

# Nanosopic Tuning via Hydrophilic and Hydrophobic Macro-RAFT

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## ABSTRACT

The motivation of this paper is to show the dependence of the morphology on the composition of the copolymers and to explore and understand the influence of morphological features in the nanoscale structure to tailor made the properties of the materials, quantifying the surface energies is of beyond the scope of study.

Primary aim is to achieve the perpendicular orientation (periodic structure inside the film plane) by removing or balancing all interfacial action.

Discussed the efforts in manipulating and controlling the orientation of the nanoscopic domains for diblock polymers of poly (2-Hydroxyethyl methacrylate) and poly (n-butyl methacrylate) with macro-RAFTs of hydrophilic PHEMA and hydrophilic BMA.

Keywords: Diblock thin films, perpendicular orientation, molar mass

## 1 INTRODUCTION

The control of orientation of the structures is a major challenge, a number of studies have been reported on thin films of lamellar and cylindrical polystyrene-poly (alkylmethacrylate) films on Si substrates, where the lamellae and cylinders have a strong tendency to orient parallel to the film surface.<sup>1</sup> Several attempts have been performed to eliminate commensurability, by e.g. applying electric fields,<sup>2</sup> or by choosing non-selective walls,<sup>3</sup> or pre-patterned surfaces<sup>4</sup> as all these approaches require additional efforts; a spontaneous formation of lateral structures would be desirable which is achieved with diblock polymer films with molar mass sufficiently high lead to the formation of nano structured surfaces.

The overall research goal of this paper was to develop a tunable novel biphasic hydrogel. To accomplish this goal, block polymers with a wide range of block lengths were synthesized with narrow molecular weight distribution using the RAFT(reversible addition-fragmentation chain transfer polymerization).living free radical polymerization technique, and the morphologies correlated with their chain lengths. One of the goals of the research was to study the nanoscopic tuning between the blocks; this was achieved.

## 2 EXPERIMENTAL PROCEDURE

There is a large interest in architectures such as block copolymers, which cannot be made via conventional free-radical polymerization. Block copolymers are generally applied as adhesives, compatibilizers, thermoplastic elastomers, etc. Traditionally, block copolymers have always been synthesized via living polymerization.<sup>5-7</sup>

Block copolymerizations were performed with two types of macroinitiators listed in Table:1 prepared via RAFT polymerization. The reactor was charged with monomer and macroinitiator mixtures of 90:10, 80:20, 50:50 molar fractions in the feed. The reaction mixture was divided into aliquots, degassed sealed with rubber septa and placed in the thermostated bath for a predetermined time at 60 °C. The reactions were stopped and the polymer was isolated by the residual monomer being evaporated off, initially in the fume cupboard to remove the bulk of the liquid and then in a vacuum oven at room temperature, and dried. Block copolymer conversions were measured gravimetrically by drying at high vacuum to constant weight.

## 2.1 Preparation of thin block polymers

Thin block polymeric films were cast from solutions in THF, DMF, Toluene, and DMAc. The solvent was evaporated very slowly for one day at room temperature either in air or solvent saturated atmosphere. The films were observed by AFM.

For our experiments we used PHEMAMI-b-BMA and BMAMI\_b\_HEMA block copolymers with molar mass ranging from 88-140K, with polydispersities  $M_w/M_n$  1.02-1.12. All block polymer material was prepared via RAFT method, with fHEMA from 0.1-0.5 and fnBMA from 0.5-0.87.

To prepare thin films, polymer solutions were coated on top of native-oxide-covered Si (100) surfaces. Prior to spin coating, the substrates were cleaved in to pieces and were cleaned with piranha solution 7/3(v/v) of 98%  $H_2SO_4$ /30%  $H_2O_2$  at 90°C for 30 min. After 15 min at 80°C in the acid bath, the substrates were taken out, rinsed in deionized water, and dried with compressed nitrogen.<sup>21</sup>

The block and random copolymers (HEMA-co-nBMA) were dissolved in appropriate solvents depending on their proportions (HPLC grade, Aldrich). The polymer concentration used were varied between 0.1 and 0.15 mg/mL to obtain nanostructured polymer surfaces. Gold-coated silicon cantilevers for very-high-resolution AFM imaging. The tips feature a high aspect ratio and an asymptotic conical shape. They have a typical radius of curvature of 10 nm, which is small compared with the structures measured (larger than 200 nm). The image acquisition was done in air at room temperature. In order to minimize tip-induced sample degradation, all measurements were performed in noncontact mode.

## 2.2 Influence of sample preparation

Three different type of preparation procedures were analyzed

### 2.2.1. Spin coating

Block polymer films can be prepared by the spin – coating technique, where drops of a solution of the polymer in a volatile organic solvent are deposited on a spinning solid surfaces (silicon wafers are used due to their uniform flatness). The polymer film spreads by centrifugal forces, and the volatile solvent is rapidly driven off.

### 2.2.2 Solvent vapor annealing

Thin films were deposited on to polishes silicon wafer by spin coating from the DMF solution. After drying, the films were exposed to tetrahydrofuran (THF) vapor or chloroform vapor to induce mobility and allow microphase separation to occur. Both solvents are good solvents for the two polymer components.

### 2.2.3. Layer prepared on water surface

Solutions of 0.1 weight % of the block copolymers in  $CS_2$  were drop casted immediately on cleaned silicon substrates in a flow –hood. Immediately after drop casting the 0.1weight % of HEMAMI-b-nBMA/ $CS_2$ . After few seconds, the turbid top-layer on the polymer solution is observed, which is attributed to water droplets floating on the polymer solution. Due to the convection of the mobile, evaporating  $CS_2$ , the water droplets move and arrange themselves into hexagonal arrangement. These hexagonally packed water droplets are stable and slowly grow during the evaporation process. The surface tension and the capillary forces keep the water droplets in their hexagonal arrangement.

## 2.2. Influence of solvents:

The solvent used to prepare the copolymer films can exert a strong influence on the morphology, mainly because the solubility of the constitutive blocks can be different, which leads to selective precipitation during the casting process. Solvents have been compared in this study. The surface morphologies has been compared for films prepared from the more and less volatile solvents and the AFM images are collected.

Thin films of nBMAMI-b-HEMA and HEMAMI-b-nBMA diblock polymers after solvent vapor annealing in different solvents. Selection of solvents address two different phenomena (1) one solvent to address the microphase formation by the spin –casting of the ultra thin block polymer thin film on silicon substrate and other solvent address the contrasting of the microphase separation which was shown by Gourinova et al.<sup>8</sup> We find different distinct difference in the resulting structures depending on the solvent used for vapor annealing and solvent extraction rate. The difference can be

understood on the basis of different swelling behavior of the respective blocks in the solvent.

Macroiniator	$M_n$	$M_w$	MWD	Tg
HEMAMI	78646	90442	1.15	108
nBMAMI	42563	46234	1.08	24

Table 1: hydrophilic and hydrophobic macroRAFT

nBMAMI-b-HEMA	Molar mass kg/mol	Mw/Mn
94:6	88	1.08
50:50	300	1.02
HEMAMI-b-nBMA		
20:80	199	1.18
10:90	113	1.13
95:5	88.4	1.1

Table 2: Diblock polymers taken for AFM charecterization

### 3 RESULTS AND DISCUSSION

More recently, polymer brushes have been used to control block copolymer film structure. Rusell and coworkers<sup>18</sup> designed a neutral surface using an end grafted PS-*co*-PMMA random copolymer brush. Furthurmore, because of the flexibility of the types of polymer chains in a polymer brush system, it is possible for those chains to adjust their configurations to reflect difference in their environment. (i.e., different lamellae in a block copolymer thin films).

#### 3.5.1 Morphology Vs f

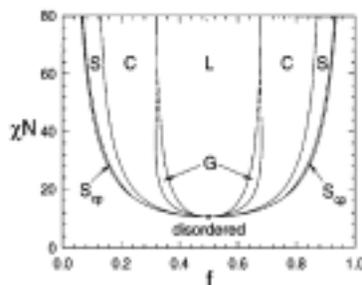


Figure 1: Phase diagram of the diblock copolymer melt L-lamellar, C-Hexagonal, S- Spherical, G-gyroid,  $S_{cp}$  -closed packed spherical.<sup>9</sup>

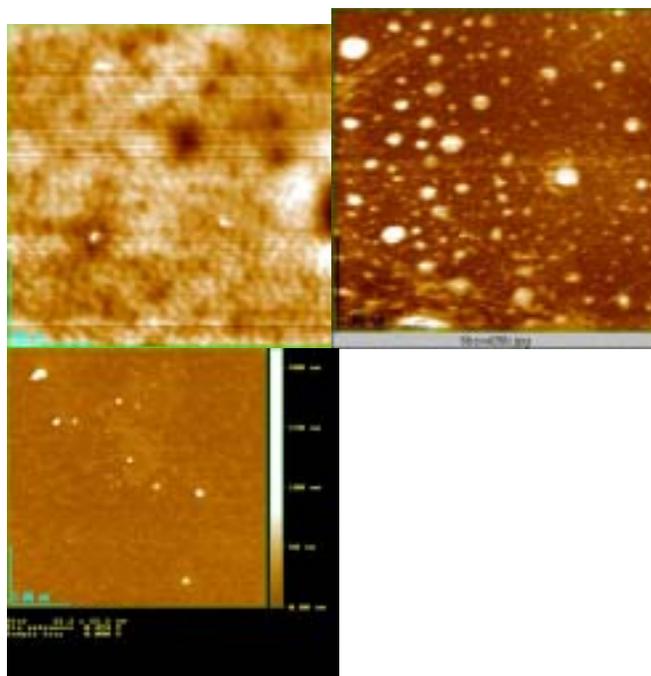


Fig 2 showing the different morphology with different fractions of BMA(a-c)

Sample	Morphology	PBMA f
22:78	C	0.78 (fig:a)
90:10	S	0.10 (fig:b)
100	S	1.00 (fig:c)

Table 3. Fractions and morphology of block polymer prepared from Hydrophilic macroRAFT

Table 4: BMAMI-b-HEMA

Sample	Morphology	PBMA f
89:11	C	0.89
45:55	L	0.55

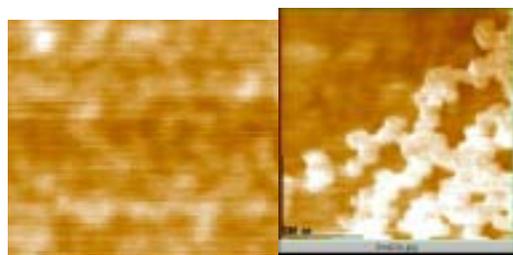


Figure 2, (a, b) showing hexagonal and sphere morphologies depending on their fractions of HEMA

Table 5: Contact angle measurements

Samples	Contact angle °
PHEMA	61± 2°
PnBMA	90
Cleaned silicon wafer	21
(BMA-b-HEMA)	
95:5	87.2
(HEMA-b-BMA)	
20:80	91.3
RR (58:42)	89.9
RR (58:42) 19 hrs	73.36

### 3.1. Contact angle measurements

To confirm hydrophilic, hydrophobic and neutral surfaces of the homopolymers and their block copolymers contact angle measurements were measured using sessile drop experiments with doubly distilled water.

## 4 CONCLUSION

Diblock polymers of approximately equal chain lengths underwent ordered phase-separated structure, showed perpendicular orientation in particular. Non preferential affinities of the copolymer segments with the interface control over the interfacial interactions was achieved by the block polymers of compositions 95:5 for nBMAMI initiated block copolymer and 20:80 for HEMAMI initiated block polymer systems.

Block polymers with and without the pre-coating of random polymers of the same polymers with 58:42 proportion suggested that both have the same neutrality surface function. (See: Table )Neutral surface functionality is confirmed by their contact angle. Depending on the experimental conditions for the film casting and annealing the orientation of the cylinders formed by the surface fully parallel organization to a fully perpendicular arrangement. The droplet diameter has a broad distribution independent of the concentration used for the spin coating. In addition, the arrangement of the droplets changes with increasing concentration. The arrangement of the droplets changes with increasing concentration. For (fig 5) the droplets are arranged into hexagonal arrays. At higher concentrations, this super structure vanishes and the droplets are 2D randomly oriented, Fig.3.8 proves the absence of a preferred orientation of the structures in real space. The formed droplets and the hexagonal droplet arrays are 2D randomly oriented and not aligned along preferential directions. Without any chemical modification tuning of the domain orientation is achieved in block polymers of compositions approximately 20:80 in HEMAMI-b-BMA and 90:10 BMAMI-b-HEMA or in other words, they work like neutral brushes (confirmed with their contact angle measurements)

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