

# Synthesis and characterization of poly(dimethylsiloxane)-block-poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate) diblock copolymers with low surface energy prepared by atom transfer radical polymerization

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## Abstract

Well-defined poly(dimethylsiloxane)-block-poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate) (PDMS-b-PHFBMA) diblock copolymers are synthesized via atom transfer radical polymerization (ATRP). The chemical composition and structure of the copolymers are characterized by nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) spectroscopy, and molecular weight measurement. Gel permeation chromatography (GPC) is also used to study the molecular weight distributions of the PDMS-b-PHFBMA diblock copolymers. The microstructure of the resulting copolymers is investigated by transmission electron microscopy (TEM). The results of TEM show that the diblock copolymers are microphase-separated if the bulk contains enough PHFBMA segments. The effect of fluorine content on the surface energy and the bulk structure is investigated by static water contact angle. Surface energy of PDMS-b-PHFBMA films is indirectly obtained from contact angle.

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**Keywords:** ATRP; PDMS-b-PHFBMA; Low surface energy; Microphase-separated structure

## 1. Introduction

Surface energy is one of the most important properties of polymers, and influences the wettability, adhesion properties, and friction properties of materials. Due to their special properties [1–4], low surface energy materials can be used in indus-

trial and commercial products, such as breathable textiles, non-wettable and nonstick materials, and antifouling coatings. Siloxane polymers and fluorinated polymers are two families of low surface energy materials. There are many ways to prepare these materials, such as anionic polymerization [5,6], group transfer polymerization (GTP) [7–9], cationic polymerization [10], and free radical polymerization [11–15]. Among them, living polymerization is a route by which to synthesize block copolymers [16], graft copolymers [17], telechelic

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polymers [18,19], and star polymers [20–22]. Living anionic polymerization has been the most extensively investigated form of living polymerization. Although the living anionic polymerization of non-polar monomers, such as butadiene and styrene, has been successfully commercialized, the need for high-purity monomers, solvents, and other reagents, requiring low temperatures and the side reaction show that living anionic polymerization of acrylic monomers would have little commercial success. ATRP is a pseudo-living radical polymerization, that is the most ideal for preparing well-defined acrylate copolymers. It has been intensely searched since its discovery in 1995 [23,24] due to its ability to control polymer architecture, molecular weight and molar mass distribution, moderate experimental condition, and its applicability to a wide range of monomers [25,26].

Siloxane polymers are highly flexible, giving them a low glass transition temperature ( $T_g$ ), high dielectric strength, low surface tension and energy, high gas permeability [27], and thermal and oxidative stability. Unfortunately, the mechanical and resistance properties to organic solvents, acids, and bases are poor [28–30]. Moreover, fluorinated polymers have some outstanding properties, and so they have become more favored. The particular merits of the fluorinated polymers include high thermal, chemical, aging, and weather resistance [31], oil and water repellency, excellent inertness, low flammability, and a low refractive index [32–36]. The application of fluorinated polymers has been greatly limited due to high price [37]. Recently, increasing attention has been paid to the combined incorporation of siloxane moieties and fluorinated groups into synthetic materials. The comprehensive properties of these materials which possess advantages from both siloxane and fluorinated polymers are better, including weather resistance, low surface energy, chemical resistance, and so on [38–41].

In previous literature, fluorosilicone polymers have been achieved mainly by two approaches: by fluorinating siloxanes, or by copolymerizing vinyl monomers containing fluorinated alkyl side groups and siloxane moieties [33,42–45]. In this paper, we use a polydimethylsiloxane macroinitiator to initiate polymerization of methacrylate monomers with fluorinated side groups to prepare fluorosilicone polymers. Although the block copolymerization of fluoroalkyl (meth)acrylates with macroinitiator had already been reported [46], the polydimethylsiloxane macroinitiator has never been

used to synthesize fluorosilicone polymers. To get diblock copolymers with a low surface energy, we design novel PDMS-*b*-PHFBMA diblock copolymers, which are then synthesized by ATRP to establish a well-defined structure. We use bromine end-capped polydimethylsiloxane (PDMS-Br) as the macroinitiator to initiate 2,2,3,3,4,4,4-heptafluorobutyl methacrylate polymerization. In the vein of molecular design, PDMS-*b*-PHFBMA diblock copolymers belong to low surface energy polymers. Accordingly, the corresponding surface properties of diblock copolymers are also investigated in this paper. PDMS-*b*-PHFBMA diblock copolymers with low surface energy can be applied as a potential anti-fouling coating.

## 2. Experimental

### 2.1. Materials

Monocarbinol-terminated polydimethylsiloxane (PDMS-OH) and 2-bromo-2-methyl-propionylbromide (98%) were obtained from A Better Choice for Research Chemicals GmbH & Co. KG (ABCR), with the former having an average molecular weight of 5000 g/mol. Triethylamine was supplied by Sinopharm Chemical Reagent Co, Ltd. (SCRC, 99%) and stored over 4-Å molecular sieves. *N*-Propylamine (98%) and pyridine-2-carboxaldehyde (99%) were obtained from ABCR GmbH & Co. KG. 2,2,3,3,4,4,4-Heptafluorobutyl methacrylate (HFBMA, 98%) purchased from Lancaster was washed with 5% aqueous NaOH solution to remove the inhibitor. Copper(I) bromide (98%) obtained from Aldrich was purified according to the method of Keller and Wyc-off [47]. All other reagents and solvents were obtained from SCRC and used without further purification.

### 2.2. Measurements

Fourier transform infrared (FTIR) spectra were obtained on an Avatar 360 FTIR spectrophotometer by a liquid sample. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) was performed on a Bruker AV400 instrument with deuterated chloroform as the solvent. Gel permeation chromatography (GPC) was performed using THF as the eluent at a flow rate of 1 mL/min with a polystyrene standard as the reference. The morphology of the PDMS-*b*-PHFBMA diblock copolymers was observed by transmission electron microscopy (TEM). The equi-

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