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Synthesis and characterization of well-defined polymer brushes grafted from silicon surface via surface reversible addition–fragmentation chain transfer (RAFT) polymerization

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Abstract

Reversible addition–fragmentation chain transfer (RAFT) polymerization was used to prepare polymer brushes grafted onto silicon wafer surface. Novel RAFT agent was prepared and immobilized on the silicon wafer surface. RAFT polymerizations were then conducted from the silicon surface to graft polymer brush to the silicon. Analysis of the polymer brush layers was conducted using ellipsometry, XPS, AFM and contact angle measurements, respectively.

Keywords: Synthesis; RAFT; Polymer brushes; Silicon surface

1. Introduction

Recently, the synthesis of surface tethered polymer brushes by a “grafting from” approach has garnered more and more attention [1–3]. To achieve a better control of molecular weight and molecular weight distribution and to synthesize block copolymer brushes, researchers have used living polymerization methods to make brushes. Several groups have reported the use of controlled/living polymerization techniques, such as cationic [4], anionic [5], ring-opening [6], atom transfer radical polymerization (ATRP) [7,8], and reversible addition–fragmentation chain transfer (RAFT) polymerization [9,10] methods, for the modification of solid substrates.

In the past few years many reports have demonstrated that polymerization with reversible addition–fragmentation chain transfer (RAFT) is an extremely versatile process due to its compatibility with a wide range of monomers and reaction conditions [11]. It is possible to take RAFT polymerization to high conversion and achieve commercially acceptable polymerization rates. Compared with the large number of reports using ATRP to prepare polymer brushes, there are surprisingly few reports on the application of RAFT techniques to the synthesis of polymer brushes, probably due to the difficulty of preparing RAFT agent anchored substrates.

In this paper we reported a novel method to graft PMMA onto silicon wafer by RAFT polymerization using the dithioester-immobilized silicon surface as RAFT agent, and to prepare structurally well-controlled polymer brush. Fig. 1 shows the method for RAFT agent immobilized on the surface of silicon wafer and PMMA chain growing from silicon wafer via surface RAFT polymerization.

2. Experimental

2.1. Materials

4,4′-Azobis-(4-cyanopentanoic acid) (Fluka, >98%), *N*-hydroxysuccinimide (Alfa Aesar, >97%) and Methyl methacrylate (MMA) (AR, Fluka) were washed with 5% NaOH, stirred over CaH_2 overnight, and distilled before use. 3-aminopropyltriethoxysilane (APTES) was obtained from Kanto Chemical Co.

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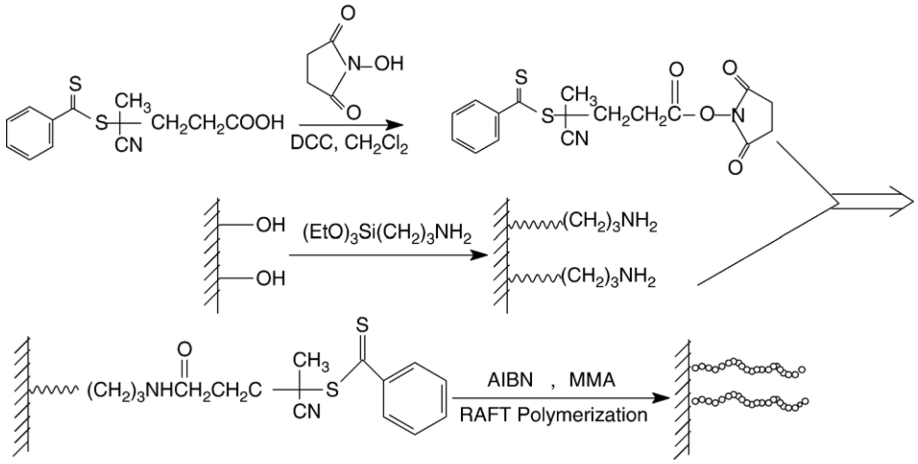

Fig. 1. Scheme for the immobilization of RAFT agent onto silicon surface and the RAFT mediated synthesis of PMMA brushes.

2.2. Synthesis of RAFT agent

According to the method of Thang et al. [11], we synthesized the compound 4-(4-cyanopentanoic acid) dithiobenzoate (CPAD). ^{1}H NMR (400 MHz, δ, ppm, CDCl$_3$): 1.95 (s, 3H, –CH$_3$), ~2.40–2.80 (m, 4H, –CH$_2$CH$_2$–), 7.40 (t, 2H, m-ArH), 7.59 (t, 1H, p-ArH), 7.91 (d, 2H, o-ArH).

Then the compound CPAD (10 mmol) and *N*-hydroxysuccinimide (10 mmol) were dissolved in 20 ml of anhydrous dichloromethane (DCM). After dicyclohexylcarbodiimide (DCC) (10 mmol) was added to the solution, the mixture was stirred at room temperature in the dark for 16 h. A white byproduct was filtrated out, and the filtrate was concentrated. The concentrated liquid was purified through a gel column with ethyl acetate:hexane (1:3, v/v) as eluent. Then the target compound 4-cyano-4-((thiobenzoyl) sulfanyl) pentanoic succinimide ester was obtained. ^{1}H NMR (400 MHz, δ, ppm, CDCl$_3$): 1.94 (s, 3H, –CH_3), ~2.30–2.75 (m, 2H, –CH$_2$–CH_2–C(CN)–(CH$_3$)–), 2.84 (s, 4H, –OC–CH_2–CH_2–CO–), 3.19 (m, 2H, –OC–CH_2–CH$_2$–C(CN)–(CH$_3$)–), 7.40 (t, 2H, m-ArH), 7.58 (t, 1H, p-ArH), 7.90 (d, 2H, o-ArH).

2.3. Wafers cleaning and silane treatment

Silicon wafers were cleaned by treatment with freshly prepared "Piranha" solution (70/30, v/v, concentrated H$_2$SO$_4$/30% aqueous H$_2$O$_2$) at 90 °C for at least 2 h and then rinsed with distilled water followed by ethanol and dried under a stream of clean nitrogen. The freshly cleaned silicon wafer was placed into a 5 wt.% toluene solution of 3-aminopropyltriethoxysilane and refluxed in a stream of nitrogen for 24 h. After the reaction, the wafer was washed twice with dried toluene, acetone and ethanol in an ultrasonic bath, and finally dried in a vacuum.

2.4. Immobilization of the RAFT agent on the silicon surface

5 pieces of the silane treated silicon wafers were introduced into the solution of 4-cyano-4-((thiobenzoyl) sulfanyl) pentanoic succinimide ester (2.0 g, 5.4 mmol) in 20 ml of anhydrous DCM. The reaction mixture was left to react at room temperature in the dark for 60 h. Then the silicon wafers were recovered from the reaction mixture and repeatedly washed with DCM, acetone in an ultrasonic bath and dried under a stream of clean nitrogen.

2.5. Formation of PMMA brushes via surface RAFT polymerization

A RAFT agent-immobilized silicon wafer was placed into a reaction flask with MMA (25 mmol), toluene (2 ml), AIBN (0.01 mmol), and free RAFT agent 4-(4-cyanopentanoic acid) dithiobenzoate (0.05 mmol). The flask was sealed under a

Table 1
Polymerization data and the surface analysis results of the MMA graft polymerized on silicon substrate via RAFT polymerization[a, b]

Sample	Time (h)	$M_{n,GPC}\times 10^{-4}$ (g/mol)	$M_{w,GPC}\times 10^{-4}$ (g/mol)	PDI[c]	Film thickness (nm)	Contact angle[d], θ(°)
Silicon–OH	–	–	–	–	0.4±0.1	2
Silicon–APTES	–	–	–	–	1.5±0.1	68
Silicon–S(C═S)R	–	–	–	–	1.8±0.1	66
Silicon–PMMA(1)	8	1.06	1.42	1.34	15.3±0.5	70
Silicon–PMMA(2)	16	1.46	1.90	1.30	18.2±0.5	72
Silicon–PMMA(3)	24	1.82	2.31	1.27	20.6±0.5	72

[a] We assume that the grafted polymers have the same molecular weights and polydispersities as the "free" polymer produced in solution.

[b] Polymerization condition: [AIBN]/[RAFT agent]/[MMA] = 1:5:2500.

[c] PDI: molecular weight distribution is calculated from M_w/M_n.

[d] Contact angle of water at room temperature on the substrate.