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FELLOWSHIP FINAL REPORT

Leveraging tunability of copolymer gradients during polymer synthesis to advance understanding of polymer self-assembly in confined geometries

Bryan S. Beckingham[1,2], Christophe Sinturel[3]

[1]LE STUDIUM Institute for Advanced Studies, 45000 Orléans, France
[2]Department of Chemical Engineering, Auburn University, Auburn AL 36849
[3]Interfaces, Confinement, Matériaux et Nanostructures (ICMN), CNRS-Université d'Orléans, UMR 7374, 1B Rue de la Férollerie, C.S. 40059, 45071 Orléans Cedex 2, France

REPORT INFO

Fellow: **Bryan S. Beckingham**
From Auburn University, USA
Host laboratory in region Centre-Val de Loire: ICMN
Host scientist: **Christophe Sinturel**
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ABSTRACT

Self-assembly of polymer materials provides a cost-effective route to preparation of materials with well-defined nanostructures (1-100 nm). Due to their ability to self-assemble, block copolymers are a particularly useful and important class of materials utilized in a wide range of applications including photonic crystals, ion conducting membranes, microfluidics, drug delivery, sensors, and nanoporous membranes, and templates for the organization of nanodots and nanowires. However, relationships between block copolymer chemistry, architecture, and thermodynamics are critical for understanding self-assembly behavior towards designing materials with target properties. This research investigated the impact of incorporation of a gradient copolymer within the block copolymer architecture for enabling additional control over self-assembly behavior in polymer thin films and how these polymer thin films can be leveraged to fabricate porous thin polymer films. Block and block-gradient copolymers were synthesized with controlled molecular size and gradient structure and their thin film structures evaluated using atomic force microscopy towards understanding relationships between the macromolecular structure and formed morphologies in thin films.

1- Introduction

Block copolymers are an important class of materials that are used for a wide range of applications.[1] Block copolymers contain large domains of chemically dissimilar repeat units and can exist in a range of states depending on the constituent blocks and surrounding environment. Critically, control over the relative block chemistry and block length dictates their resulting physical and phase behavior. In particular, block copolymers can microphase-separate into specific morphologies due to incompatibility between the chemically dissimilar blocks. This inter-block separation occurs at macromolecular length scales (tens of nanometers) due to covalent bonding between the blocks preventing bulk phase separation. The degree of immiscibility (segregation strength) between polymer segments is enthalpic and determined by the block chemistry and temperature. Typically, block copolymers are ordered at low temperature and disorder upon heating above the order-disorder transition temperature (T_{ODT}). This project will investigate additional control over self-assembly behavior by incorporating compositionally controlled blocks within these block copolymer architectures, yielding systems ordered at the chain level through compositional control and ordered at the micron scale through block copolymer self-assembly.

There has been some prior research investigating the role gradient distributions play in the self-assembly behavior of block copolymers.[2,3] Previous studies have tended toward two approaches yielding two distinct block copolymer architectures: (1) gradient copolymers where depending on the relative reactivity either a single large gradient spanning the entire polymer chain is formed or due to preferential kinetics each end is near-pure with short and sharp gradient between.[4] Alternatively, (2), a deliberately synthesized, short gradient, or taper, block is inserted in the middle of a diblock copolymer—i.e. architectures such as A-b-(A-grad-B)-B and A-b-(B-grad-A)-b-B)—forming tapered or reverse tapered block copolymers where the taper block leads to varying effects on self-assembly behavior depending on the direction and strength of the gradient.[2,3,5] For instance in A-A/B-B tapered block copolymers the taper tends to decrease the segregation strength leading to increased interfacial breadth between the pure phases of the microphase separated morphology.

Notably, the block gradient architecture has many possibilities depending on the structure of the gradient. This gradient can span the entire block and compositionally go from pure A to B or it can be compositionally mixed at each end with a shorter and shallower gradient. Compositionally control of this gradient copolymer block thereby provides additional opportunities for tuning segregation strength, self-assembly behavior, and physical properties. Unfortunately, the impact of these different gradient features is not well understood such that there remains a large opportunity space to investigate and many research questions and hypotheses to be addressed.

Here, block gradient copolymers of controlled molecular size and gradient structure are synthesized and their morphology in thin films investigated using atomic force microscopy (AFM). gradient shape, compositional variation, and polymer length.

2- Experimental details

Styrene, cyclohexane, deuterated chloroform, and tetramethylsilane were purchased from EMD Millipore Corporation. Isoprene was obtained from Acros Organics. *Sec*-Butyllithium (1.4 M in cyclohexane) and di-*n*-butylmagnesium (1.0 M in heptane) were used as received from Sigma-Aldrich. 1,1 Diphenylethylene and *n*-butyllithium (2.0 M in cyclohexane) were used as received from Alfa Aesar. Methanol and chloroform were used as received from VWR International, and *tert*-butyllithium (1.7 M) was used as received from TCI America. Cyclohexane was stirred over diphenylhexyllithium (an adduct of *sec*-butyllithium and 1,1-diphenylethylene), degassed via freeze–pump–thaw (FPT) cycles, and vacuum-transferred prior to use. Isoprene was stirred over *n*-butyllithium, degassed via FPT, and vacuum-transferred prior to use. **Caution !** *n*-Butyllithium, *sec*-butyllithium, and *tert*-butyllithium are pyrophoric and moisture-sensitive materials and should be handled with appropriate care. Styrene was stirred over di-*n*-butylmagnesium, degassed via FPT, and vacuum-transferred prior to use. Methanol was degassed via FPT cycles prior to use.

Polymers were synthesized in 100 mL of solvent consisting of 94 v/v% cyclohexane and 6 v/v% TEA at ~15 wt% final solids content. Glass reactors were flamed out under vacuum, rinsed with *n*-butyllithium (*n*-BuLi) and subsequently with cyclohexane prior to charging with initiator (*sec*-BuLi) in a nitrogen-filled glovebox. A 94/6 v/v mixture of cyclohexane/triethylamine was stirred over diphenylhexyllithium (adduct of *s*-BuLi and 1,1-diphenylethylene), degassed via freeze–pump–thaw cycles, and vacuum transferred directly into the reactor. Styrene ans isoprene monomers were handled similarly, though isoprene monomer was stirred over *n*-BuLi. Polymerizations were performed 30 °C. For each of the block–gradient copolymers, an aliquot of the reaction mixture was collected immediately prior to the second monomer charge to permit separate characterization of the first block and the final copolymer. Upon completion, the polymerization was terminated by injection of degassed methanol. Copolymers were precipitated in an adequate amount of methanol, dried under nitrogen, and then in a vacuum oven overnight at room temperature

Gel permeation chromatography (GPC) was conducted at a flow rate of 1 ml/minute using a Malvern Viscotek VE 1122 solvent delivery system equipped with dual Agilent PLgel mixed-C columns (7.5 mm ID and 300 mm length) maintained at 30 °C. A Viscotek VE 3580 refractive index (RI) detector was used for detection. Samples were prepared by dissolving each sample in HPLC grade tetrahydrofuran (THF) (VWR BDH Chemicals) at a concentration of 1 mg mL^{-1}. The solutions were double filtered through 20 µm filters, and 200 µL aliquots were injected. Polystyrene-equivalent molecular weight was determined using a calibration developed using Agilent EasiVial GPC/SEC calibration standards (12 monodisperse polystyrenes) that cover molecular weights from 162 – 500000 Da.

^1H Nuclear magnetic resonance (NMR) spectroscopy was performed using a 500 MHz Burker Spectrophotometer. Samples were prepared by dissolution in deuterated chloroform (VWR BDH Chemicals) and the ^1H NMR spectra were collected for 16 scans.

Polymer thin films were formed on silicon substrates from varied concentration solutions. The substrates (1 cm x 1 cm) were first cleaned under sonication using acetone and ethanol.

Atomic Force Microscopy (AFM) was used to examine surface of the film for identification of phase separated morphologies through the diffefences in phase stiffness. AFM imaging was performed in air at room temperature in tapping mode on AFM Dimension Icon with ScanAsyst from Bruker.

3- Results and discussion

A series of block-random copolymers were synthesized via sequential monomer addition using anionic polymerization. Each block-gradient copolymer included a polystyrene block and a gradient block where their relative fraction and the gradient block composition was varied. Targets for the block-gradient copolymer syntheses are given in Table 1.

Table 1 : Target Block-gradient Copolymers

Name	**Gradient block wt %**	**PS content in gradient block wt.%**	**Target phases**
PS-grad 1	50	40	lamellar
Ps-grad 2	27	20	cylinder
Ps-grad 3	27	30	cylinder
Ps-grad 4	11	30	spheres
Ps-grad 5	11	20	spheres
Ps-grad 6	50	20	lamellar
Ps-grad 7	50	30	lamellar

In order to establish a desired compositional gradient in the gradient block the copolymers were synthesized in a cosolvent mixture that included 94 vol.% cyclohexane and 6 vol.% triethylamine. In previous work evaluating the impact of solvent mixtures on compositional gradients by the Beckingham research group established reactivity ratios for this cosolvent mixture which allow for prediction of the compositional gradient based on the feed monomer compositions (styrene and isoprene) using the copolymer equation (Equation 1), where r_A and r_B are the reactivity ratios for the A and B chain ends and f_A and f_B are the instantaneous molar feed composition of A and B monomers (where $f_B = 1–f_A$) and F_A is thereby the relative velocity of A-monomer incorporation into the copolymer over an infinitesimally small change in conversion which approximate the composition of the growing copolymer for infinetesimal changes in conversion.[6]

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2} \qquad \text{Eq. (1)}$$

Example compositional drift profiles for the gradient block in PS-grad- are shown in Figure 1, where F_S is the instantaneous polystyrene content in the polymer chain plotted against the gradient block fractional conversion. Reactivity ratios r_S and r_I of 0.39 and 2.27 respectively were utilized.[6]

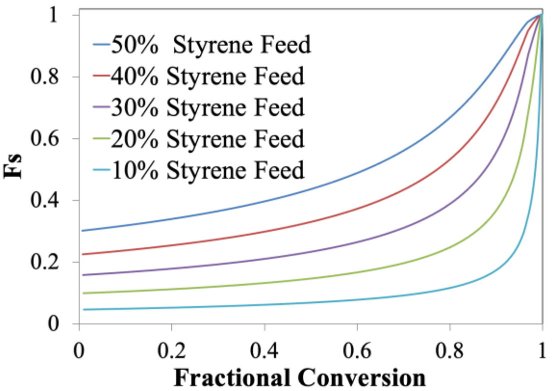

Figure 1. Compositional drift profiles for different initial monomer feed compositions.

Synthesized block copolymers were characterized for purity and molecular size using gel permeation chromatography (GPC) ; example chromatograms shown in Figure 2.

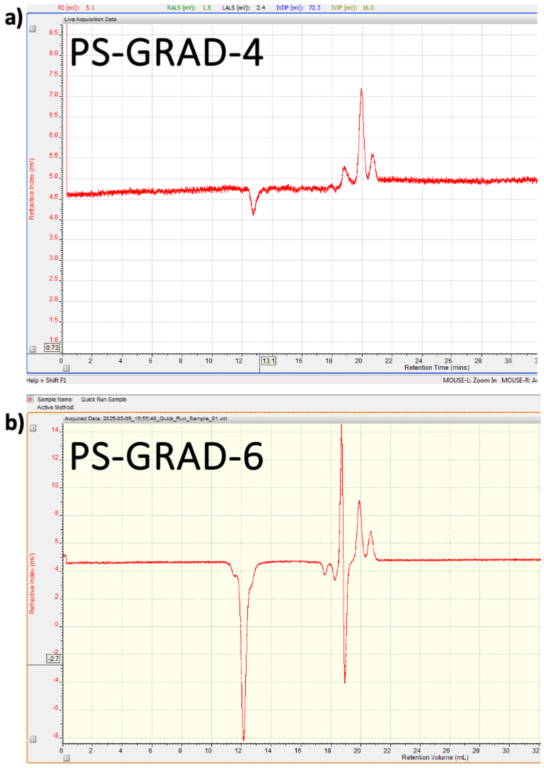

Figure 2. Example GPC chromatograms for the synthesized block-gradient copolymers. Shown are the final synthesized polymers for PS-Grad-4 and PS-Grad-6.

In these chromatograms the down-facing peaks on the left are the copolymer signals. In the case of PS-Grad-4, a single peak is observed consistent with a clean synthesis of a block-gradient copolymer and the elution time corresponded to a polystyrene-equivalent molecular weight of 80 kg/mol. This elevated molceular weight versus the target is indicative of initiator termination either in the supply or during addition to the polymerization reactor. In the case of PS-Grad-6 there are slight shoulders on the signal at both longer and shorter elution times that we attribute to the presence of terminated first block and coupled block-gradient copolymer during the synthesis.

For examining the relative compositions of the incorporated monomers 1H NMR spectroscopy was used. An example 1H NMR spectra is shown in Figure 3 for the first block aliquot (gradient block) for the synthesis of PS-Grad-3.

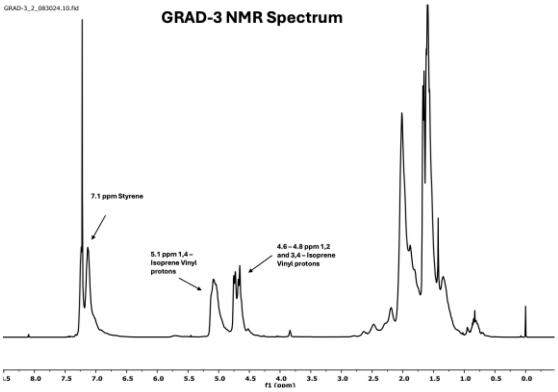

Figure 3. 1H NMR spectra of the gradient block from the PS-GRAD-3 synthesis.

A significant amount of experimentation with the formation of spin-coated and solvent-annealed thin films was performed. Initial trials focused on fabrication of thin films of varied thicknesses by varying the solution concentrations (mg polymer/mL solvent) for spin coating as well as the time and speed (rpm) of the spin coating process. A majority of the final characterized films were prepared using 20 mg/mL solutions of the block-gradient copolymers in toluene. Solvent annealing to improve the observed phase separation was performed using tetrahydrofuran for varying amounts of solvent exposure time (30 seconds to 180 seconds). A key insight that allowed for better AFM imaging of these particular samples was a transition to using QNM mode or Quantative Nanomechanics mode. Whereas standard AFM looks generally at the surface texture, by examining the mechanics at the AFM tip we were able to better resolve differences between the phases. An example is shown in Figure 4 for PS-Grad-3 where there are distinct regions of dark and light in both the height (Figure 4a) and modulus (Figure 4b) though more distinct in the modulus image. While the adopted morphology is faint this provides evidence of phase separation.

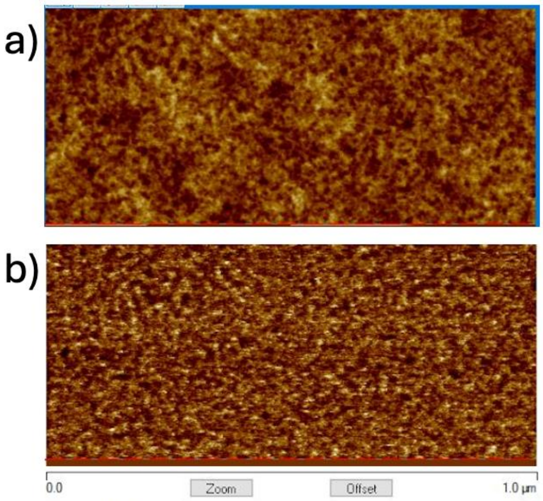

Figure 4. AFM images of PS-Grad-3 spin coated from 15 mg/mL solutions in toluene at 3k rpm and solvent annealed for 2 minutes in THF vapor. a) Height image and b) DMT modulus. Both images are 1 micron in width.

4- Conclusion

A series of block-random copolymers were synthesized, characterized for macromolecular properties, and processed into thin films for characterization by atomic force microscopy. AFM imaging techniques were refined in order to visualize the differences between the two polymer phases, and phase separated morphologies were obsesrved. Additional polymer syntheses and characterization are planned in order to better understand the formation of these morphologies as several of the investigated block-gradient copolymers examined in this study contained undesireable homopolymer from the synthesis.

5- Perspectives of future collaborations with the host laboratory

The collaboration between Dr. Beckingham and Dr. Sinturel at ICMN aims to continue through exchange of materials and expertise towards achieving deeper understanding of these types of materials. Dr. Beckingham and his students have been working to prepare additional block and block-gradient copolymers, characterize their macromolecular properties, and conduct preliminary studies before sending material to ICMN to leverage Dr. Sinturel's expertise in solvent annealing and thin film characterization.

6- Articles published in the framework of the fellowship

There have not, as yet, been any manuscripts derived from the research conducted during the fellowship.

7- Acknowledgements

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