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Synthesis of poly(methyl methacrylate)-*b*-poly(*N*-isopropylacrylamide) (PMMA-*b*-PNIPAM) amphiphilic diblock copolymer brushes on halloysite substrate via reverse ATRP

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Abstract

A series of well-defined copolymer brushes grafted from the halloysite substrate by reverse atom transfer radical polymerization (RATRP) were studied. A sufficient amount of peroxides as initiating moieties were firstly introduced onto the surface of halloysite substrate. Then the monomer methyl methacrylate (MMA) was polymerized via RATRP at a mild temperature using $CuCl_2$ as a catalyst, 2,2′-bipyridine (bpy) as a ligand, and cyclohexanone as a solvent. The XPS and SPM results indicated that the PMMA chains grafted from the halloysite substrate. The kinetic studies revealed that there was a linear increase in $\mathrm{Ln}([M]_0/[M])$ with polymerization time. Moreover, the fact that the growth of *N*-isopropylacrylamide (PNIPAM) block from the PMMA-grafted halloysite (halloysite-*g*-PMMA) surface using the PMMA modified halloysite substrate as the macroinitiator provided further evidence of the existence of “living” chain ends in the halloysite-*g*-PMMA hybrid material.

Keywords: Halloysite; RATRP; Kinetic studies; Macroinitiator; “Living” chain ends

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1. Introduction

Radical polymerization is the most significant and efficient procedure to synthesize polymers in laboratory and in industry. But it could not control the molecular and molecular weight distribution. The breakthrough was occured in 1995 when Sawamoto et al. [1] and Matyjaszewski et al. [2] found the novel polymerizable method—ATRP. ATRP is one of the most promising systems, a series of well-defined polymers could be synthesized via this controlled polymerization [3–10]. However, ATRP usually exhibits two drawbacks in the initiation system. Firstly, the choice of the initiator

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(R–X) is limited. Secondly, some catalysts such as CuBr are unstable expose to the air and moisture. Therefore, a so-called reverse atom transfer radical polymerization (RATRP) has been developed rapid recently [11–17]. However, the preparation of well-defined polymer-grafted inorganic particles via RATRP is rarely reported yet [18–20].

So far, very few literatures are reported on halloysite [21–23]. Halloysite, a clay mineral, occurs frequently in nature as ultramicroscopic hollow cylinders. It has an empirical formula of $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$, 1:1 layer aluminosilicate. A mismatch in the periodicity between the oxygen sharing tetrahedral SiO sheets and adjacent octahedral AlO sheets in the 1:1 layer structure of halloysite results in curvature (roll-up) giving these clay particles a hollow cylindrical shape [21]. Considering the polymer brushes from halloysite substrate has not been reported yet. In the present paper, the structurally well-defined, polymer/halloysite hybrids were prepared by modifying the halloysite surface with peroxide groups via RATRP.

2. Experimental section

2.1. Materials

Halloysite (325 mesh, dasanded and dried) was purchased from Xingtai county, Heibei, China. MMA (Shanghai chemical Reagent plant) was distilled under reduced pressure and stored in a refrigerator prior to use. PNIPAM (Aldrich chemical Co.) was purified by recrystallization from *n*-hexane/toluene. All solvents and other chemicals were of reagent grade and were used as supplied without further purification.

2.2. Introduction of peroxide groups onto halloysite

2.2.1. Halloysite substrate preparation

Halloysite was activated by treatment with 20% HCl at 80 °C for 2 h and was then rinsed with distilled water to pH 7 and then dried at 50 °C.

2.2.2. Preparation of halloysite carried 3-chloropropyltrimethoxysilane

Halloysite (6 g) was dissolved in 45 mL xylene and 1.5 mL distilled water, the mixture was stirred at room temperature for about 15 min. Then 7 mL 3-chloropropyltrimethoxysilane was added, the reaction mixture was heated at 80 °C for about 11 h. After the reaction, the product was isolated by filtration and dried under vacuum. The powder was extracted with toluene for 24 h to remove the free 3-chloropropyltrimethoxysilane and vacuum-dried at 50 °C, obtaining halloysite carried 3-chlopropyltrimethoxysilane.

2.2.3. Introduction of peroxide groups onto halloysite substrate

Fig. 1 shows the introduction of peroxide groups onto the surface of halloysite and the polymerization of MMA initiated by the peroxide groups. A detailed description of the introduction of peroxide groups onto the surface of halloysite is given: The halloysite carried 3-chlopropyltrimethoxysilane (6.0 g) was added into a dry 200 mL round-bound-bottom flask equipped with a magnetic stirrer. Then diosane (90 mL), TBHP (12 mL) were charged followed by the addition of 0.3 g sodium bicarbonate. The mixture was stirred under nitrogen at 20 °C in the dark for 12 h. After the reaction, the product was washed with methanol three times and dried at 20 °C in vacuum for 24 h.

2.2.4. Determination of peroxide groups on halloysite substrate

The halloysite having peroxide groups (0.2 g) and acetic anhydride (10 mL) were charged into a dry 50 mL flask followed by the addition of 0.5 g potassium iodide, and the mixture was stirred for 20 min. Then isolated iodide was titrated with 0.1 mol L^{-1} sodium hyposulfite using starch as an indicator. The content of peroxide groups introduced onto the halloysite was determined to be 0.2 mmol g^{-1}.

2.3. Graft polymerization of MMA

Halloysite having peroxide groups (0.19 g), $CuCl_2$ (0.06 g) and 2,2′-bipyridine (0.115 g) were charged into a tree-neck round-bottom flask equipped with a magnetic stirrer. The flask was subsequently evacuated and flushed with nitrogen three times. Then degassed monomer MMA 8 mL was injected and the solution was further degassed by nitrogen purging and the reactions was carried out in a oil bath at 70 °C for various reaction time. The resulting solution was diluted with THF and the polymer-grafted halloysite composite was separated by centrifugation. The product was precipitated in a large excess of methanol, yielding a white powder quantitatively. The halloysite with chemisorbed and grafted PMMA was separated from the mixture followed by extracting with THF. After completely removing the chem-