



# Thermally switchable thin films of an ABC triblock copolymer of poly(*n*-butyl methacrylate)-poly(methyl methacrylate)-poly(2-fluoroethyl methacrylate)

Shanju Zhang<sup>a,1</sup>, Zhan Liu<sup>a</sup>, David G. Bucknall<sup>a,\*</sup>, Lihong He<sup>b</sup>, Kunlun Hong<sup>b</sup>, Jimmy W. Mays<sup>b</sup>, Mark G. Allen<sup>c</sup>

<sup>a</sup> School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, United States

<sup>b</sup> Center for Nanophase Materials Sciences and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

<sup>c</sup> School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0765, United States

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## ABSTRACT

The thermo-responsive behavior of polymer films consisting of novel linear triblock copolymers of poly(*n*-butyl methacrylate)-poly(methyl methacrylate)-poly(2-fluoroethyl methacrylate) (PnBuMA-PMMA-P2FEMA) are reported using differential scanning calorimetry (DSC), atomic forcing microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and contacting angle (CA) measurements. The surface morphology, wettability and chemical structure of thin films of these triblock copolymers on silicon wafers as a function of temperature have been investigated. It has been shown that the wettability of the films is thermally switchable. Detailed structural analysis shows that thermo-responsive surface composition changes are produced. The underlying mechanism of the thermoresponsive behavior is discussed.

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## 1. Introduction

Design of a polymer surface layer can produce a predictable surface response under defined conditions. The latest advances in this area have resulted from the on-going search for smart surfaces which display two distinct surface properties, such as switching between hydrophobic or hydrophilic, acidic or basic, conductive or non-conductive and adhesive or repellent [1–7]. These smart surfaces possess interfacial properties that are capable of undergoing reversible changes under the influence of an external stimulus such as temperature, pH, light, or electrical fields. Intensive studies in this area of adaptive or responsive surfaces have led to a number of different approaches, forefront of which has been the use of a wide variety of functional polymers [8], polymer blends [9], block copolymers [10] and polymer brushes [11].

The micro-phase separation in block copolymers leads to a rich variety of nanostructures depending on the number of constitutive blocks and their relative volume fraction [12–14]. The ordering or orientation of the domains of the blocks and there-

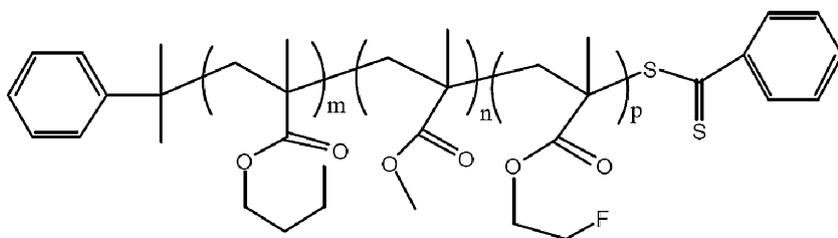
fore the resulting surface composition of the films is influenced by preferential surface interactions [15–18]. Preferential segregation of the blocks to a substrate as well as a free surface occurs due to the surface energy differences of the respective components. Utilization of this property has been used in creating, for example, stimuli responsive thin films of diblock copolymers consisting of hydrophilic and hydrophobic blocks [19–21]. In the dry state the lower surface energy hydrophobic component migrates to the air surface and the hydrophilic component to the substrate. Upon exposure to water there is a reconstruction of the film and at equilibrium the hydrophilic blocks are present on the surface.

Thermo-responsive smart surfaces of block copolymers have attracted ever-increasing attention in the past decade because of their potential applications in sensors, drug delivery, microfluidics and actuators. *N*-substituted poly(acrylamides) based block copolymers are the most studied thermo-responsive polymers [2,22]. In water, the *N*-substituted poly(acrylamides) block undergoes a coil-to-globule transition as the temperature increases around the lower critical solution temperature (LCST). Below the LCST, the polymer chains form extended conformations due to their hydrogen bonding with water via the amide groups. Above the LCST, the amide-water hydrogen bonds are disrupted and polymer chains collapse into a globule. It is found that the content of hydrophobic blocks can significantly affect the thermo-responsiveness [22].

\* Corresponding author. Tel.: +1 404 894 2535; fax: +1 404 894 8780.

E-mail addresses: [shanju.zhang@yale.edu](mailto:shanju.zhang@yale.edu) (S. Zhang), [bucknall@gatech.edu](mailto:bucknall@gatech.edu) (D.G. Bucknall).

<sup>1</sup> Current address: Yale University, New Haven, CT 06511, United States.



Scheme 1.

In this work, we demonstrate thermo-responsive behavior of thin films consisting of the novel triblock copolymer of poly(*n*-butyl methacrylate)-poly(methyl methacrylate)-poly(2-fluoroethyl methacrylate). The surface components and structures of triblock copolymer films at different temperatures are investigated by means of atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and contacting angle (CA) measurements.

## 2. Experimental

The PnBuMA–PMMA–P2FEMA triblock copolymers (Scheme 1) were synthesized using reversible addition-fragmentation chain transfer (RAFT) polymerization. The details of the synthesis can be found elsewhere [23].

The structures of block terpolymers were confirmed by  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR. The resonance peaks of the methylene groups from PnBuMA, PMMA and P2FEMA blocks were identified, respectively, in  $^1\text{H}$  NMR spectroscopy, while the resonance peak of the fluorine group was identified in  $^{19}\text{F}$  NMR spectroscopy. Detailed structural characterization can be found in our recent paper [23].

Thin films of the triblock copolymers were prepared by spin-coating from 2 wt.% solutions in tetrahydrofuran (THF) on to silicon wafers at 3000 rpm. All films were dried under vacuum for 24 h. The dried films were annealed in vacuum at different temperatures for 1 h. After heat-treatment, the films were rapidly moved onto a cold metal plate in order to quench the structure to room temperature.

DSC measurements (TA-Q200) were carried out using a scanning rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. The surface morphology and structure of polymer films were studied using atomic force microscopy (Pacific Nanotechnology) operated in a tapping mode under ambient conditions. Images of each sample were recorded in both height- and phase-contrast modes. X-ray photoelectron spectroscopy (XPS) analysis was performed using a model SSX-100 photoelectron spectrometer (Surface Science Instruments) with Al  $K\alpha$  radiation (1486.6 eV). Static contact angles were measured by the sessile drop method using a VCA-Optima surface analysis system (AST Products, Inc.) at room temperature, with water drops (1  $\mu\text{l}$ ) applied to the polymer surfaces using a micro-liter syringe.

## 3. Results and discussion

The data for molecular weights, polydispersity and glass transition temperatures of homopolymers, diblock copolymers and triblock copolymers used in the experimental studies are shown in Table 1. The typical DSC curves are shown in SI-Figure 1. The diblock copolymer PnBuMA–PMMA showed two glass transition temperatures ( $T_g$ ) at  $\sim 33^\circ\text{C}$  and  $\sim 120^\circ\text{C}$ , corresponding to the soft PnBuMA region (low  $T_g$ ) and the hard PMMA region (high  $T_g$ ). The triblock copolymer PnBuMA–PMMA–P2FEMA also exhibited two  $T_g$ 's at  $\sim 33^\circ\text{C}$  and  $\sim 105^\circ\text{C}$ . The  $T_g$  at  $\sim 33^\circ\text{C}$  as for the diblock copolymer is associated with the soft PnBuMA phase-rich region and the  $T_g$  at  $\sim 105^\circ\text{C}$  is from the hard PMMA–P2FEMA regions. Only

one  $T_g$  at  $\sim 105^\circ\text{C}$  was obtained for the PMMA–P2FEMA blocks, indicating miscibility between PMMA and P2FEMA blocks. This result is consistent with blend miscibility of P2FEMA and PMMA homopolymers [24].

PMMA and PnBuMA are known to show an upper critical solution temperature (UCST) phase behavior [25], whilst PMMA and P2FEMA blends show LCST behavior [24]. P2FEMA is known to be totally immiscible with PnBuMA [24]. This combination of phase behaviors potentially provides this ternary polymer system with completely reversible thermally controlled morphology. Since the UCST and LCST for these polymers are  $160^\circ\text{C}$  and  $230^\circ\text{C}$ , respectively [24,25], we treated the films of the triblock copolymer PnBuMA–PMMA–P2FEMA at  $100^\circ\text{C}$  and  $250^\circ\text{C}$  for investigating effect of temperature on the surface composition.

Fig. 1 shows typical tapping-mode AFM height mode images from the triblock copolymer films on the silicon wafer with different thermal histories. The as-prepared thin film showed a honeycomb-like morphology (Fig. 1a), which is attributed to the fast solvent evaporation during the spin-coating. The average surface roughness over an area of  $5\ \mu\text{m} \times 5\ \mu\text{m}$  of the film was 9.8 nm. When the films were annealed at an elevated temperature, the increase in chain mobility allows block copolymer microphase separation to occur. Since silicon forms a silicon dioxide layer when in contact with air, the PMMA block will migrate to the substrate due to the higher polarity of PMMA compared to PnBuMA and P2FEMA [26]. After thermal annealing for one hour at  $100^\circ\text{C}$  and  $250^\circ\text{C}$ , respectively, the films were quenched to room temperature. The quenched surfaces of the films at  $100^\circ\text{C}$  and  $250^\circ\text{C}$  exhibited similar morphologies consisting of flat terraces with holes of different lateral sizes ranging between 200 nm and 600 nm (Fig. 1b and c). This morphology corresponds to the typical morphology of the block copolymer forming lamellae parallel to the surface [27–29]. This is expected, since this phenomenon is analogous to that observed for a diblock copolymer lamella with preferential surface segregation [30]. The holes appeared in the lamella because the film thickness is not commensurate with the lamella period dimension. The typical height image analysis is shown in SI-Figure 2. The average surface roughness over an area of  $5\ \mu\text{m} \times 5\ \mu\text{m}$  of the film after annealing is reduced to 3.8 nm.

The thermo-responsibility of the polymer film was investigated through determination of the wettability of the thin films quenched from  $100^\circ\text{C}$  and  $250^\circ\text{C}$  using the water contact angle (WCA) measurements. The surface phase reconstruction is expected to result in differences in surface energies, depending on the chemical

**Table 1**  
Characterization of homopolymers, diblock copolymers and triblock copolymers.

Polymers	$M_n$ (g mol $^{-1}$ )	$M_w$ (g mol $^{-1}$ )	$M_w/M_n$	$T_g$ ( $^\circ\text{C}$ )
PnBuMA	19,900	23,600	1.18	32
PMMA	19,390	20,810	1.07	121
P2FEMA	13,000	–	–	90
PMMA–P2FEMA	40,000	–	–	105
PnBuMA–PMMA	42,000	49,300	1.18	33/120
PnBuMA–PMMA–P2FEMA	58,200	93,800	1.61	34/105

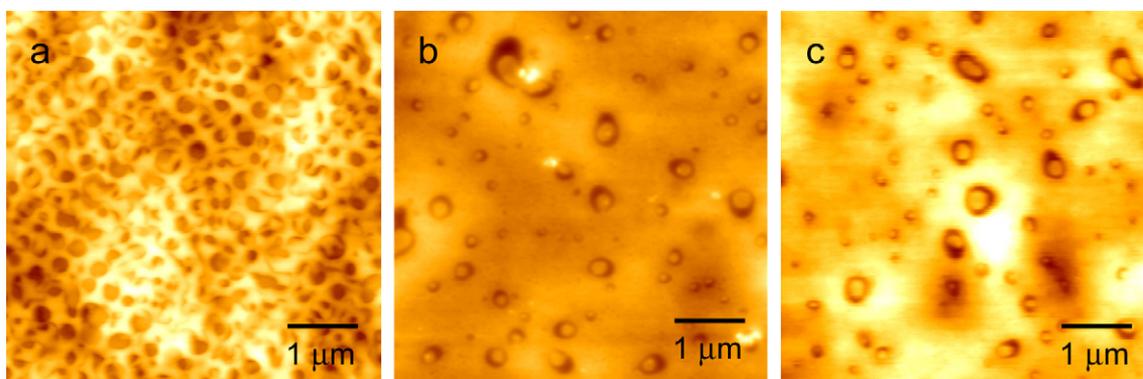


Fig. 1. AFM height image of the triblock copolymer on the silicon wafer. (a) as-prepared film, (b) quenched from 100 °C and (c) quenched from 250 °C.

nature of the surface component. The WCA (neutral deionized water droplets) on the films of the pure homopolymers at room temperature were measured as  $74 \pm 3.2^\circ$ ,  $86 \pm 2.1^\circ$ , and  $93 \pm 1.8^\circ$  on the films of pure PMMA, P2FEMA and PnBuMA, respectively (Fig. 2). The increase in WCA with increasing the side chain length in the polymer is expected, since the side chain consists of nonpolar aliphatic groups. However, the effect of the fluorine in P2FEMA on the surface energy is smaller than what may initially be expected, presumably because the fluorine group does not fully decorate the surface.

For the triblock copolymer, the WCA of the film quenched from 100 °C is  $99.1 \pm 1.0^\circ$ , which is close to that of PnBuMA (Fig. 3a). At an annealing temperature of 250 °C, the WCA of the quenched film decreased down to  $89.4 \pm 1.0^\circ$ , which is close to that of P2FEMA (Fig. 2b). Furthermore, when the polymer film treated at 250 °C was further annealed at 100 °C, the WCA changed from  $89.4 \pm 1.0^\circ$  back to  $95.8 \pm 1.4^\circ$ . This phenomenon indicates that the polymer films

on silicon wafers exhibit reversible thermo-responsive wettability. This reversible change of WCAs with temperature is attributed to the chemical component change on the film surface at 100 °C and 250 °C. At 100 °C, the P2FEMA and PMMA blocks are miscible and are therefore in the disordered state (one phase region) and hence form a layer next to the substrate. In addition, the PnBuMA block is immiscible with the PMMA block at this temperature and is phase-separated from it and therefore forms the surface layer. At 250 °C, the PnBuMA and PMMA blocks are in the disordered state and therefore form the layer next to the substrate, whilst the P2FEMA block forms the surface segregated layer due to phase separation. Due to this inherent phase behavior of the triblock copolymer, wettability changes in temperature result from reversible switching in the surface structure.

X-ray photoelectron spectroscopy (XPS), was used to determine the chemical structures of the film surfaces. Fig. 4 shows both sur-

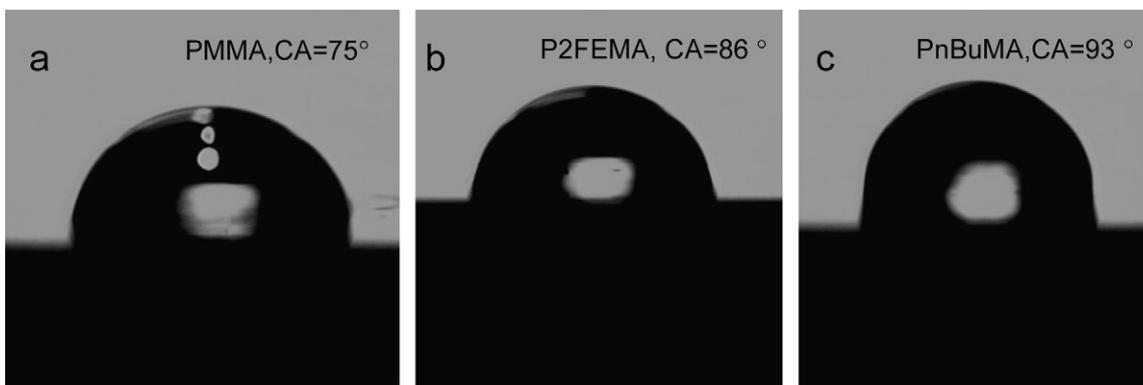


Fig. 2. Water droplet profiles and contact angles for PMMA, P2FEMA and PnBuMA on the silicon wafers.

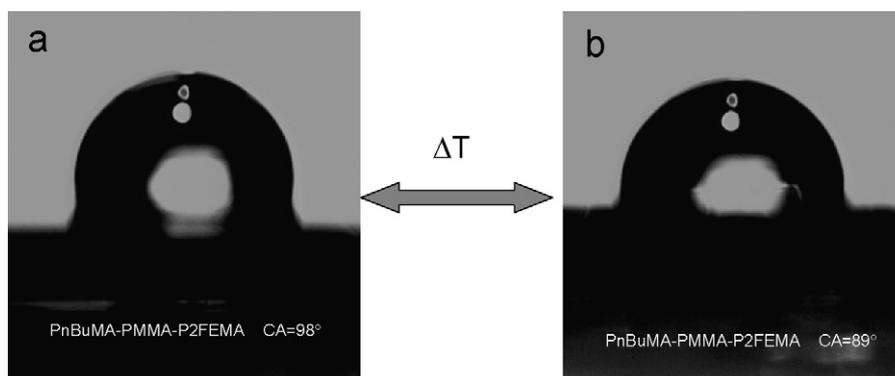
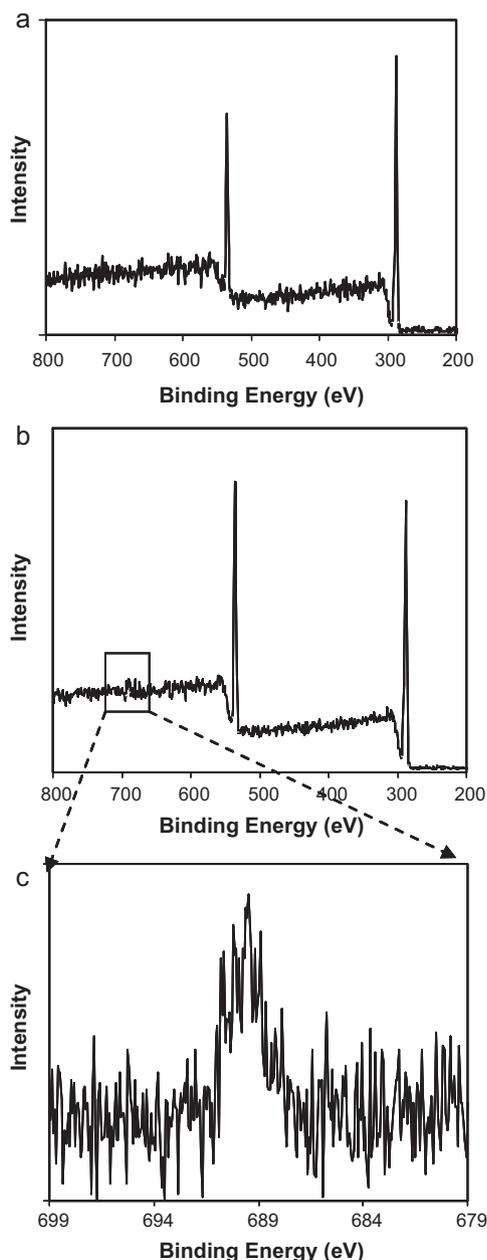


Fig. 3. Change of water contact angles for the triblock copolymer on the silicon wafer quenched from different temperature (a) 100 °C and (b) 250 °C.

**Table 2**  
XPS data of the PnBuMA–PMMA–P2FEMA films at different temperatures.

Samples	Annealing temperature (°C)	C1s		O1s		F1s	
		Binding energy (eV)	Atom (%)	Binding energy (eV)	Atom (%)	Binding energy (eV)	Atom (%)
PnBuMA–PMMA–P2FEMA	100	293.4	77.3	541.2	22.7	–	–
PnBuMA–PMMA–P2FEMA	250	292.5	72.5	540.1	26.1	690.7	1.4

vey and high-resolution XPS spectra for the triblock copolymer films quenched from 100 °C and 250 °C. The corresponding data resulting from quantitative analysis of XPS spectra are summarized in Table 2. No signals indicative of the silicon wafer were detected on any of the samples, demonstrating that no dewetting of the polymer films or hole formation were evident. The film quenched from 100 °C exhibited two sharp peaks at ~290 eV and ~540 eV (Fig. 4a), corresponding to carbon 1s (C<sub>1s</sub>) and oxygen 1s (O<sub>1s</sub>), respectively



**Fig. 4.** XPS spectra for the triblock copolymer quenched from different temperature. (a) 100 °C, (b) 250 °C and (c) high resolution of (b).

[31]. No additional peak indicative of the fluorine was observed. As shown in Table 2, the atomic percentages are close to theoretical values of PnBuMA, indicating that the surface of the polymer film quenched from 100 °C is dominated by the PnBuMA component. This result is entirely consistent with the CA measurements. The polymer film quenched from 250 °C showed both C<sub>1s</sub> and O<sub>1s</sub> peaks as well as an additional low intensity peak located at ~690 eV, which is unique to fluorine 1s (F<sub>1s</sub>) (Fig. 4b). The high-resolution F<sub>1s</sub> spectrum (Fig. 4c) consisting of a single peak at 688.5 eV is in agreement with the previous reports [32,33]. The observed F<sub>1s</sub> peak of the polymer film quenched from 250 °C indicates that the film surface has changed from PnBuMA to P2FEMA and confirms the CA results. When this polymer film was subsequently annealed again at 100 °C, the F<sub>1s</sub> peak of the polymer film disappeared while the percentages of C<sub>1s</sub> and O<sub>1s</sub> are close to those of PnBuMA.

It should be noted that the percentage of F<sub>1s</sub> detected for the polymer film quenched from 250 °C is only 1.4%, which is far from the theoretical value of 10% for P2FEMA. The decrease of the fluorine content at the surface is not clear, but could partly be attributed to the incomplete phase-separation of the polymer blocks due to the long time required to reach equilibrium [6]. A more likely explanation is that surface defluorination has occurred under X-ray irradiation. Previous reports on the XPS measurements of fluorine-containing polymers such as polytetrafluoroethylene (PTFE) [34,35] and poly(vinylidene fluoride) (PVDF) [32,33] showed significantly reduced signals of F<sub>1s</sub> at the surface, with HF elimination the dominant mode of fluorine loss [32,33].

#### 4. Conclusions

We have designed and investigated a novel triblock copolymer PnBuMA–PMMA–P2FEMA for fabricating thermally reversible smart films. The molecular design is based on the miscibility among three blocks of the copolymer which show UCST and LCST type phase behavior. Wettability studies show that the polymer film has a high contact angle at 100 °C and low contact angle at 250 °C. These results coupled with XPS analysis illustrate that the mechanism of thermo-responsive switching is driven by the miscibility between PnBuMA and P2FEMA blocks. The concept of utilizing polymer miscibility for fabricating smart films described in this work could be applicable to other triblock copolymers and may find potential applications in various fields such as adhesion, actuators, microfluidics and drug delivery.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apsusc.2011.06.098.

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