

# A novel approach to magneto-responsive polymeric gels assisted by iron nanoparticles as nano cross-linkers†

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**A new route for the preparation of magneto-responsive polymeric gels involving iron nanoparticles as nano cross-linkers has been described.**

Although other stimuli-responsive polymer gels such as temperature-, pH- or analyte-sensitive gels have received much attention,<sup>1</sup> preparation of magneto-responsive gels remains a challenging field. Magnetic gels (ferrogels) are a new class of soft polymer materials exhibiting properties controlled by magnetic fields. Due to their shape and size distortion ability in a magnetic field, these magnetic stimuli-responsive polymer networks are of interest for artificial muscles, actuators and micromanipulators.<sup>2</sup> Superparamagnetic gels (e.g. 10 nm sized ferrit nanocrystals in a polymer network) are potential candidates as agents for electromagnetic hyperthermia that is a recently developed method for cancer therapy.<sup>3</sup> Furthermore, the magneto-elastic properties of magnetic gels can be applied to the manufacture of sensors, switches, various separations, membranes and drug delivery systems.<sup>4</sup>

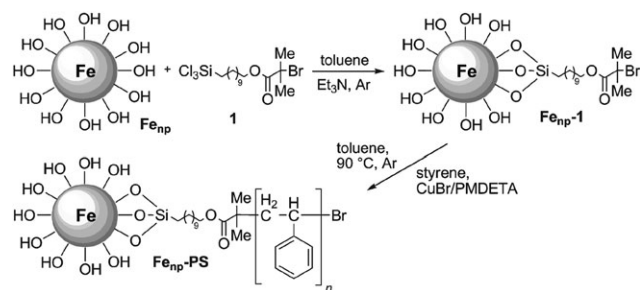
Magnetic gels which have been fabricated by *in situ* precipitation of different iron-containing particles so far do not involve chemical bonds between the magnetic particles and the cross-linked polymer matrix.<sup>2–7</sup> The question arises whether the termination of propagating radicals situated on different magnetic particles allows the formation of a polymer network? In other words, whether a covalently cross-linked polymeric gel can be synthesized without using conventional cross-linkers? With this problem in mind we attempted to prepare a covalently cross-linked polymer network in which magnetic nanoparticles act as cross-linking points. Iron nanoparticles were chosen as model magnetic particles because their magnetization is higher than those measured for different iron-oxide species.<sup>8</sup>

Generally, there are two approaches to chemically attaching polymer chains to the surface of inorganic particles: (1) the “grafting to” method;<sup>9</sup> end-functionalized polymer chains

react with surface groups and (2) the “grafting from” method<sup>10</sup> in which polymer chains grow *in situ* from initiator molecules that have been pregrafted to the surface of inorganic particles. Among various controlled radical polymerization methods (e.g. NMRP, RAFT, LAP) increasing attention has been placed on atom transfer radical polymerization (ATRP) because of its high tolerance to most functional groups.<sup>11</sup>

Herein, we demonstrate the first surface-initiated ATRP from iron nanoparticles as a novel approach to prepare magneto-responsive gels. To fabricate highly dense polymer-grafted iron nanoparticles we divided the process into three steps (Scheme 1): (1) synthesis of nano-sized iron particles ( $\text{Fe}_{\text{np}}$ ), (2) immobilization of ATRP initiator onto  $\text{Fe}_{\text{np}}$  and (3) conducting polymerization from initiator-grafted  $\text{Fe}_{\text{np}}$ . Iron nanoparticles were synthesized according to a modified literature method† by adding sodium borohydride to an aqueous solution of iron(III) chloride.<sup>12</sup>

Radical polymerization initiator [11-(2-bromo-2-methylpropionyloxy)undecyltrichlorosilane (**1**) was synthesized<sup>13</sup> and grafted onto  $\text{Fe}_{\text{np}}$  by the reaction between the surface accessible OH groups on the  $\text{Fe}_{\text{np}}$  and the trichlorosilyl anchoring group of **1**. Since initiator **1** was applied in excess to obtain the highest surface coverage as possible, the non-immobilized and physically absorbed initiator molecules had to be removed entirely because “free” initiators may cause polymerization in solution. To avoid this undesirable side reaction initiator-grafted iron nanoparticles ( $\text{Fe}_{\text{np}}\text{-I}$ ) were repeatedly washed with different organic solvents and water.‡ The amount of surface-attached initiator was estimated on the basis of thermogravimetric analysis ( $2.91 \text{ nm}^2 \text{ initiator}^{-1}$ ).† ATRP processes were carried out using  $\text{Fe}_{\text{np}}\text{-I}$  suspended in a mixture of styrene and toluene in the presence of CuBr and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) as catalyst precursors giving a magneto-responsive gel.§ Both the shape and the length of the  $\text{Fe}_{\text{np}}\text{-PS}$  gel could be influenced by

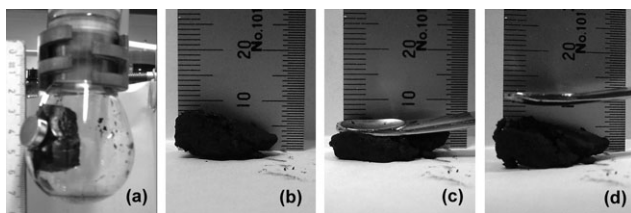


**Scheme 1** Synthetic steps for preparation of PS-grafted  $\text{Fe}_{\text{np}}$ .

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† Electronic supplementary information (ESI) available: Preparation of  $\text{Fe}_{\text{np}}$ , and thermogravimetric analysis of  $\text{Fe}_{\text{np}}\text{-I}$ , TEM image of bare  $\text{Fe}_{\text{np}}$  and XRD pattern of  $\text{Fe}_{\text{np}}$  and  $\text{Fe}_{\text{np}}\text{-PS}$ . See DOI: 10.1039/b717721f



**Fig. 1** Illustration of (a) magnetic and (b), (c) and (d) elastic features of a magneto-responsive gel prepared by ATRP of styrene.

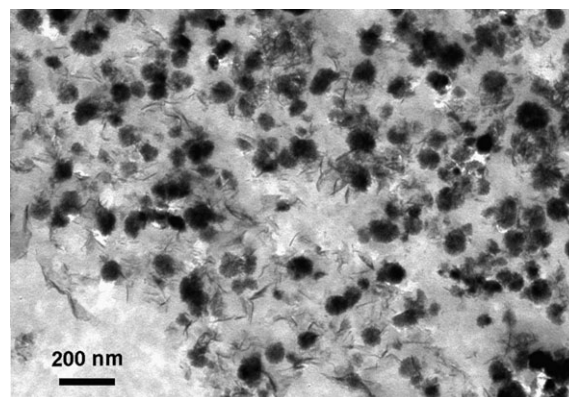
a permanent magnet as shown in Fig. 1a. Although the elasticity of the obtained  $\text{Fe}_{\text{np}}$ -PS gel has been proved (Fig. 1b–d) further measurements should be done in view of establishing the magnetoelastic properties thoroughly.<sup>2</sup> On the basis of the experimental conditions summarized in Table 1 the concentration of iron nanoparticles ( $c_{\text{m}}$ ) seems to influence the appearance of the resultant composite material significantly. While radical induced polymerization of styrene resulted in the formation of a magnetic gel (Fig. 1a) at 0.25 or 0.12  $\text{g mL}^{-1}$  nanoparticle concentration, no gelation was observed at  $c_{\text{m}} = 0.03 \text{ g mL}^{-1}$  under the experimental conditions indicated in Table 1 (entries 1, 2 and 3). It must be added here that bulk ATRP of a styrene and 1,4-divinylbenzene (DVB) mixture did not provide gel in the absence of  $\text{Fe}_{\text{np}}$  under the same experimental conditions (entry 5). In a control experiment we also performed the surface-initiated ATRP of styrene adding DVB as a cross-linker and we observed gel formation after 6 hours confirming that  $\text{Fe}_{\text{np}}$  play a significant role in the gelation as functional cross-linkers.

The obtained magnetic gels were purified by Soxhlet extraction to remove the chemically not bonded polymer chains, then investigated by transmission electron microscopy (TEM).<sup>¶</sup> An interesting conclusion can be drawn from the comparison of TEM images of bare Fe particles (Fig. S3<sup>†</sup>) and  $\text{Fe}_{\text{np}}$ -PS gel (Fig. 2). Unmodified iron particles with average diameter 50 nm are arranged as necklace shaped aggregates over 1000 nm caused by secondary aggregation. The authors believe that the particles obtained by this procedure are well dispersed in suspension but that rapid solvent evaporation during the preparation of TEM samples induces secondary aggregation.<sup>14</sup> In contrast,  $\text{Fe}_{\text{np}}$  were observed to have fine dispersion at average 68 nm with a few agglomerates only in  $\text{Fe}_{\text{np}}$ -PS gel. These findings clearly prove that surface modification of the particles hinders the secondary aggregation,

**Table 1** Experimental conditions and appearance of the products prepared by surface-initiated ATRP on  $\text{Fe}_{\text{np}}$

Entry <sup>a</sup>	Time/h	$c_{\text{m}}/\text{g mL}^{-1b}$	Cross-linker	Product
1 <sup>c</sup>	24	0.25	—	Gel
2 <sup>c</sup>	24	0.12	—	Gel
3 <sup>c</sup>	24	0.03	—	Suspension
4 <sup>d</sup>	6	0.2	DVB	Gel
5 <sup>de</sup>	6	—	DVB	Solution

<sup>a</sup> Solvent : monomer ratio (v/v) = 1 : 1, 90 °C. <sup>b</sup>  $c_{\text{m}} = \text{wt}_{\text{Fe}_{\text{np}}}/(V_{\text{toluene}} + V_{\text{monomer(s)}})$ ,  $\text{wt}_{\text{Fe}_{\text{np}}} = \text{weight of Fe}_{\text{np}}$ . <sup>c</sup>  $[\text{styrene}]_0 : [\text{CuBr}] : [\text{PMDETA}] = 150 : 1 : 1$ . <sup>d</sup>  $[\text{styrene}]_0 : [\text{DVB}]_0 : [\text{CuBr}] : [\text{PMDETA}] = 105 : 4 : 1 : 1$ . <sup>e</sup> Bulk polymerization in the absence of  $\text{Fe}_{\text{np}}$ .



**Fig. 2** TEM images of magnetic gel.

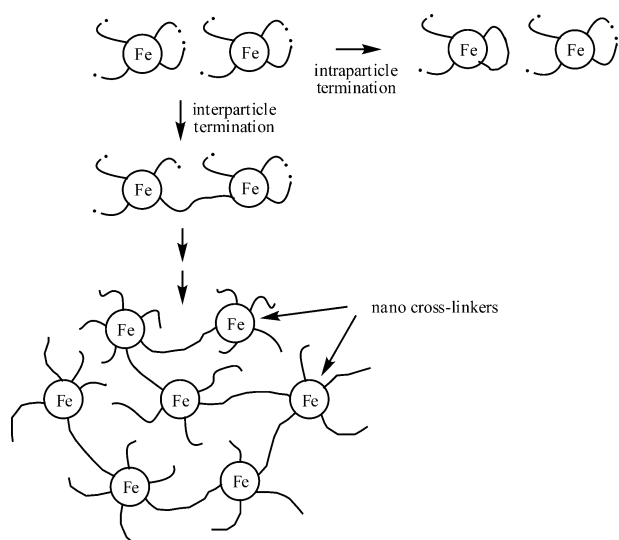
allowing fine dispersion and ensuring the stability of the nanoparticles in solid phase.

To determine the exact chemical composition of the magnetic nanoparticles, X-ray diffraction (XRD) measurements were performed using both bare  $\text{Fe}_{\text{np}}$  and  $\text{Fe}_{\text{np}}$ -PS. An XRD pattern of bare  $\text{Fe}_{\text{np}}$  and  $\text{Fe}_{\text{np}}$ -PS shown in Fig. S2<sup>†</sup> confirmed that the fraction of Fe-oxide (hydroxide) species is below the detection limit of the X-ray diffraction method.<sup>15</sup>

Generally, polymer gelators possess functional groups that interact with each other *via* non covalent interactions including H-bonds,  $\pi$ - $\pi$  stacking and van der Waals interactions, providing the necessary driving forces for gelation.<sup>16</sup> Lack of functional groups in PS that may participate in H-bonds preclude its self-aggregation into a gel, consequently  $\text{Fe}_{\text{np}}$ -PS cannot be considered as a physical gel and the mechanism of the network formation must be explained in a different way.

Von Werne and Patten reported that in surface-initiated radical polymerization reactions there are four possible termination modes: termination between free chains in solution, termination between a free chain and a surface bound chain, termination between chains on the same particle (intraparticle termination) and termination between chains on different particle surfaces (interparticle termination, Scheme 2).<sup>17</sup> Occurrence of intraparticle termination could be supposed if propagating radicals are close to each other on the surface, while interparticle termination has the spatial requirement that two particles must collide in a special orientation where two propagating radical ends can meet. Since the surface coverage of  $\text{Fe}_{\text{np}}$  ( $2.91 \text{ nm}^2 \text{ initiator}^{-1}$ )<sup>†</sup> is one order of magnitude lower than those measured on silica nanoparticles ( $0.34 \text{ nm}^2 \text{ initiator}^{-1}$ ),<sup>18</sup> the probability of interparticle termination should be higher than that of intraparticle termination. The present unique polymer network involving  $\text{Fe}_{\text{np}}$  as cross-linking points is established by interparticle termination reactions of the growing free radicals situated on neighboring  $\text{Fe}_{\text{np}}$ . According to our best knowledge this is the first magneto-responsive polymer network that has been fabricated without adding any conventional cross-linking agent.

We have described a new route for preparing magneto-responsive gels involving iron nanoparticles as functional cross-linkers by surface-initiated ATRP. The current work has a number of significant advantages over traditional preparation methods of magneto-responsive gels, namely that the



**Scheme 2** Schematic illustration for termination reactions on the particle surfaces giving a cross-linked network.

polymer matrix is chemically bound to the  $\text{Fe}_{\text{np}}$ , the ability to attach peculiar polymer architectures (e.g. block copolymers) with a high variety of end functionalities, and furthermore that the formation of the polymer network does not require the addition of a conventional cross-linking agent. Application of the present approach to prepare biocompatible/biodegradable magneto-responsive gels and hydrogels is underway in our laboratory and will be published in forthcoming papers.

## Notes and references

‡ *Grafting of ATRP initiator (1) to the surface of iron nanoparticles.* 3 g of iron nanopowder were dispersed in 20 mL toluene and the solution was deoxygenated by bubbling through argon for 15 minutes. 0.105 g (0.231 mmol) [11-(2-bromo-2-methyl)propionyloxy]undecyltrichlorosilane (**1**) were added and the suspension was stirred for 10 minutes. Then 0.07 g  $\text{Et}_3\text{N}$  (0.692 mmol) were added and the stirring was continued under inert atmosphere for 24 hours. After immobilization of **1** the suspension was diluted with toluene and  $\text{Fe}_{\text{np}}$  were separated by a magnet. Then the particles were re-suspended in 8 mL toluene, the suspension was stirred for 5 minutes and the toluene was decanted. This washing process was repeated using methanol, water, methanol and dichloromethane (each three times). Finally, the purified  $\text{Fe}_{\text{np}}\text{-1}$  were dried under vacuum and stored at room temperature under argon when not in use. It is noteworthy, that after the above detailed washing process, Soxhlet extraction with dichloromethane for 24 hours did not further reduce the organic content of  $\text{Fe}_{\text{np}}\text{-1}$  confirming that purification was successful.

§ *Surface-initiated ATRP of styrene on  $\text{Fe}_{\text{np}}\text{-1}$ .* 0.103 g (0.593 mmol) PMDETA were added to a mixture of 10 mL toluene and 10 mL styrene, then the solution was mixed with 0.6–5 g of initiator-grafted iron nanoparticles (depending on  $c_m$  in Table 1). The suspension was purged with argon and 0.085 g (0.593 mmol)  $\text{CuBr}$  were added. The mixture was degassed by three freeze–pump–thaw cycles, then the flask was placed in an oil bath with a preset temperature of 90 °C. After 24 hours the gel was removed from the mold, then Soxhlet extraction was carried out to purify the product albeit the solvent did not penetrate deeply to the gels.

¶ *Samples for the TEM analysis of magnetic gels were prepared by ultramicrotoming of both dry and swollen gels. Swollen gels were embedded in epoxy resin and thin sections (approximately 70 nm) were microtomed using an LKB ultramicrotome at room temperature with a diamond knife.*

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