



# Tadpole-shaped magnetic block copolymer: Self-assembly induced increase of magnetic susceptibility



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## ABSTRACT

Self-assembly induced increase of magnetic susceptibility for the tadpole-shaped block copolymer based on paramagnetic  $\text{FeCl}_4$  pyridinium was reported in this work. The tadpole-shaped block copolymer was prepared by sequential reversible addition-fragmentation chain transfer polymerization of styrene (St) and 4-vinylpyridine (4VP) at the presence of chain transfer agent-modified polyhedral oligomeric silsesquioxanes (POSS). The corresponding magnetic block copolymer (POSS-PSt-*b*-QP4VP( $\text{FeCl}_4$ )) was obtained by quaternization of 4VP and complexation with  $\text{FeCl}_3$ . The prepared block copolymer was paramagnetic with magnetic susceptibility of  $15.4 \times 10^{-6} \text{ emu g}^{-1}$ , as investigated by superconducting quantum interference device. Surprisingly, the magnetic susceptibility of the block copolymer was almost doubled ( $27.5 \times 10^{-6} \text{ emu g}^{-1}$ ) after self-assembly in thin film. Since the composition of the block copolymer is unchanged, the increase of the susceptibility should be generated by the self-assembly, which makes the magnetic  $\text{FeCl}_4^-$  more ordered. And, self-assembly will be an efficient and convenient method in improving magnetic properties of such polymers.

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## 1. Introduction

Self-assembly of block copolymers is a facile method to prepare ordered nanostructures. And, polymer materials with specific morphologies or patterns, such as vesicles, micelles, tubes, bamboos and nanoparticles in solution as well as long-range ordered bulk/film with spherical, cylinder, lamellar, hexagonal, and tetragonal phase were prepared by the self-assembly of block copolymers with different chemical and physical structures [1–11]. The highly ordered structures generated from self-assembly could bring about variation to the physical structures, and thus endow the self-assembled block copolymers with functional properties and applications. Xiao and co-authors reported the controlled release of sugar from the self-assembled glycopolymerosomes to regulate blood glucose level without insulin drugs [12]. And, smart  $\text{K}^+$  responsive micelles were prepared by the self-assembly of block copolymers, which showed potential in targeted intracellular delivery of drugs [13]. Additionally, self-assembled bulk and films are available in nanolithography [14–17] and surface patterning [18–21]. For example, sub-10 nm space patterns were efficiently

prepared by nanolithography of self-assembled polystyrene-block-poly(methyl methacrylate) copolymer [22]. Meantime, as the physical structure of block copolymers was changed by self-assembly, the corresponding physical property of the self-assembly should be different, which will endow the block copolymers with new functionalities. Grubbs et al. reported the one dimensional photonic crystals by the layer by layer self-assembly of brush block copolymers, which showed special optical properties [23–25]. Our group have prepared the anti-icing and anti-fogging surfaces by the self-assembly of block copolymers [26–28], and the versatile surface properties were presented after self-assembly.

On the other hand, giant block copolymer with polyhedral oligomeric silsesquioxanes (POSS) as one block showed great potential in the preparation of ordered structures. A giant surfactant with acid-functionalized POSS as hydrophilic head and polystyrene (PSt) as hydrophobic tail was self-assembled in solution to generate micelles, worms and particles by varying the composition of the solutions [29]. The tadpole-shaped POSS-poly(acrylic acid) polymer self-assembled to nanoparticles in solution [30]. Furthermore, highly ordered lamellae, hexagonal, and body-centered cubic structures were prepared by the self-assembly of tadpole-shaped polymers with group-functionalized POSS as head and PSt as tail [31]. And, nanothick sheets with micron size were prepared by tadpole-shaped poly(ethylene glycol) with POSS as head [32]. The

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self-assembly of tadpole-shaped polymers with POSS as head showed not only highly ordered structures with large scale but also shorter spacing between the polymer chains.

As well known, the magnetic property of inorganic magnets is related closely to their physical structures. The difference between paramagnetism and ferromagnetism is the degree of magnetic ordering of the magnetic domains. For example,  $\text{Fe}_2\text{O}_3$  with  $\alpha$ -type crystal is paramagnetic [33–35], while  $\text{Fe}_2\text{O}_3$  with  $\gamma$ -type crystal is ferromagnetic [36–38]. The difference in magnetism is derived from the crystal structure and magnetic ordering of the inorganic magnet. If magnetic groups were introduced into the block copolymers with POSS as head and polymer as tail, the self-assembly induced highly ordered structures with sub-10 nm could be expected to favor design and preparation of new magnetic polymers since the magnetism is much related with the ordered physical structures.

Recently, magnetic ionic liquid, which shows a strong response to magnetic field, has been discovered by Hayashi and Hamaguchi via mixing 1-butyl-3-methylimidazolium chloride with  $\text{FeCl}_3$  [39]. The magnetic property is generated from the high spin of  $\text{Fe}^{3+}$  in  $\text{FeCl}_4^-$ . Döbbelin et al. reported the synthesis of the paramagnetic poly(ionic liquid) containing  $\text{FeCl}_4^-$  and tetrabromoferrate  $\text{FeBr}_4^-$  [40]. We have prepared paramagnetic homo- and block copolymers based on  $\text{FeCl}_4^-$  by ring-opening metathesis polymerization. Although the ferric content in block copolymer is lower than that in homopolymer, the block copolymer showed higher magnetic susceptibility than the homopolymer [41]. However, most of the magnetic ionic liquids and poly(ionic liquid)s were paramagnetic, which mean a low ordered magnetic structure. As discussed above, self-assembly of block copolymers is an effective and convenient method to prepare ordered physical structures, which will be helpful in improvement of the magnetism of magnetic poly(ionic liquid)s.

Herein, we proposed the tadpole-shaped block copolymers based on paramagnetic  $\text{FeCl}_4^-$  pyridinium with POSS as head. The modified chain transfer agent (CTA) with POSS molecule was used to prepare POSS-containing amphiphilic block copolymer, POSS-polystyrene-*b*-poly(4-vinylpyridine) (POSS-PSt-*b*-P4VP), by sequential reversible-addition fragmentation chain transfer (RAFT) polymerization as shown in Scheme 1. And, well-defined magnetic block copolymer was prepared by quaternization of the P4VP block followed by ion exchange to chloride and complexation with  $\text{FeCl}_3$ . The self-assembly of the magnetic block copolymer was studied in thin film. And, self-assembly induced improvement in magnetism was expected and discussed.

## 2. Experimental section

### 2.1. Materials

Aminopropyl-isobutyl polyhedral oligomeric silsesquioxane (APOSS) was purchased from Hybrid Plastics Company, and used as received. 2, 2'-Azobisisobutyronitrile (AIBN) was obtained from Tianjin Kemio Chemical Reagent Co. Ltd., China, and used after recrystallization from ethanol. Styrene (St) and 4-vinylpyridine (4VP) were stirred over  $\text{CaH}_2$  overnight and distilled under reduced pressure prior to use. Methyl iodide (99%, Tianjin Bichenglan Chemical Reagent Factory),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (99%, Tianjin Shuangchuan Chemical Reagent Factory), ion exchange resin (Amberlite IRA-400(Cl), Alfa Aesar) were used as received. The RAFT agent S-1-dodecyl-S'-( $\alpha$ ,  $\alpha'$ -dimethyl- $\alpha'$ -acetic acid) trithiocarbonate (DDMAT) was synthesized according to a procedure described previously [42]. Unless specified, all other reagents were purchased from commercial sources and used without further purification.

### 2.2. Synthesis of POSS-CTA

APOSS (805.3 mg, 0.9 mmol) was dissolved in 5 mL anhydrous dichloromethane (DCM), and 0.3 mL new distilled pyridine was added. A solution of freshly prepared acyl chloride of DDMAT (497.3 mg, 1.3 mmol) in 5 mL anhydrous DCM was slowly added to the above mentioned APOSS solution at 0 °C. After stirring for 12 h at room temperature under nitrogen, the mixture was filtered and the solvent was removed from the filtrate by rotary evaporation. The residue was purified by a silica gel chromatography with ethyl acetate/petroleum ether (v/v, 1:4) as eluent. The resultant product was crystallized in petroleum ether. Yield: 80%.

### 2.3. Synthesis of POSS-PSt

A mixture of St (2.73 mL, 24.6 mmol), POSS-CTA (100.0 mg, 0.08 mmol), AIBN (2.7 mg, 0.02 mmol) and tetrahydrofuran (THF, 2.50 mL) were added into a 25 mL Schlenk tube equipped with a stir bar and sealed with a rubber septum. After three freeze-pump-thaw cycles, the mixture was reacted at 70 °C for 18 h under the protection of nitrogen. The polymerization was quenched by open to air and diluted with THF. The polymer was precipitated in excessive amount of methanol and dried under vacuum at room temperature to a constant weight. Yield: 54%.  $M_{n,NMR} = 17600$ ,  $M_{n,GPC} = 17700$ , PDI = 1.18.

### 2.4. Synthesis of block copolymer POSS-PSt-*b*-P4VP

In a 25 mL Schlenk tube equipped with a stir bar, POSS-PSt (1.000 g, 0.06 mmol), 4VP (1.82 mL, 17.0 mmol), AIBN (1.9 mg, 0.01 mmol), and *N,N*-dimethylformamide (DMF, 2.50 mL) were charged. The mixture was degassed by three freeze-pump-thaw cycles, and then reacted at 80 °C for 10 h. The polymerization was quenched at the end of the polymerization by opening to air. The polymer was precipitated in excessive amount of *n*-hexane for three times and dried under vacuum at room temperature to a constant weight. Yield: 61%.  $M_{n,NMR} = 38600$ ,  $M_{n,GPC} = 38100$ , PDI = 1.31.

### 2.5. Synthesis of magnetic block copolymer POSS-PSt-*b*-QP4VP( $\text{FeCl}_4$ )

In a 25 mL round bottom flask charged with POSS-PSt-*b*-P4VP (400.0 mg, containing 2.1 mmol 4VP group) THF (2.0 mL) solution, methyl iodide (0.6 mL, 9.7 mmol) was added dropwise under rapid stirring. The mixture was refluxed for 24 h at 50 °C. At the end of the reaction, the reaction mixture was concentrated by rotary evaporation, and the product was obtained by precipitating in diethyl ether for three times. POSS-PSt-*b*-QP4VP with chloride as counter ion was prepared by ion exchange in the presence of ion exchange resin (IRA-400) followed by filtration and rotary evaporation. Finally, the magnetic block copolymer (POSS-PSt-*b*-QP4VP( $\text{FeCl}_4$ )) was synthesized by complexing  $\text{FeCl}_3$  with POSS-PSt-*b*-QP4VP at the molar ratio of  $\text{FeCl}_3$ :  $\text{N}^+$  of ca.1:1 in methanol. The magnetic block copolymer was purified by precipitation in excessive amount of diethyl ether for three times followed by vacuum dry. Yield: 95%.

### 2.6. Self-assembly of POSS-PSt-*b*-QP4VP( $\text{FeCl}_4$ )

In the sample preparation, POSS-PSt-*b*-QP4VP( $\text{FeCl}_4$ ) was dissolved in DMF at a concentration of 2 mg/mL, and the solution was spin coated onto silicon substrates to prepare the thin film samples. After solvent evaporation, the thin film samples were annealed in  $\text{H}_2\text{O}$  vapor at room temperature for three days in a chamber.

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