the mixture and refluxed for 1 h. Then, the obtained solid was easily separated from the reaction mixture by an external magnet and washed with deionized water and ethanol three times and dried overnight in vacuum at 80 °C.

The same procedure applied for the preparation of poly(AMPS-co-AA)@Fe3O4 was also repeated for the preparation of poly(AMPS-co-AA) without addition of Fe3O4 nanoparticles. In this case, the polymer formed in the first step was collected by filtration, washed three times with ethanol, and dried overnight in vacuum at 60 °C.

2.4. Preparation of 3,3’-(4-Nitrobenzylidene)-bis-(4-hydroxycoumarin) as a Typical Procedure for the Synthesis of Bis-coumarines

A mixture of 1 mmol of 4-nitrobenzaldehyde, 2 mmol of 4-hydroxycoumarin, 0.04 mmol of poly(AMPS-co-AA)@Fe3O4, and 3 mL of toluene was heated at 90 °C. After the completion of the reaction (monitored by TLC), the catalyst was removed by an external magnet and washed with toluene (2 × 5 mL) and the filtrate was concentrated on a rotary evaporator under reduced pressure. The crude product was recrystallized from ethanol to give the pure 3,3’-(4-nitrobenzylidene)-bis-(4-hydroxycoumarin).

3. Results and Discussion

3.1. Synthesis of Poly(AMPS-co-AA)@Fe3O4

Poly(AMPS-co-AA)@Fe3O4 was synthesized by free radical polymerization of AA and AMPS monomers.
in the presence of Bz₂O₂ initiator followed by the reaction with Fe₃O₄ nanoparticles (Scheme 1). The acidic sites loading in poly(AMPS-co-AA)@Fe₃O₄ obtained by means of acid–base titration was found to be 1.1 mmol/g.²⁷,²⁸ For comparison purposes, poly(AMPS-co-AA) was also prepared via the same procedure applied for the preparation of poly(AMPS-co-AA)@Fe₃O₄ without addition of Fe₃O₄.

3. 2. Characterization of Poly (AMPS-co-AA)@Fe₃O₄

Figure 1 shows the FT-IR spectra of Fe₃O₄, poly(AMPS-co-AA), and poly(AMPS-co-AA)@Fe₃O₄. The IR spectral data of Fe₃O₄ show two characteristic peaks at 425 and 567 cm⁻¹, which are due to Fe–O stretching vibrations (Figure 3a).³¹ As shown in Figure 3b, the IR spectrum of poly(AMPS-co-AA) exhibits peaks at 3346 and 3428 cm⁻¹ (N–H vibrations of amide groups), 1663 cm⁻¹ (C=O vibrations of carbonyl groups), and 1208 cm⁻¹ (S=O vibrations of sulfonic groups).²⁷,²⁸ Also, the IR spectrum of poly(AMPS-co-AA)@Fe₃O₄ displayed peaks at 3422, 1658, and 1185 cm⁻¹ which are assigned to stretching vibrations of NH and NH₂, C=O, and S=O, respectively (Figure 3b). In IR spectrum of poly(AMPS-co-AA)@Fe₃O₄ the appearance of peaks at 429 and 574 cm⁻¹, attributed to Fe–O stretching vibrations, indicates that Fe₃O₄ nanoparticles were attached to the polymer chains.

Thermal data obtained from TGA analysis are presented in Figure 2. In TGA curves of Fe₃O₄ and poly(AMPS-co-AA)@Fe₃O₄, a slow mass loss observed between room temperature and 150 °C could be related to the removal of surface adsorbed water, the remaining solvent, and residual monomers. The second step weight loss starting from 180 °C in TGA curve of Fe₃O₄ could be attributed to thermal crystal phase transformations of Fe₃O₄ to Fe₂O₃. In the case of poly(AMPS-co-AA)@Fe₃O₄, the second step weight loss starting from 180 °C could be related to thermal oxidation of Fe₃O₄ and also the decomposition of amide and 2-methylpropane sulphonic acid pendant groups. The last weight losses in TGA curves of poly(AMPS-co-AA)@Fe₃O₄ at about 360 °C was likely due to the degradation of the polymer backbone. Based on the char yield of poly(AMPS-co-AA)@Fe₃O₄ at 800 °C and assuming that the final residues are mainly Fe₃O₄ and

![Scheme 1. Synthetic pathways for poly(AMPS-co-AA) containing Fe₃O₄ nanoparticles.](image)

![Figure 1. FT-IR spectra of Fe₃O₄ (a), poly (AMPS-co-AA) (b), and poly(AMPS-co-AA)@Fe₃O₄ (c).](image)

![Figure 2. TGA curves of Fe₃O₄ (a) and poly(AMPS-co-AA)@Fe₃O₄ (b).](image)
Fe₃O₄, the anchoring amount of Fe₃O₄ in poly(AMPS-co-AA)@Fe₃O₄ is about 20 wt.%. The relatively high char yield of poly(AMPS-co-AA)@Fe₃O₄ also indicates that the incorporation of Fe₃O₄ into the polymer chains imparts significant thermal stability to the resulting poly(AMPS-co-AA)@Fe₃O₄.

Figure 3 shows the SEM images of synthesized samples. Figure 3a indicates that the most of Fe₃O₄ nanoparticles are monodisperse and have a spherical crystal morphology with a diameter range between 40–50 nm. With comparison of SEM micrographs of the magnetic poly(AMPS-co-AA) (Figure 3c) with poly(AMPS-co-AA) (Figure 3b), it can be deduced that the polymer chains clearly loaded on Fe₃O₄ nanoparticles.

EDS analyses of poly(AMPS-co-AA) and poly(AMPS-co-AA)@Fe₃O₄ are shown in Figure 4. EDS of poly(AMPS-co-AA)@Fe₃O₄ shows that there are no impurities in this catalyst and confirms the presence of S and Fe elements (Figure 4b).

Figure 5 shows the XRD patterns of Fe₃O₄ nanoparticles and poly(AMPS-co-AA)@Fe₃O₄. The XRD pattern of Fe₃O₄ nanoparticles (Figure 5a) exhibited the peaks at 2θ = 30.21, 35.52, 43.32, 53.61, 57.09, 62.63, 71.19, and 74.20° that could be assigned to 220, 111, 311, 400, 422, 511, 440, and 442 planes of Fe₃O₄, respectively. Due to
the agreement with the card no. 88-0315, it seems the resultant particles are pure magnetite. The crystal size of the particles was calculated by line broadening from the XRD pattern using the Debye–Scherrer formula and they were estimated to be between 20–25 nm. The weaker diffraction lines of poly(AMPS-co-AA)@Fe₃O₄ (Figure 5b) compared with Fe₃O₄ nanoparticles indicate that the Fe₃O₄ nanoparticles were covered by amorphous polymer.

Magnetic properties of the samples were also studied. Hysteresis loops of Fe₃O₄ nanoparticles and poly(AMPS-co-AA)@Fe₃O₄ are depicted in Figure 6. The Fe₃O₄ nanoparticles exhibited ferromagnetic behavior in saturation magnetization of 63.53 emu/g and a coercivity of 1.76 Oe at room temperature (Figure 6a).

The results showed that the saturation magnetization value of poly(AMPS-co-AA)@Fe₃O₄ (Figure 6b, 48 emu/g) was lower than Fe₃O₄ nanoparticles due to the interaction of polymer and Fe₃O₄ nanoparticles.

3. 3. Catalytic Application of Poly(AMPS-co-AA)@Fe₃O₄ in the Synthesis of Biscoumarins

After synthesis of poly(AMPS-co-AA)@Fe₃O₄ we tried to convert aldehydes to the corresponding biscoumarins in the presence of this catalyst. To optimize the reaction conditions, initially, the condensation reactions of benzaldehyde (1 mmol) with 4-hydroxycoumarin (2 mmol) in the presence of different molar ratios of poly(AMPS-co-AA)@Fe₃O₄ in various solvents and also under solvent free conditions were studied. The results indicate that this reaction goes well in toluene and the product was obtained in excellent yield in the presence of 0.04 mmol of the catalyst at 90 °C. After establishing the optimal conditions, in order to prove the generality of this method, a variety of aromatic aldehydes bearing electron-deficient or electron-rich substituents on the aromatic ring (Table 1, entries 1–7), heteroaromatic aldehydes such as 2-thienyl and 2-furanyl carbaldehyde (entries 8, 9), and aliphatic aldehydes (entries 10–12) reacted with 4-hydroxycoumarin to give the corresponding biscoumarin products in excellent yields. 1H NMR spectrum of the product 3,3’-(4-nitrobenzylidene)-bis-(4-hydroxycoumarin) is shown in Figure 7.
To determine the extent of sulfuric acid groups leaching from poly(AMPS-co-AA)@Fe₃O₄, one test was performed. Poly(AMPS-co-AA)@Fe₃O₄ was added to toluene and the mixture was stirred for 2 h at 90 °C. Then, the catalyst was removed by using magnetic field and the filtrate was analyzed for its acid content, which showed a negligible release of the acidic sites. The filtrate was found to be inactive in the reaction of aldehydes with 4-hydroxycoumarin. Thus, this leaching test suggested that the poly(AMPS-co-AA)@Fe₃O₄ catalyst was a true heterogeneous catalyst without significant acid moieties leaching.

Scheme 2 shows a possible mechanism for the preparation of biscoumarins using poly(AMPS-co-AA)@Fe₃O₄. First, the acidic nature of catalyst may facilitate the enolization step of 4-hydroxycoumarin. Second, nucleophilic addition of 4-hydroxycoumarin to the activated aldehyde followed by loss of H₂O generates intermediate I, which is further activated by poly(AMPS-co-AA)@Fe₃O₄. Then, the 1,4-nucleophilic addition of a second molecule of 4-hydroxycoumarin on the activated intermediate I, in the Michael addition fashion, affords the biscoumarin product. Based on this mechanism, it is clear

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Time (min.)</th>
<th>Yield (%)</th>
<th>M.P. (°C)</th>
<th>Obs.</th>
<th>Lit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzaldehyde</td>
<td>15</td>
<td>97</td>
<td>226–230</td>
<td>230–232²⁰</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4-Methylbenzaldehyde</td>
<td>19</td>
<td>94</td>
<td>263–267</td>
<td>266–268²⁰</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4-Methoxybenzaldehyde</td>
<td>20</td>
<td>96</td>
<td>238–240</td>
<td>242–244⁹⁹</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4-Bromobenzaldehyde</td>
<td>19</td>
<td>96</td>
<td>266–268</td>
<td>265–267²⁰</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4-Hydroxybenzaldehyde</td>
<td>22</td>
<td>95</td>
<td>224–226</td>
<td>222–224⁹⁹</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4-Nitrobenzaldehyde</td>
<td>10</td>
<td>97</td>
<td>227–230</td>
<td>232–234⁹⁹</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3-Nitrobenzaldehyde</td>
<td>10</td>
<td>97</td>
<td>236–239</td>
<td>236–238⁹⁹</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2-Thienyl carbaldehyde</td>
<td>20</td>
<td>96</td>
<td>211–213</td>
<td>210⁹⁹</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2-Furanyl carbaldehyde</td>
<td>21</td>
<td>95</td>
<td>205–207</td>
<td>202⁹⁹</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Cinnamaldehyde</td>
<td>27</td>
<td>94</td>
<td>275–279</td>
<td>279–281²⁸</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>3-Phenylpropionaldehyde</td>
<td>30</td>
<td>94</td>
<td>188–191</td>
<td>190¹⁷</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Butyraldehyde</td>
<td>33</td>
<td>94</td>
<td>121–125</td>
<td>123¹⁷</td>
<td></td>
</tr>
</tbody>
</table>

Isolated yields. All products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples.

**Scheme 2.** Suggested mechanism for the preparation of biscoumarins catalyzed by poly(AMPS-co-AA)@Fe₃O₄.

Cat.: Poly (AMPS-co-AA)@Fe₃O₄
that in the cases of electron withdrawing groups present on the aromatic aldehyde (Table 1, entries 6, 7), the 1,4-nucleophilic addition of a second molecule of 4-hydroxycoumarin on the activated intermediate I is more favored which can finally cause the decrease of reaction time for these types of aldehydes when reacting with 4-hydroxycoumarin.\textsuperscript{27,33} We believe that the catalytic efficiency of poly(AMPS-co-AA)@Fe\textsubscript{3}O\textsubscript{4} may be attributed to the acidic hydrogen (SO\textsubscript{3}H) as well as Lewis acid properties of Fe\textsubscript{3}O\textsubscript{4} nanoparticles.

Very recently, we have introduced carbon nanotube-supported butyl 1-sulfonic acid groups as a heterogeneous catalyst for the synthesis of 1,8-dioxo-octahydroxanthene.\textsuperscript{32} Along this line and based on the above encouraging results, we tried to examine the applicability of poly(AMPS-co-AA)@Fe\textsubscript{3}O\textsubscript{4} for the synthesis of 1,8-dioxo-octahydroxanthenes and 12-aryl-9,9-dimethyl-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Entry & Reaction conditions & Time (min.) & Yield (%) \textsuperscript{a} \\
\hline
1 & Piperidine, EtOH, r.t. & 240 & 92\textsuperscript{17} \\
2 & Tetrabutylammonium bromide, H\textsubscript{2}O, 100 °C & 25 & 92\textsuperscript{18} \\
3 & I\textsubscript{2}, H\textsubscript{2}O, 100 °C & 25 & 97\textsuperscript{19} \\
4 & Sodium dodecyl sulfate, H\textsubscript{2}O, 60 °C & 138 & 90\textsuperscript{20} \\
5 & 1-Buthyl-3-methylimidazolium tetrafluoroborate, 70 °C & 120 & 84\textsuperscript{21} \\
6 & 1-Ethyl-(3-sulfopropyl)-benzimidazolium trifluoromethanesulfonate, 70 °C & 120 & 95\textsuperscript{22} \\
7 & p-Dodecylbenzenesulfonic acid/piperidine, H\textsubscript{2}O, r.t. & 360 & 89\textsuperscript{23} \\
8 & 3-Methyl-1-(4-sulfonic acid)butylimidazolium hydrogen sulfate, 70 °C & 30 & 92\textsuperscript{24} \\
9 & B(HSO\textsubscript{4})\textsubscript{3}, EtOH/H\textsubscript{2}O, 70 °C & 6 & 86\textsuperscript{25} \\
10 & Polyvinyl pyrrolidone-nickel nanoparticles, ethylene glycol, r.t.\textsuperscript{b} & 15 & 93\textsuperscript{26} \\
11 & [Poly(4-vinylpyridine)--BuSO\textsubscript{3}H]Cl-xAlCl\textsubscript{3}, toluene, 90 °C & 36 & 95\textsuperscript{27} \\
12 & [Poly(4-vinylpyridine)--BuSO\textsubscript{3}H]HSO\textsubscript{4}, toluene, 90 °C & 48 & 93\textsuperscript{28} \\
13 & Cellulose sulfonic acid, H\textsubscript{2}O, reflux & 120 & 90\textsuperscript{29} \\
14 & Poly(AMPS-co-AA)@Fe\textsubscript{3}O\textsubscript{4}, toluene, 90 °C & 15 & 97 \\
\hline
\end{tabular}
\caption{Comparison results of poly(AMPS-co-AA)@Fe\textsubscript{3}O\textsubscript{4} with other catalysts reported in the literature in the condensation of benzaldehyde with two equivalents of 4-hydroxycoumarin.}
\end{table}

\textsuperscript{a} Isolated yields. \textsuperscript{b} With 4-nitrobenzaldehyde.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{recyclability.png}
\caption{Recyclability of poly(AMPS-co-AA)@Fe\textsubscript{3}O\textsubscript{4} (0.04 mmol) in the reaction of benzaldehyde (1 mmol) with 4-hydroxycoumarin (2 mmol) in toluene at 90 °C after 15 min.}
\end{figure}

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{xanthene.png}
\caption{Preparation of xanthene derivatives using poly(AMPS-co-AA)@Fe\textsubscript{3}O\textsubscript{4}.}
\end{scheme}

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nes and 12-aryl-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-ones were obtained in high yields in ethanol at room temperature in the presence of 0.05 mmol of poly(AMPS-co-AA)@Fe3O4 (Scheme 3). It is worth noting that, to the best of our knowledge, relatively few examples were reported on the synthesis of xanthene derivatives at room temperature. Usually, these reactions need high temperatures, long time or an additional source of energy (ultrasound or microwave irradiation).34–36

Finally, we investigated the reusability of the poly(AMPS-co-AA)@Fe3O4 catalyst, and it was found that the catalyst could be completely recovered and used again at least six times without any noticeable loss of catalytic activity (Figure 8).

In comparison with selected previously known protocols employed for the synthesis of biscoumarins, poly(AMPS-co-AA)@Fe3O4 showed that in addition to having the general advantages attributed to the solid catalysts it has a much higher activity evident in the terms of high yields reached after short reaction times and at mild reaction conditions (Table 2).

4. Conclusion

In this study the coating of Fe3O4 nanoparticles with sulfonated polyacrylamide has been described. Magnetization measurements showed that the obtained poly(AMPS-co-AA)@Fe3O4 particles have paramagnetic properties. Poly(AMPS-co-AA)@Fe3O4 showed good catalytic activity in a one-pot domino Knoevenagel-type condensation/Michael reaction between aldehydes and 4-hydroxycoumarin, aromatic aldehydes with dimedone, and aromatic aldehydes with dimedone and β-naphthol. Work-up of these reactions is a “green” process because the catalyst was easily separated from the reaction media by the application of an external magnetic source. The high thermal and chemical stabilities of the catalyst, easy preparation, handling, and recycling of the catalyst, high yields achieved, and short reaction times needed are the other obvious advantages of the present method.

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6. References


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Povzetek
S polimerizacijo ustreznih monomerov in z nadaljnjo reakcijo s Fe₃O₄ nanodelci smo pripravili magnetitne delce s sulfoniranim poliakrilamidnim ovojem. Karakterizacijo dobljenega katalitskega materiala smo izvedli s Fourierjevo transformacijsko infrardečo spektroskopijo (FT-IR), termično gravimetrijo (TGA), vrstično elektronsko mikroskopijo (SEM), energijsko disperzijsko spektroskopijo (EDS), rentgensko difrakcijo (XRD) in vibracijsko magnetometrijo (VSM). Ugotovili smo, da pripravljeni polimer vsebuje 1.1 mmol na gram kislih SO₃H ostankov. Katalitsko učinkovitost polimera smo raziskali na primeru sinteze biskumarinskih derivatov, ki smo jih pripravili z dvokomponentno enolono domino Knoevenaglovo kondenzacijo z sledečo Michaelovo reakcijo med aldehidi in 4-hidroksikumarinom. Biskumarine smo pripravili z visokimi izkoristki in s kratkimi reakcijskim časi. Izolacije so bile zelo enostavne. Katalizatorji so stabilni (pri sobnih pogojih), z njimi je enostavno ravnati in jih je moč ponovno uporabiti.

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