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Surface-initiated atom transfer radical polymerization of methyl methacrylate on magnetite nanoparticles

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Abstract

The synthesis of magnetite nanoparticles coated with a well-defined graft polymer is reported. The magnetite nanoparticles with an initiator group for copper-mediated atom transfer radical polymerization (ATRP), 2-(4-chlorosulfonylphenyl) ethyltrichlorosilane (CTCS) chemically bound on their surfaces were prepared by the self-assembled monolayer-deposition method. The surface-initiated ATRP of methyl methacrylate (MMA) was carried out with the CTCS-coated magnetite nanoparticles in the presence of free (sacrificing) initiator, *p*-toluenesulfonyl chloride. Polymerization proceeded in a living fashion, exhibiting first-order kinetics of monomer consumption and a proportional relationship between molecular weight of the graft polymer and monomer conversion, thus providing well-defined, low-polydispersity graft polymers with an approximate graft density of 0.7 chains/nm^2. The molecular weight and polydispersity of the graft polymer were nearly equal to those of the free polymer produced in the solution, meaning that the free polymer is a good measure of the characteristics of the graft polymer. The graft polymer possessed exceptionally high stability and remarkably improved dispersibility of the magnetite nanoparticles in organic solvent.

Keywords: Atom transfer radical polymerization; Graft polymerization; Magnetic nanoparticle

1. Introduction

Recently, there has been increased interest in coating surfaces of magnetic nanoparticles with polymer materials for various functionalities. Such polymer-coated nanoparticles find many applications in various fields, e.g. ferrofluid, magnetic resonance imaging contrast enhancement, biological and mineral separation and so on [1–5]. In many of these applications, the magnetic nanoparticles respond external magnetic fields, whereas the polymer shell carries various functionalities. In other words, polymer-coated magnetic nanoparticles suitable for a number of applications can be prepared simply by changing properties of the polymer shell. On the other hand, for practical applications, the polymer shell is required to have good stability, high concentration of functional groups and controlled structures such as chain-length and its distribution. Therefore, it would be rewarding to establish a method to prepare polymer coatings on magnetic nanoparticles not only satisfying the above-mentioned requirements but also applicable to a large variety of polymers.

Several methods have been developed to prepare polymer-coatings on nanoparticles, e.g. physical adsorption of polymers, emulsion polymerization in the presence of nanoparticles, and the so-called ‘grafting to’ and ‘grafting from’ methods [6–9]. The ‘grafting from’ strategy is a promising candidate to achieve both high stability of polymer layer and high graft density. Surface-initiated graft polymerization has been extensively studied [9–32], but it usually results in a poor control of chain-length and its distribution [10–14]. Recently, living polymerization techniques were successfully applied to surface-initiated graft polymerization to prepare a dense polymer layer with controlled structures [9,15–33]. Some research groups have explored the applicability of living radical polymerization (LRP), which has been attracting much attention as a new

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route to well-defined polymers with low polydispersities [9,20–33]. Its clear advantage over other polymerization techniques may be the applicability to a large variety of monomers without involved procedures including perfect removal of water and other impurities and protection and deprotection of reactive groups. Synthesis of polymer-coated magnetic nanoparticles by means of LRP methods has been reported. Matsuno et al. reported synthesis of poly(styrene)-grafted magnetite nanoparticles by nitroxide-mediated polymerization method [32]. They showed that poly(styrene) with low polydispersities can be grafted onto the magnetite nanoparticles. However, applicability of the nitroxide method is mostly limited to homopolymers of styrene and its derivatives, and random copolymers containing them [34,35]. The atom transfer radical polymerization (ATRP) is a powerful variant of LRP, which can be applied to a large variety of monomers, e.g. styrenes, (meth)acrylates, (meth)acrylamides, (meth)acrylic acids, and so on [36]. Vestal et al. reported synthesis of poly(styrene)-grafted $MnFe_2O_4$ nanoparticles by copper-mediated ATRP method [33]. In their work, however, little was studied about polymerization processes and characteristics of the grafted poly(styrene) chains, e.g. graft density, chain-length and its distribution. Such information is inevitable to extend surface-initiated ATRP on magnetic nanoparticles over various monomers, since careful choice of polymerization conditions is essential to synthesize polymers with well-defined structures [37]. Detailed studies on surface-initiated ATRP on magnetic nanoparticles are, therefore, of particular importance to develop high performance polymer-coated magnetic nanoparticles.

In this work, we have applied copper-mediated ATRP technique to graft polymerization of methyl methacrylate (MMA) on magnetite (Fe_3O_4) nanoparticles with an ATRP initiator, 2-(4-chlorosulfonylphenyl) ethyltrichlorosilane (CTCS), immobilized on their surfaces (Fig. 1). We will discuss immobilization of CTCS on the magnetite nanoparticles, polymerization mechanism of MMA, characteristics of the grafted poly(MMA)(PMMA) chains, and properties of the PMMA-coated magnetite nanoparticles thus-obtained.

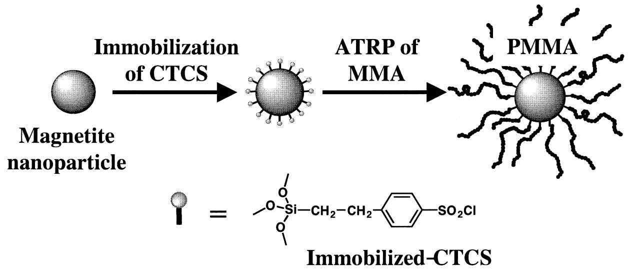

Fig. 1. Schematic representation for the synthesis of polymer-coated magnetite nanoparticle by surface-initiated ATRP.

2. Experimental section

2.1. Materials

Magnetite nanoparticles (MP, average size: 60 nm, standard deviation: 17%) were kindly donated by Toda Kogyo, Japan and used as received. The surface of MP was not covered by any organic compounds like surfactant. The specific surface area estimated by the BET method is reported to be 20.2 m^2/g. The MMA obtained from Nacalai Tesque, Japan was distilled under reduced pressure over CaH_2 before use. A 50 wt% CTCS solution in dichloromethane was obtained from Gelest, USA and used as received. *p*-Toluenesulfonylchloride (TsCl), copper bromide (CuBr, 99.0%), L-(−)-sparteine (Sp), aqueous HF solution (46%), and trioctylmethylammonium chloride (TOC) were purchased form Nacalai Tesque, Japan and used without further purification. Unless otherwise specified, all other reagents were purchased from commercially available sources and used as received.

2.2. Immobilization of initiator and graft polymerisation

CTCS was immobilized on the surface of MP by the self-assembled monolayer-deposition method; namely 1 g of MP was mixed with dehydrated toluene (40 ml), to which 1.3 mmol of CTCS was added. The reaction mixture was kept at room temperature under irradiation of ultrasonic wave for 3 h. Thus-obtained CTCS-immobilized magnetite nanoparticle (MP-CTCS) was washed four times with tetrahydrofuran (THF) and dried in vacuum.

The graft polymerization was carried out as follows; a degassed diphenyl ether solution containing CuBr (32.5 mM), Sp (65 mM), MMA (5 M), free initiator (TsCl, 5 mM) and MP-CTCS (20 mg/ml-solution) was sealed in a glass tube under vacuum and heated for various periods of time (t) at 70 °C. Sp is a ligand coordinating with Cu, providing a homogeneous ATRP system for MMA [38]. After polymerization, a small amount of the sample solution filtered through a 0.2 μm pore-size filter was subjected to the gel permeation chromatographic (GPC) measurement. The PMMA-grafted magnetite nanoparticles (MP-PMMA) were washed with THF by several dispersion-centrifugation cycles to remove free PMMA produced from the free initiators.

2.3. Cleavage of the graft polymer from the magnetite nanoparticles

PMMA chains of MP-PMMA were cleaved as follows; 100 mg of MP-PMMA was vigorously stirred in a poly(ethylene) flask containing 3.5 ml of toluene, 3.5 ml of 5 wt% aqueous HF solution and 8 wt% of TOC as a phase transfer catalyst. After 2 h, the aqueous layer was removed, and 3.5 ml of 5% aqueous HF solution containing 8 wt% of TOC was added and stirred for further 2 h. This procedure was repeated until no impurities could be detected by GPC measurement. The organic layer containing cleaved polymer was washed with aqueous $NaHCO_3$ solution and water, filtered to remove solid impurities, and then subjected to the GPC measurement.

2.4. Measurements

The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the free polymer produced in the solution and those of the graft polymer cleaved from the magnetite nanoparticles were determined by PMMA-calibrated GPC (8010 high-speed liquid chromatograph, Tosoh, Japan). THF was used as eluent, and the temperature was kept at 40 °C. Sample detection and quantification were made with a Tosoh refractive-index detector, RI-8020. Monomer conversion (C) was estimated from the amounts of PMMA produced in the solution (free polymer) and on the magnetite nanoparticle (graft polymer). For Fourier transform infrared (FTIR) spectroscopy (KBr, pellet), a BioRad FTS 6000 Fourier Transform Infrared Spectrometer (BioRad Laboratories, USA) was used.

3. Results and discussion

3.1. Preparation of MP-CTCS

We developed here the self-assembled monolayer-deposition method to prepare the MP carrying chlorosulfonyphenyl groups suitable for copper-mediated ATRP. This method is based on a ligand-exchanging reaction between the protecting surfactants on the MP and CTCS. It is believed that the chlorosilyl group of CTCS react with the hydroxyl groups on the MP to form a covalent Si–O–Fe bond. The introduction of CTCS onto MP was confirmed by FTIR analysis. Fig. 2 shows the FTIR spectra of MP and MP-CTCS. The spectrum of MP-CTCS has a new absorption peak at 1380 cm^{-1} (indicated by arrow), which can be assigned to the S=O stretching of CTCS. Since our method is based on the reactions between the chlorosilyl groups of CTCS and the hydroxyl groups on the MP surface, it should be applicable to various MPs with surface hydroxyl groups.

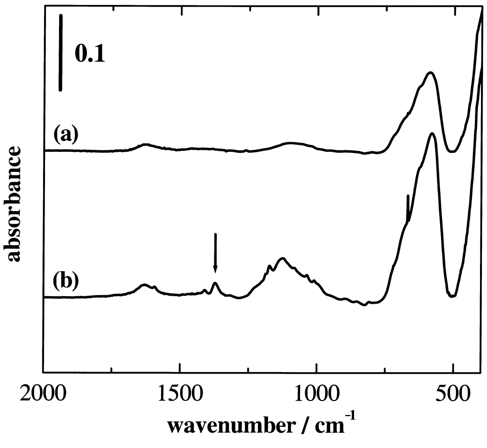

Fig. 2. FTIR spectra of (a) MP and (b) MP-CTCS.

3.2. Surface-initiated ATRP of MMA on magnetite nanoparticle

The MP-CTCS was subsequently subjected to copper-mediated ATRP of MMA. We paid particular attention to the following two points: first, the polymerization solution was constantly shaken to prevent precipitation of the MP during the course of polymerization, as the size of the MP was relatively large (ca. 60 nm). Second, we carried out the polymerization in the presence of the free (sacrificing) initiator of TsCl. The free initiator was added to self-adjust the concentration of the Cu^{II} complex, as described elsewhere [20].

Fig. 3 shows the first-order kinetic plot of the conversion of MMA. The plot can be approximated by a straight line. The linear relationship reveals that the concentration of the propagating species is constant during the course of polymerization. After polymerization, MP-PMMA was washed to remove the free PMMA and subjected to the cleavage processes including the two-step addition of HF and TOC. By using a standard PMMA sample, it was confirmed that the cleavage process gave no damage on the PMMA chain. The PMMA cleaved off the MP was subjected to GPC analysis to determine M_n and M_w/M_n. In Fig. 4, M_n and M_w/M_n of the cleaved graft polymer and the free polymer simultaneously produced from the free initiator are plotted as a function of monomer conversion C. For both polymers, M_n increased proportionally to C and the M_w/M_n values remained fairly low, smaller than 1.2. This confirms that the graft polymerization was well controlled as the free ATRP of MMA in solution. These M_n values are almost equal to the theoretical values ($M_{n,theo}$) calculated with the monomer to initiator molar ratio and C.

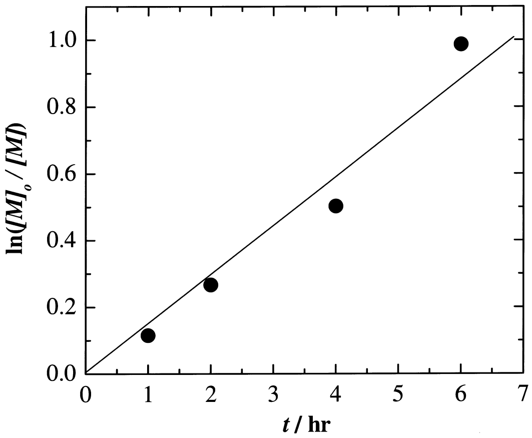

Fig. 3. Plot of $\ln([M]_0/[M])$ vs polymerization time, t. Here, $[M]_0$ and $[M]$ are the monomer concentrations in the polymerization solution at times 0 and t, respectively. The solid line is a guide to eyes.

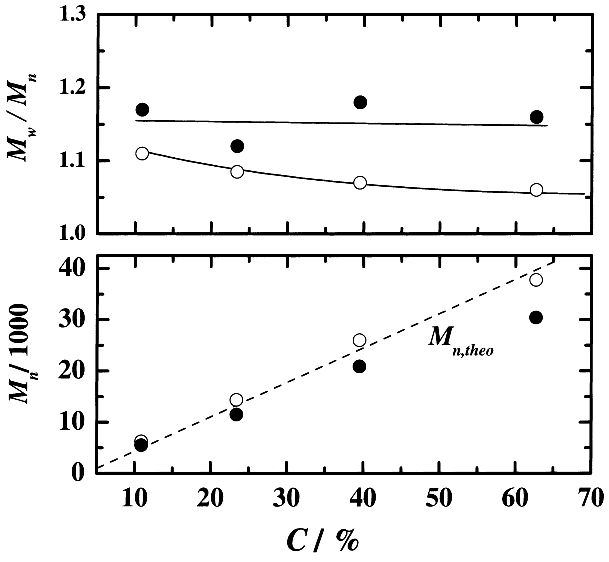

Fig. 4. Plots of M_n and M_w/M_n of the cleaved (●) and the free (○) polymers vs monomer conversion C. The broken line represents $M_{n,theo}$ calculated from the monomer to initiator ratio and C. The solid lines are guide to eyes.

Fig. 4 also shows that the M_n and M_w/M_n values of the graft polymer are nearly the same as those of the free polymer. This means that the M_n and M_w/M_n of the free polymer approximate those of the graft polymer.

In order to estimate the amount of PMMA grafted on MP, FTIR spectrum was measured. As Fig. 5 shows, a sharp absorption peak characteristic of the ester group of PMMA is clearly observed at 1735 cm^{-1} (indicated by arrow). The amount (in grams) of the graft polymer per 1 g of MP-PMMA (W, in unit of PMMA(g)/MP-PMMA(g)) can be evaluated by referring to the absorption peak characteristics of MP at around 600 cm^{-1}. The FTIR spectrum of a physical mixture of prescribed amounts of PMMA and MP was used to calibrate data. For precise estimation of W, no free polymer should remain in the MP-PMMA samples. To check this, graft polymerization was carried out with untreated MP, i.e. the MP without CTCS. The FTIR analysis of the samples showed complete absence of PMMA after the washing process described in Section 2. Fig. 6 shows that W is proportional to M_n of the graft polymer. This suggests that the graft density, the number of graft chain per unit area, is constant during the course of polymerization. From the slope of the line, the graft density is estimated to be about 0.7 chains/nm^2 on the basis of the BET-estimated surface area (20.2 m^2/g). This value is comparable to the values obtained for other surface-initiated LRP systems [20–22]. All these results suggest that the surface of magnetite nanoparticle was successfully covered with a high-density PMMA brush.

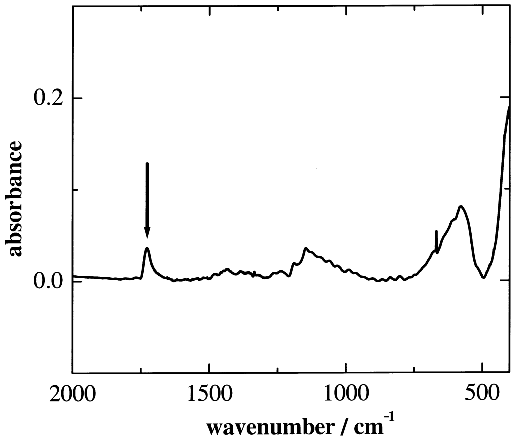

Fig. 5. FTIR spectrum of MP-PMMA (polymerization time $t = 4$ h).

For practical applications, the dispersibility of the polymer-coated MP is primarily important. Fig. 7 shows the photos of 0.01 wt% chloroform dispersions of MP, MP-CTCS and MP-PMMA. After 15 h, MP and MP-CTCS were almost precipitated, whereas MP-PMMA was still well dispersed. Thus grafting of PMMA has improved dispersibility. MP-CTCS has a relatively hydrophobic surface with affinity to chloroform like MP-PMMA. Nevertheless, there is a large difference in dispersability between MP-CTCS and MP-PMMA. This result suggests that the solvent-swollen PMMA layer of MP-PMMA acts as a stabilizing layer to sterically prevent coagulation.

Stability of the grafted polymer is another important factor. Toluene dispersion of MP-PMMA was heated to reflux for 12 h, and the amount of the grafted PMMA, evaluated by FTIR analysis, was found unchanged within an experimental error. This confirms the exceptionally high stability of the grafted PMMA layer on the magnetite nanoparticles.

4. Conclusions

The MP with CTCS, which has ATRP-initiating ability, can be prepared by the self-assembled monolayer-deposition method. This method should be applicable to various MPs with surface hydroxyl groups. ATRP of MMA using the CTCS-functionalized MP proceeded in a living fashion

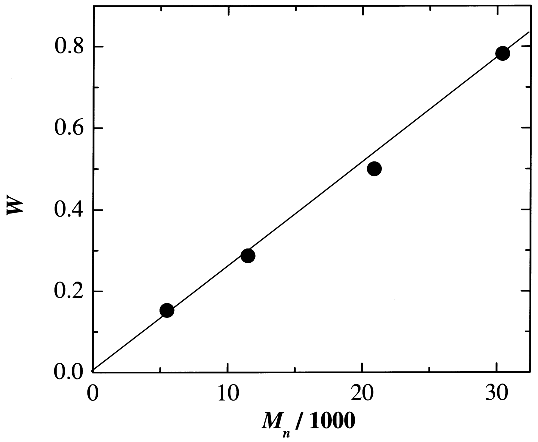

Fig. 6. Plots of grafted amount W vs M_n of graft polymer. The solid line is a guide to eyes.

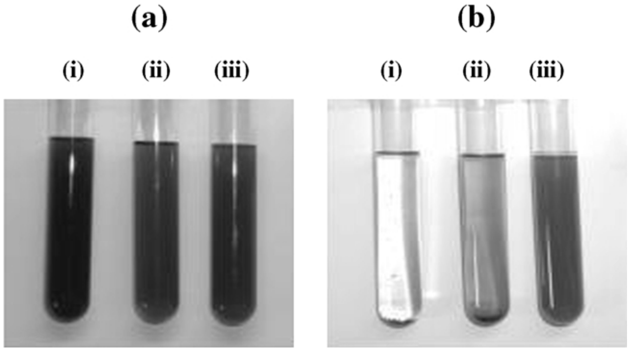

Fig. 7. Photos of 0.01 wt% chloroform dispersions of (i) MP, (ii) MP-CTCS and (iii) MP-PMMA (polymerization time $t = 6$ h), taken at (a) 0 h and (b) 15 h after preparation.

on the MP surface as well as in the bulk solution in the presence of free initiator. IR and GPC analyses revealed the following points: (i) polymerization exhibits a first-order kinetics of monomer consumption indicating that the concentration of the propagating species is constant during the course of polymerization. (ii) The M_n and M_w/M_n values of the graft polymer are nearly the same as those of the free polymer. (iii) The amount of the grafted polymer increases proportionally to monomer conversion and hence the M_n of the graft polymer. The proportionality suggests a constant and high graft density (about 0.7 chains/nm^2). It was also revealed that stability of the grafted PMMA layer is exceptionally high and the grafting of PMMA largely improves dispersibility of the magnetite nanoparticles in organic solvent. Since ATRP can be applied not only to homopolymerizations but also to block and/or random copolymerizations of a variety of monomers, this work will open up a new and versatile route to the synthesis of a wide range of high-performance polymer-coated MPs.

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