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Controllable synthesis of nanosilica surface-grafted PMMA macromonomers via catalytic chain transfer polymerization

Zhen Lu, Jiyi Wang, Qing Li, Li Chen, Su Chen *

State Key Laboratory of Material-Oriented Chemical Engineering and College of Chemistry and Chemical Engineering, Nanjing University of Technology, No. 5 Xin Mofan Rd., Nanjing 210009, PR China

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ABSTRACT

Catalytic chain transfer polymerization (CCTP) has emerged as an efficacious method to produce low-molecular weight polymers. In this paper, we reported the first controllable synthesis of nanosilica surface-grafted poly(methyl methacrylate) (PMMA) (SI-PMMA) macromonomers by using bis(aqua)bis((difluoroboryl)-dimethylglyoximato)cobalt(II) (CoBF) as a chain transfer catalyst via CCTP. In a typical run, we firstly prepared functionalized nanosilica by using 3-(trimethoxysilyl)propylmethacrylate (MPS) as the coupling agent, allowing naosilica containing unsaturated double bonds in end groups. Subsequently, SI-PMMA macromonomers were prepared by PMMA surface-grafted onto the functionalized nanosilica via CCTP. The as-prepared products were characterized by Fourier transforms infrared (FT-IR) spectrum, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Fourier transforms Raman (FT-Raman) spectrum and gel permeation chromatography (GPC). We also investigated the dependence of macromonomers on CoBF concentrations.

1. Introduction

During the past decade, controllable fabrication of inorganic–organic polymer hybrid composites based on the molecular level has been extensively investigated due to their potential applications, such as electrochemical sensors, drug carriers and nanocomposites materials [1–7]. However, it seems to be difficult to obtain well-dispersed inorganic–organic nanocomposites owing to the strong tendency of aggregation among inorganic nanoparticles, which may serve to depress properties of nanocomposites. To this end, considerable efforts have been devoted to the design and controlled fabrication of well-defined inorganic–organic polymer hybrids. There are two principle approaches for attaching polymer chains onto surfaces of nanoparticles, involving chemisorptions [8], covalent attachment of end-functionalized polymers to a reactive surface (“grafting to”) [9] and in situ monomer polymerization with monomer growth of polymer chains from immobilized initiators (“grafting from”) [10,11]. Among these methods, the “grafting from” approach offers the most promising method in the synthesis of inorganic–organic polymer hybrids with high grafting density. Recently, several research groups have reported the synthesis of inorganic–organic polymer hybrids via “grafting from” method, such as anionic [12–15], cationic [16–18], radical [19,20], ring-opening polymerization (ROP) [21–24], atom transfer radical polymerization (ATRP) [25–29], reversible addition-fragmentation chain transfer polymerization (RAFT) [30–33] and frontal polymerization (FP) [34–39]. Dubois and co-workers [21] reported the ring-opening polymerization of ε-caprolactone initiated from amine or hydroxyl groups spreading over the surface of silica. Fukuda et al. [25] developed a useful route to the modification of silica particles by surface-initiated ATRP and synthesized hybrid nanoparticles with a monodisperse silica core and a well-defined concentrated PMMA brush. Most recently, Pan et al. [30] presented a method for preparation of RAFT agent anchored nanosilica surface, and synthesized

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* Corresponding author. Tel./fax: +86 25 83587194.
E-mail address: chensu@njut.edu.cn (S. Chen).

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polystyrene (PS) grafted silica particles through RAFT polymerization. Chen et al. [34,35] reported a facile method for fabrication of nanosilica–polymer nanocomposites via FP and positional assembly [40].

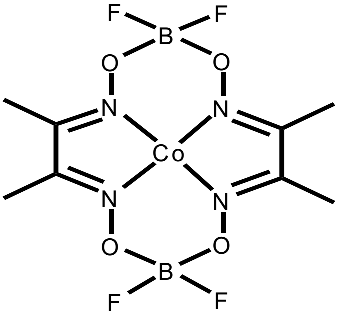
Although a wealth of methods have been applied on incorporating polymer onto silica surface, there are few reports on preparation of nanosilica–polymer nanocomposites by using the method of catalytic chain transfer polymerization (CCTP). CCTP has emerged as a very efficient technique for producing vinyl end-functionalized low-molecular weight polymers via free-radical polymerization [41–43], which based upon the property of certain low-spin Co(II) complexes to catalyze the chain transfer to monomer reaction. Up to now, CCTP has been only applied in the synthesis of graft or block copolymers with low-molecular weight, which can be used in a bulk or conventional emulsion process. However, the utilization of CCTP to fabricate nanosilica surface-grafted polymer macromonomers has not been described. Our preliminary works on nanosilica–polymer nanocomposites focused on how to obtain well-dispersed polymer nanocomposites by the assembly between nanosilica functionalized with low-molecular chemical agents and polymers [34,35,40,44,45]. We believe nanosilica macromonomer hybrids containing vinyl end-functionalized groups prepared by CCTP may have numerous potential applications, such as further preparation of well-defined high performance inorganic–organic network hybrids.

In the present paper, we first described the synthesis of nanosilica surface-grafted poly(methyl methacrylate) (PMMA) (SI-PMMA) macromonomers via CCTP. Since silica nanoparticles are easy to aggregate in the polymer matrix owing to their high surface area and surface energy, we firstly use 3-(trimethoxysilyl)propylmethacrylate (MPS) as the coupling agent to prepare vinyl-functionalized nanosilica. Subsequently, dangling double bonds to some extent remain on the surface of functionalized nanosilica particles, allowing them to further graft into PMMA matrix in situ. Finally, controllable synthesis of well-defined SI-PMMA macromonomers with terminal unsaturated double bond via CCTP has been successfully carried out. FT-IR, FT-Raman, TGA, SEM and GPC results of SI-PMMA macromonomers prepared by CCTP were thoroughly characterized.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) (Aldrich, 99%) was purified by the distillation under reduced vacuum to remove inhibitor. The initiator, 2,2′-azoisobutyronitrile (AIBN) (Aldrich), was purified by recrystallization from methanol. The coupling agent 3-(trimethoxysilyl)propylmethacrylate (MPS) (Aldrich) were used as received. The monomer MMA and toluene (Aldrich) were sparged with high purity nitrogen (BOC Gas) at least 2 h prior to use. Spherical silica nanoparticles (diameter = 35 nm, BET = 160 m^2, Mingri) were dried at 110 °C under vacuum for 8 h prior to use. The cobalt catalyst bis(aqua)bis((difluoroboryl)-dimethylglyoximato)-cobalt(II) (CoBF, as seen in Scheme 1) was prepared as the literature [46]. CoBF was analyzed using elemental analysis (C: 22.86%, N: 13.4%, H: 3.89%).



Scheme 1. Structure of cobalt catalyst CoBF.

2.2. Synthesis of MPS functionalized nanosilica (SI-MPS)

Five grams of dried spherical nanosilica (SI) was firstly dispersed in 150 g of toluene and stirred vigorously for 2 h, and then the mixture was mixed with 5.0 g MPS at 110 °C for 12 h with vigorous stirring under nitrogen. After isolation and wash with fresh toluene for five times, the free MPS was completely removed. Finally, the nanosilica functionalized with MPS (SI-MPS) containing double bonds on the surface of nanosilica, which can further polymerize with MMA monomers, were done.

2.3. Synthesis of nanosilica surface-grafted PMMA (SI-PMMA) macromonomers via CCTP

In a typical run, SI-MPS (0.6 g), AIBN (0.15 g), MMA (30 g), CoBF (0 mg, 0.13 mg, 0.38 mg, 0.63 mg, respectively) and toluene (70 g) were placed in a flask equipped with a magnetic stirrer under oxygen-free conditions by six freeze–pump–thaw cycles. The flask was consecutively evacuated and purged with nitrogen for six times. Then, the reaction mixture was placed in water bath maintaining isothermal reaction condition at 60 °C. After 1 h, the reaction was quenched in an ice bath and followed by the addition of methanol (10 mL). The products SI-PMMA macromonomers were then isolated by centrifugation and washing recycles, twice with toluene, twice with acetone and four times with toluene/acetone (1/1 v/v) mixtures. After dried under vacuum at ambient temperature overnight, the SI-PMMA macromonomers were done.

2.4. Characterization

The chemical structure of SI-PMMA macromonomers was analyzed by Fourier transform infrared (FT-IR) spectrum in the range of 400–4000 cm^{-1} using a Nicolet 6700 spectrometer (KBr disk, 64 scans, 4 cm^{-1} resolution). Fourier transforms Raman (FT-Raman) spectra were performed on a NXR FT-Raman Module by sharing interferometer installed in the FT-IR bench. The Raman optics system is comprised of Nd: YVO_4 laser operating at 1064 nm, sample holders, an InGaAs detector and a CaF_2 beam spliter.