



# Syntheses and morphologies of fluorinated diblock copolymer prepared via RAFT polymerization



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## ABSTRACT

Block copolymers (BCPs) consisting of fluorinated and non-fluorinated blocks can show interesting morphology, because of the presence of two dissimilar blocks. In this investigation BCPs of methyl methacrylate (MMA) and 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA), (PMMA-*b*-PHFBA) were synthesized via reversible addition fragmentation chain-transfer (RAFT) polymerization using 2-cyano-2-propyl dithiobenzoate (CPBT) as chain transfer agent (CTA). Gel permeation chromatography (GPC) and <sup>1</sup>H NMR analyses confirmed the synthesis of well-defined BCP. TEM and XRD analyses showed lamellar stacking in the BCP. Surface morphology and topography of the BCP were analyzed by SEM and AFM analyses. The morphology of the BCP in THF and methyl ethyl ketone (MEK) solvent mixture was studied by TEM analysis. Morphology of the BCP varied from lamellar to spherical micelles with the variation of THF-MEK ratio in the solution, as evidenced by TEM and DLS analyses.

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## 1. Introduction

Block copolymers (BCPs) are interesting materials with distinct phase separated morphologies. BCPs are composed of different polymer chains bonded in different ways like linear, branched, star etc. [1]. The properties of the BCPs depend on the length of different blocks as well as the nature of the different blocks like soft-hard, hydrophilic-hydrophobic, oleophilic-oleophobic etc. The different polymeric architecture of BCPs can form variety of ordered structures and morphologies. The self-assembled micro-domains and phase separated morphologies of the BCPs make them applicable as surface modifying agents [2,3]. The micro-domain structures can be tuned by changing the block length of the BCPs and also by changing the solvents according to the solubility parameters of the respective blocks [4]. Nanophase separated BCPs have ordered morphologies. BCPs have potential applications in numerous fields; like, in shape memory materials, surface coating, nanotechnology and drug delivery [5–9]. The industrial applications of BCPs are in thermoplastic elastomers (TPEs), foams, adhesives, shoe soles, paints and coatings.

BCPs have the ability to self-assemble into organized micro domain structures in suitable solvents [10–12]. Crystallization within the BCP micro domain is an important issue, since it can

change the block copolymer morphology. The structural development of BCPs depends on micro phase separation and micro domain crystallization [13–15]. The simplest class of BCP is linear diblock copolymer (AB). Being composed of two immiscible blocks, A and B, they can adopt the following equilibrium microphase morphologies, basically as a function of composition; spheres, cylinders, double gyroid, lamellae etc. [13–16].

Till the development of controlled radical polymerization (CRP) in 1990s, BCPs were usually prepared by living ionic polymerizations [1], which require very stringent reaction conditions like, low temperature, complex reaction set-up and ultrapure solvents as well as monomers. Recent advances in CRP techniques like, atom transfer radical polymerization (ATRP) [17–20], iodine transfer polymerization (ITP) [21–27], nitroxide mediated polymerization (NMP) [28–30], reversible addition fragmentation chain-transfer (RAFT) polymerization [31–35] etc. help in synthesizing different types of copolymers (diblock, triblock, star etc.) of varying architectures and block length. They are tolerant to adventitious impurities and can be carried out at wide range of temperatures. RAFT polymerization has been found to be very versatile process for the polymerization of fluoroacrylates [36]. There are several reports on the synthesis of fluorinated copolymers like random, graft and block copolymers [37–46].

Fluoropolymers have unique properties due to the presence of electronegative fluorine atoms in the main chain or in the pendant group [47]. The poly(fluoro acrylates) have hydrophobic and

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lipophobic property, because of the strong electronegativity of the fluorine atom and the helical chain structure of the fluorinated pendant group [48]. Furthermore, poly(fluoro acrylate) BCPs exhibit unique surface properties like low surface energy, excellent thermal and chemical resistance, low refractive index, low dielectric constant etc. [40,47–50]. For these reasons poly(fluoro acrylate)s are widely used in different applications like surface active agents, surface coatings, as additives etc. [37]. In the BCPs of fluorinated and non-fluorinated polyacrylates there is thermodynamic incompatibility which leads to the self-organization through micro phase separation between the two blocks [13]. These BCPs have applications in photonics optical materials, organic printed electronics and low refractive index polymer for cladding layer in optical wave guides.

2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) is an interesting fluoroacrylate monomer which has long fluoro alkyl pendant group [51]. In this investigation, we have reported the synthesis of BCP of 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) and methyl methacrylate (MMA) via RAFT polymerization and studied the bulk morphology using TEM, SEM, AFM and XRD analyses. The morphology of this hydrophobic and oleophilic BCP in a mixture of solvents has also been studied by using TEM analysis. To the best of our knowledge there is no report on the preparation and morphological study of the BCPs of HFBA and MMA via RAFT polymerization.

## 2. Experimental

### 2.1. Materials

2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) and methyl methacrylate (MMA) were purchased from Sigma–Aldrich, USA, and were purified by vacuum distillation. Initiator, 2,2'-azobisisobutyronitrile (AIBN) and the RAFT reagent, 2-cyano-2-propylbenzodithioate (CPBT) were purchased from Sigma–Aldrich, USA and were used as received. The solvent, 1,4-dioxane was purified by passing through alumina column prior to use. Tetrahydrofuran (THF) and methyl ethyl ketone (MEK) were purchased from Merck and were distilled prior to use. The solvent n-hexane was purchased from Merck and was used as such.

### 2.2. Characterization

The molecular weight and dispersity ( $\bar{D}$ ) of the polymers were determined by Gel Permeation Chromatography (GPC) using a Viscotek GPC equipped with a RI detector (model VE 3580). Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 ml/min. Linear and narrow disperse poly(methyl methacrylate) (PMMA) was used as calibration standard.

$^1\text{H}$  NMR spectra of the polymers were recorded on a Bruker 200 MHz nuclear magnetic resonance (NMR) instrument using  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as internal standard.

FT-IR spectra of polymer were carried out using a Perkin-Elmer, Inc. version 5.0.1 spectrophotometer. The polymer sample in chloroform was film cast onto KBr cells and then the IR spectra were recorded. FT-IR spectra were recorded in the range of 4000–400  $\text{cm}^{-1}$ .

DSC analysis was carried out using TA Instrument (DSC Q100 V8.1 Build 251) under nitrogen atmosphere at a heating rate 10  $^\circ\text{C}/\text{min}$  within a temperature range of  $-100^\circ\text{C}$  to  $+180^\circ\text{C}$ .

Scanning Electron Microscopy (SEM) analysis of the BCP film was performed on JEOL JSM5800 (JEOL, Japan) scanning electron microscope with Oxford EDS Detector. The microscope has tungsten hairpin filament and a maximum acceleration voltage of 30 kV. Before analysis the polymer film was coated by gold sputtering to avoid the charging mechanism.

The morphology of the BCP in bulk and in different mixture of solvents was studied by TEM (Analytical TEM: FEITM, USA, Type 5022/22, Technai G2 20 S-Twin) operated at an accelerated voltage of 120 kV. For the bulk morphology the BCP film was ultra-microtomed to a size of 300 nm and was placed on carbon coated copper grid for analysis. For morphology, the polymer film was dissolved in THF-MEK solvent mixture and was drop-cast on 300 mesh carbon coated copper grid. The grids were quickly dried by keeping the grid on a hot plate at 60  $^\circ\text{C}$ .

The X-ray diffraction analysis was performed using a Rigaku Dmax 2500 diffractometer with a Co target (0.179 nm) at room temperature. The system consisted of a rotating anode generator, operated at 40 kV and 30 mA current and a wide angle goniometer. The samples were scanned at  $2\theta$  of  $2^\circ$  to  $40^\circ$  at the step scan mode (step size  $0.03^\circ$ , preset time 2 s), and the diffraction pattern was recorded using a scintillation counter detector.

The phase morphology of BCPs was obtained using AFM (Agilent Technologies, USA) Model: Multiview-1000<sup>TM</sup>; 70  $\mu\text{m}$  AFM/NSOM scanner equipped with Nd: YAG Laser. Prior to AFM analysis the block copolymer solution in THF/MEK mixture was cast on cleaned silicon wafers. The silicon wafers of [100] orientation was cut into pieces followed by cleaning in 1,2-dichloromethane in ultrasonic bath for 15 min, washed several times with Millipore water, dried under argon flow. Afterwards, the BCP solution was cast onto the silicon wafers. They were dried under hood, annealed under solvent vapor of THF/MEK (4:1 v/v) mixture and the AFM images were recorded. The phase morphology was imaged using AFM in tapping mode using silicon cantilevers. Each sample was scanned at three different locations on the grid.

The particle size of the block copolymer micelles was determined by dynamic light scattering (DLS). The DLS analysis was carried out on a Zetasizer Nano ZS90 (Malvern instrument, UK) using a 4 mW He-Ne laser ( $\lambda = 632.8 \text{ nm}$ ). The detector angle is fixed at  $90^\circ$ .

### 2.3. Synthesis of PMMA-macro RAFT agent using 2-cyano-2-propyl dithiobenzoate (CPBT) as RAFT agent

The RAFT agent, CPBT (23.9 mg, 0.10 mmol) and 1,4-dioxane (2 mL) were introduced into the Schlenk tube equipped with a stirring bar and under nitrogen atmosphere. MMA, monomer (2.7 g, 27 mmol) was added to the mixture. Finally, AIBN (4.4 mg, 0.027 mmol) dissolved in a small amount of solvent (1.4 dioxane) was added into the reaction tube under nitrogen atmosphere. The reaction tube was heated at 70  $^\circ\text{C}$  under constant stirring for 8 h. The polymer obtained was dissolved in THF and was purified by precipitation into hexane. Conversion = 81%,  $M_{n,GPC} = 18,500 \text{ g/mol}$  and  $\bar{D} = 1.18$ . This PMMA was used as macro-RAFT agent for the synthesis of BCP with HFBA.

### 2.4. Preparation of block copolymers of poly (methyl methacrylate) and poly (2,2,3,3,4,4,4-heptafluorobutyl acrylate) (PMMA-b-PHFBA) using PMMA as macro-RAFT agent

In a typical recipe, for the preparation of block copolymer containing poly (methyl methacrylate) (PMMA) and poly (2,2,3,3,4,4,4-heptafluorobutyl acrylate) (PHFBA), PMMA macro-RAFT agent (0.11 g, 0.006 mmol) ( $M_{n,GPC} = 18,500 \text{ g/mol}$ ) was dissolved in 1,4-dioxane (4 mL) in a Schlenk tube. The monomer, HFBA (470 mg, 1.87 mmol) and the initiator, AIBN (0.97 mg, 0.006 mmol) were added subsequently to the Schlenk tube under nitrogen atmosphere. Finally, the Schlenk tube was plunged into the oil bath preheated at 80  $^\circ\text{C}$ . The reaction was carried out for 9 h. Conversion = 63%,  $M_{n,GPC} = 57,400 \text{ g/mol}$  and  $\bar{D} = 1.23$ . Similarly

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