Progress in Organic Coatings 97 (2016) 122–132

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Synthesis of fluorinated block copolymer and superhydrophobic cotton fabrics preparation

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ARTICLE INFO

Article history:
Received 17 November 2015
Received in revised form 1 April 2016
Accepted 1 April 2016

Keyword:
Fluorinated block copolymer (FPGs)
ATRP
Superhydrophobic
Durability

ABSTRACT

Fluorinated block copolymers, hexafluorobutyl methacrylate-block-poly(glycidyl methacrylate) (HFBMA-*b*-PGMAs, FPGs) were synthesized by atom transfer radical polymerization (ATRP) and applied to fabricating hydrophobic cotton fabrics. Since the HFBMA block provided low surface free energy and the PGMA blocks served as anchors with cotton fibers, the FPGs modified cotton fabrics showed excellent water repellency. The results indicated that nano- and microscale rough structures were created with combining HFBMA blocks onto surfaces of micro-sized cotton fibers. Since the HFBMA blocks were chemically bound to the cotton fibers by epoxy groups of PGMA blocks, the modified cotton fabrics possessed long-term high stability and durability. Furthermore, the important cotton fabric parameters such as tensile strength, color, and haptics were all unaffected by the FPGs modification, which revealed potential for applications.

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1. Introduction

Block copolymers consist of two or more different blocks arranged in a random or alternating sequence have unique microphase separation and aggregation properties, which result in their widespread applications as adhesives, surfactant, emulsifiers, barrier materials, impact modifiers, and materials for gene and drug delivery [1–5]. Besides the common properties of block copolymers, fluorinated block copolymers have low surface energy, superior oil and water repellence as well as low dielectric constant, and have attracted significant attention over the past few decades [6–11].

Many techniques have been used to synthesize well-defined block copolymers, atom transfer radical polymerization (ATRP) as one of the most significantly important methods has been employed in the synthesis of a wide range of block copolymers with narrow polydispersity index, architectures, functionalities and well-defined compositions [12–16]. The common usage is a sequential preparation of nonfluorinated segment followed by the ATRP polymerization with fluorinated monomers. Although there are many approaches for the synthesis of fluorinated block copolymers by ATRP, the polymerization with nonfluorinated monomers based on fluorinated macroinitiator has still been few reported [17–19].

Fluorinated blocks behaved a number of unique properties including hydrophobicity and low surface energy, as well as high chemical and thermal resistance are very interesting and promising, and they have been broadly applied to high-performance paint and varnish in the textile, paper, leather, construction, automotive and aerospace industries, optics, and microelectronics [20–24]. Up to the present, commercial products of fluorinated acrylates are mainly random copolymers, and the fluorinated units are distributed randomly in polymer backbone, so the fluorine effect on the surface free energy cannot get the best. It was found that the efficiency of fluorine could also be maximized by anchoring the fluorinated group at the end of the molecular chain [25–28]. Therefore, in order to achieve desirable surface properties, design and rearrange the molecular structure is an effective approach. Fluorinated acrylates are one of the most widely used fluorides. Converting them into initiators will both widen the initiators used for ATRP and introduce its excellent properties to the copolymers. Sun et al. synthesized a new fluorinated macroinitiator of hexafluorobutyl methacrylate-Br and prepared series of fluorinated block copolymers with different fluorine contents from the macroinitiator by the AGET ATRP [27].

Coating hydrophilic cotton fabrics with hydrophobic moieties may turn the fibers superhydrophobic, and have attracted great interest within the scientific community and industry for their

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http://dx.doi.org/10.1016/j.porgcoat.2016.04.001
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unique characteristics such as self-cleaning, antifouling, and drag reduction [29–35]. The simplest method to coat cotton fabrics is to polymerize hydrophobic monomers and crosslink the resultant polymers around the cotton fibers. If a suitable block copolymer both have anchor group and hydrophobic segment, the anchoring group would be covalently linked to the cotton fibers and the other hydrophobic block would render the desired water-repellency to the textile. A latest research indicated that fluorinated block copolymer contained poly(glycidyl methacrylate) (PGMA) block behaved excellent superhydrophobic property, and PGA block served as an anchor and formed covalent bonds with the surfaces of cotton fibers [36].

Based on the above considerations, in this paper, a new macroinitiator of HFBMA-Br, and series of well-defined fluorinated diblock copolymers of poly 2,2,3,4,4,4-hexafluorobutyl methacrylate-block-poly(glycidyl methacrylate)(HFBMA-*b*-PGMA, FPGs) were prepared by ATRP. The surface properties of FPGs modified cotton fabrics were also studied. The results showed that the cotton fabrics coated with FPGs exhibited excellent superhydrophobic property, and the method demonstrated in this paper might has potential application prospect for the superhydrophobic surface fabrication.

2. Experimental

2.1. Materials

2,2,3,4,4,4-Hexafluorobutyl methacrylate (HFBMA) was purchased from Aladdin Reagent Co., Ltd., China. Hydrobromic acid in acetic acid (44 wt%) was supplied Alfa Aesar. Glycidyl methacrylate (GMA) was purchased from Aladdin Reagent Co., Ltd., China, and purified by passage through acolumn of alumina powder to remove the inhibitor before it was vacuum-distilled and stored in a refrigerator prior to usage. Cuprous bromide (CuBr) was purchased from Aladdin Reagent Co., Ltd., China, and stirred in acetic acid at 80 °C for 24 h, washed three times with methanol, then dried under vacuum overnight at room temperature before use. *N*,*N*,*N*,*N*-pentamethyldiethylenetriamine (PMDETA) was purchased from Sigma-Aldrich. Cyclohexanone, diphenyl ether, dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane(CH_2Cl_2), diethyl ether, and hexane were all analytical grade and used as received.

2.2. Synthesis of bromo-terminated HFBMA initiator (HFBMA-Br)

HFBMA-Br was synthesized by the reaction of HFBMA and excess hydrobromic acid in acetic acid. A typical procedure is described as follows: HFBMA (2.5 g) and hydrobromic acid in acetic acid (24.2 g) were put into a flask with an apparatus for dealing with tail gas, the reaction mixture was stirred at 20 °C for 24 h, the products were extracted by water and CH_2Cl_2, neutralized the pH of the oil liquid with sodium carbonate then dried over anhydrous magnesium sulfate. The crude product was isolated as a slight yellow liquid after removed from the solvent and then concentrated by rotary evaporator. The concentrated liquid purified by silica gel column chromatography using ethyl acetate/petroleum ether (1:5 v/v) as the eluent. After removed the solvents by a rotary evaporator and dried in vacuum oven at 40 °C for 24 h. HFBMA-Br was obtained as a slight yellow liquid at a yield of 23%. ^1H NMR (400 MHz, $CDCl_3$, δ): 4.85–5.01 (H, -C*H*F), 4.49–4.51 (2H, -OC*H*$_2$-), 3.52–3.55 (2H, -C*H*$_2$Br), 2.97–3.02 (1H, -C*H*), 1.34–1.35 (3H, -C*H*$_3$).

2.3. Synthesis of HFBMA-terminated PGMA copolymers (FPGs)

HFBMA-terminated PGMA copolymers, HFBMA-PGMA$_{10}$ (FPG$_1$), HFBMA-PGMA$_{20}$ (FPG$_2$) and HFBMA-PGMA$_{30}$ (FPG$_3$) were prepared via ATRP by using HFBMA-Br as the macroinitiator and CuBr/PMDETA as the catalyst system. A typical procedure for HFBMA-PGMA$_{10}$ is described as follows: the schlenk tube was purged with dry argon for 30 min, then degassed diphenyl ether (5.0 mL), HFBMA-Br (0.33 g), GMA (1.42 g) CuBr (0.143 g) were added to the schlenk tube, degassed via three freeze-thaw-pump cycles and back-filled with argon. Then degassed PMDETA (0.347 g) was injected into the flask using a degassed syringe, and the tube was then immersed in a preheated oil bath at 30 °C for 2 h. The experiment was stopped by immersing the tube into liquid nitrogen and then exposing the contents to air. The resultant viscous reaction mixture was diluted with CH_2Cl_2 (50 mL) and passed through a short neutral alumina column (200 mesh) in order to remove copper catalyst. The filtrate was subsequently added into cold hexane to precipitate the polymer. It was redissolved in CH_2Cl_2 and precipitated into hexane again. The precipitate was dried under vacuum for 10 h to yield 1.33 g of PGMA$_{50}$ in a 94% yield. HFBMA-PGMA$_{20}$ (FPG$_2$) and HFBMA-PGMA$_{30}$ (FPG$_3$) were prepared analogously, except the use of different GMA to initiator molar ratios (HFBMA-PGMA$_{20}$ with molar ration 20:1, and HFBMA-PGMA$_{30}$ with molar ration 30:1).

2.4. Cotton fabrics modification with FPGs

In a typical procedure, 20 mL of FPGs in THF at 1 mg mL^{-1}, 5 mg mL^{-1} and 10 mg mL^{-1} separately, with 50 μL of TEA and 0.02 g of benzyltrimethylammonium chloride were all loaded into a flask, then cotton fabrics (3.0 cm × 2.5 cm) were sealed and stirred at 60 °C for 30 min. Subsequently, the cotton fabrics were removed from the flask and rinsed three times with enough THF. The resulting cotton fabrics were first naturally dried at room temperature in desiccator, then dried in an oven at 100 °C for 2 h. All of the modified cotton fabrics described in this study was treated similarly.

2.5. Characterization

The FT-IR spectra were recorded on a Nicolet 5100 spectrometer by potassium bromide (KBr) sample holder method in the fundamental region of 400–4000 cm^{-1}. ^1H NMR spectra were obtained on a Bruker DMX-400 spectrometer. Deuterated chloroform ($CDCl_3$), or deuterated dimethyl sulfoxide (DMSO-d_6) was used as the solvent. The number average molecular weights (Mn), the weight average molecular weights (Mw), and polydispersity index (Mw/Mn) values of the polymers were determined at 30 °C using a Waters 1515 size exclusion chromatography (SEC) system equipped with a Waters 2414 refractive index (RI) detector, and monodispersed polystyrene (PS) was used as standards. DMF solution was used as eluent, and passed through a 0.45 mm Polytetrafluoroethylene (PTFE) filter before analysis. The energy disperse spectroscopy (EDS) and surface morphologies of the original cotton fabrics were characterized with a scanning electron microscope (SEM, Hitachi, S-4800) that was operated at an accelerating voltage of 2.0 kV. The samples were affixed onto an aluminum SEM-holder and coated with a thin layer of gold before observation. Atomic force microscopy (AFM) measurement was performed using a Multimode 8 SPM AFM system (Bruker, USA) using the ScanAsyst TM mode. The samples were fixed onto the surface of an AFM-holder. X-Ray photoelectron spectroscopy (XPS) measurement was performed using a Surface Science Instruments X-ray Photoelectron Spectrometer/ESCA (ESCALAB 250, produced by Thermo Fisher Scientific), which was operated at a base pressure of 2×10^{-9} mbar. The samples were irradiated with monochromatic Al Ka X-rays using an elliptical X-ray spot size of 500 mm and a power of 15 KV and 150 W. The standard take-off angle used for this analysis was 58, which produced a maximum analysis depth in the range of 1–5 nm.

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