# Soft Matter

# ARTICLE

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# Self-Assembly of Gradient Copolymers Synthesized in Semi-Batch Mode by Nitroxide Mediated Polymerization

Ian Bennett, Kevin Wylie, and Milan Marić\*

The effect of diffuse compositional interfaces on copolymer self-assembly was studied via gradient copolymers (GCP). Poly((methyl methacrylate)-*grad*-(styrene)) (PMMA-grad-PSt) copolymers were synthesized in semi-batch mode using nitroxide-mediated polymerization (NMP) with varied monomer injection protocols to produce different diffuse interfaces (number average molecular weights (M<sub>n</sub>) ranged from 62 000 g mol<sup>-1</sup> to 94 000 g mol<sup>-1</sup> with dispersities (Đ) between 1.35 and 1.59). The GCPs were spun into thin films on substrates made neutral by poly(St-*ran*-MMA-*ran*-hydroxyethyl methacrylate) terpolymers and annealed at elevated temperature to produce vertically oriented microphase-separated domains. The GCPs were found to have domain spacing larger than equivalent monodipseres BCPs, due to their polydisperse nature. This effect was partially offset by the decrease in enthalpic interaction parameter  $\chi$  due to the gradient. GCPs synthesized with a single-injection protocol (i.e. less diffuse interfaces) were found to self-assemble into ordered domains. However, GCPs synthesized with long injection times (i.e. more diffuse interfaces) exhibited poor selfassembly attributed to their predicted statistical-copolymer-like middle sequence, which caused a reduction of the effective  $\chi$ .

## Introduction

Recently, nanolithographic technologies based on selfassembling materials have been receiving significant attention from both industrial(1–3) and academic perspectives.(4–6) Block copolymer (BCP) thin films have been shown to selfassemble into periodic structures with a characteristic size well below 50 nm.(7) The emergence of self-assembled BCPs has coincided with the difficulties in traditional photolithographic techniques, which become increasingly complex and costly due to the continued trend of miniaturization.(8)

Diblock copolymers can exhibit a wide range of morphologies that occur through microphase separation due to the immiscibility of the two distinct monomeric components. Lamellar, gyroid, hexagonally packed cylinders, and body-centered spheres are all possible equilibrium arrangements. (9-11) This equilibrium depends primarily on the relative volume fraction of each species (f), the degree of polymerization (N) and the thermodynamic incompatibility of the two species, described by the Flory-Huggins enthalpic interaction parameter (χ). Poly(styrene-*block*-methyl methacrylate) (PSt-b-PMMA) is one of the most commonly used BCPs for self-assembly, partly due to the similarity of their surface tensions, making vertical orientation relatively

#### simple.(12)

Vertical orientation of the BCP domains is generally desired, although it does introduce a number of defect structures such as dislocations and disinclinations in the plane of the film.(13) Several different methods have been developed to address this: mechanical flow fields,(14-16) electric fields,(17,18) solvent annealing,(19) and chemically neutral surfaces.(20-22) In particular, random copolymer brushes are a commonly used technique in order to render a neutral surface and achieve vertical orientation. These brushes, which have a finely tuned composition, are covalently bonded to the substrate to prevent them from diffusing into the BCP film. The grafting is typically achieved through a dehydration reaction between hydroxyl groups on the polymer and the native oxide of the substrate. Pinning using hydroxyl groups positioned at the ends of polymer chains used to take excessively long, in excess of 48 h,(20) but has been reduced to a few hours.(22) More recently, rapid thermal annealing of polymer thin films has been shown to further reduce the annealing time to several minutes.(23)

In contrast to BCPs, gradient copolymers (GCP) are defined by a continuously varying composition along the polymer chain. They have emerged in the past two decades as a possible alternative to BCPs for many applications.(24) Controlled/living radical polymerization (CRP) is one of the most commonly employed methods to obtain gradient copolymers with excellent chain-to-chain compositional heterogeneity.(24) Gradient copolymer synthesis is carried out either as a batch or semi-batch process. In a batch reaction, monomer pairs with sufficiently different reactivity ratios must



<sup>&</sup>lt;sup>a.</sup> Dept. of Chemical Engineering, McGill Institute of Advanced Materials (MIAM) McGill University, 3610 University Street, Montreal, QC Canada H3A 0C5.

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be chosen and the reaction must be allowed to proceed to very high conversion. In a semi-batch or "forced" butyl[1(d polymerization, the second monomer is gradually added to the reaction system, changing the composition of the reaction mixture.(25,26) GCPs provide an advantage over traditional BCPs via CRP for large scale processing by reducing the number of reaction steps (i.e. the intermediate purification and characterization step required for BCP synthesis is avoided). Further, GCPs like the related tapered block copolymers, via

Further, GCPs like the related tapered block copolymers, via manipulation of the gradient profile, allow modulation of segregation strength, which in turn can influence mechanical properties and domain spacing.(27,28) However, the minimum order-disorder transition temperature (ODT) for GCPs changes as a function of the gradient length, becoming higher as the gradient length grows.(29)

In this study, poly((MMA-ran-St)-grad-St) (simplified as P(MMA-grad-St)) hyperbolic gradient copolymers were synthesized via NMP using a semi-batch method where styrene was injected over a certain period of time to a PMMArich initiating species with a small fraction of styrene comonomer initially ~ 5-10 mol% to aid in control of the polymerization (i.e. high chain end fidelity and narrow molecular weight distribution. This is the controlling comonomer approach pioneered by Charleux and coworkers using commercially available alkoxyamine unimolecular initiators).(30) One class of gradients was produced by injecting all of the styrene at once, resulting in "blocky" gradients. The other was produced by injecting styrene over an extended period of time to produce more gradual, smoother gradients (herein classified as smooth gradients). (29,31,32) Thus, we present here a process to attain an industrially scaleable, NMP process with commercial initiators to make GCPs that would exhibit similar self-assembly as carefully designed, more rigorously prepared BCPs using classical living polymerization methods.

We aim specifically to study the effect of diffusive transitions on the self-assembly of hyperbolic GCPs made by NMP and determine the limit for self-assembly for such copolymers. This will then serve as a launching point to study such systems to achieve longer-range order and use further processing techniques such as e-beam lithography.

#### **Experimental Section**

#### Materials

Styrene (St,  $\geq$ 99%), methyl methacrylate (MMA, 99%), 2hydroxyethyl methacrylate (HEMA,  $\geq$ 99%), calcium hydride (CaH<sub>2</sub>, 95%, reagent grade), and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, Brockmann Type I, basic) were purchased from Sigma-Aldrich. Methanol ( $\geq$ 99.8%, ACS reagent grade), tetrahydrofuran (THF,  $\geq$ 99.9%, HPLC grade), and toluene ( $\geq$ 99.5%, ACS reagent grade) were purchased from Fisher Scientific. Chloroform-d<sub>1</sub> (99.8% deuteration) was purchased from MagniSolv. All of the above compounds were used as received. St, MMA and HEMA were purified by passing through a column of basic aluminum oxide mixed with 5 wt% calcium hydride, and stored in a sealed flask under a head of nitrogen until required. 2- ((*tert*butyl[1(diethoxyphosphoryl)-2,2-dimethylpropyl]amino)oxy)-2-methylpropionic acid (BlocBuilder, 99%) was obtained from Arkema. N-hydroxysuccinimide (NHS, 98%), and N,N'dicyclohexylcarbodiimide (DCC, 99.9%) were purchased from Sigma-Aldrich and used in conjunction with BlocBuilder to synthesize the succinimidyl ester terminated alkoxyamine BlocBuilder (NHS-BlocBuilder) using the same procedure described by Vinas *et al.*(33) Silicon wafers were purchased from University Wafer.

Synthesis of Statistical Terpolymer Brush. The Statistical copolymer used was synthesized by nitroxide-mediated polymerization (NMP) following similar procedures adapted from Nealey et al.(22) A typical formulation follows. A mixture of NHS-BlocBuilder initiator (0.0805 g, 0.168 mmol), St (4.6792 g, 44.93 mmol), MMA (8.1498 g, 81.50 mmol), and HEMA (0.2574 g, 1.980 mmol) was purged with nitrogen for 30 minutes at room temperature. The mixture was heated to 100°C for 2 hours while maintaining the nitrogen purge. Aliquots were taken periodically for analysis by <sup>1</sup>H NMR and GPC. The contents were then cooled and the resulting copolymer was precipitated in methanol, decanted, and dried under vacuum at 50°C overnight to obtain the final copolymer (3.16 g, 24% yield),  $M_n$ = 39 000 g mol<sup>-1</sup>, D = 1.25 (by GPC relative to linear PMMA standards in THF at 40 °C). The mol fraction of St in the terpolymer (F<sub>St</sub>) was determined by <sup>1</sup>H NMR spectroscopy to be 0.53, and the mol fraction of HEMA (F<sub>HEMA</sub>) was 0.01.

#### **Block Copolymer Synthesis.**

Synthesis of P(MMA-ran-St) Macroinitiator. The macroinitiator (M1) was synthesized by NMP with a target molecular weight at complete conversion of 42 000 g mol<sup>-1</sup>. The copolymerization method to make an essentially pure PMMA block (with a low concentration ~ 5-10 mol% of controlling co-monomer such as St) was adapted from Charleux et al.(30) A mixture of NHS-BlocBuilder initiator (0.0704 g, 0.147 mmol), St (0.6956 g, 66.88 mmol), and MMA (6.9820 g, 69.82 mmol) was purged with nitrogen for 30 minutes at room temperature. The mixture was heated to 90°C for 90 minutes while maintaining the nitrogen purge. Aliquots were taken periodically for analysis by <sup>1</sup>H NMR and GPC. The contents were then cooled and the resulting copolymer was precipitated in hexane, decanted, and dried under vacuum at 50°C overnight to obtain the final copolymer (37% conversion, 1.82 g, 24% yield),  $M_n$  = 28 000 g mol<sup>-1</sup>, D = 1.27 (by GPC relative to linear PMMA standards in THF at 40 (°C). Fst was determined by <sup>1</sup>H NMR spectroscopy to be 0.15.

**Chain Extension of Macroinitiator.** The block copolymer (B1) was synthesized by chain extension of macroinitiator M1. A mixture of St (22.72 g, 218.5 mmol), and macroinitiator M1 (1.8784 g, 0.068 mmol) was purged with nitrogen for 30 minutes at room temperature. The mixture was heated to 110°C for 3 hours while maintaining the nitrogen purge. Aliquots were taken periodically for analysis by <sup>1</sup>H NMR and GPC. The contents were then cooled and the resulting

polymer was precipitated in methanol, decanted, and dried under vacuum at 50°C overnight to obtain the final copolymer (1.85 g, 7.5% yield),  $M_n$  = 58 000 g mol<sup>-1</sup>, D = 1.37 (by GPC relative to linear PMMA standards in THF at 40 °C). F<sub>st</sub> was determined by <sup>1</sup>H NMR spectroscopy to be 0.76.

Synthesis of Blocky Gradient Copolymers. The blocky GCPs used were synthesized by NMP in semi-batch mode following similar procedures, adapted from Gray et al.(34) The polymerization procedure for sample G1 is described below. A mixture of NHS-BlocBuilder initiator (0.0706 g, 0.185 mmol), St (0.7125 g, 6.85 mmol), and MMA (7.1325 g, 71.3 mmol) was purged with nitrogen for 30 minutes at room temperature. The mixture was heated to 90°C for 1.5 hours while maintaining the nitrogen purge. St (21.58 g, 208 mmol) previously purged was then added and the temperature was raised to 110°C for 3 hours. Aliquots were taken periodically throughout the reaction for analysis by <sup>1</sup>H NMR and GPC. The contents were then cooled and the resulting polymer was precipitated in methanol, decanted, and dried under vacuum at 50°C overnight to obtain the final copolymer (2.32 g),  $M_n$  = 94 000 g mol<sup>-1</sup>, Đ = 1.59 (by GPC relative to linear PMMA standards in THF at 40 °C).  $F_{St}$  was determined by <sup>1</sup>H NMR spectroscopy to be 0.76.

Synthesis of Smooth Gradient Copolymers. Smooth GCPs were synthesized by NMP in semi-batch mode with slow injection of the second monomer. The polymerization procedure for sample G5 is described below as an example. A mixture of NHS-BlocBuilder initiator (0.0721 g, 0.151 mmol), St (0.7271 g, 6.99 mmol), and MMA (7.5600 g, 75.60 mmol) was purged with nitrogen for 30 minutes at room temperature. The mixture was heated to 90°C for 30 minutes while maintaining the nitrogen purge. Previously purged St (21.98 g, 211 mmol) was delivered at a rate of 0.206 ml min<sup>-1</sup> using a syringe pump for 2 hours while the temperature was steadily increased at a rate of 10°C hour<sup>-1</sup>. The pump was then switched off and the reaction proceeded for 1 hour at 110°C. Aliquots were taken periodically throughout the reaction for analysis by <sup>1</sup>H NMR and GPC. The mixture was then cooled and the resulting polymer was precipitated in methanol, decanted, and dried under vacuum at 50°C overnight to obtain the final copolymer (17% conversion, 3.22 g, 11% yield),  $M_n$  = 64 000 g mol<sup>-1</sup>, Đ = 1.44 (by GPC relative to linear PMMA standards in THF at 40 °C). F<sub>st</sub> was determined by <sup>1</sup>H NMR to be 0.71.

**Substrate Preparation.** Silicon(100) wafers were cut into approximately 1.5 cm<sup>2</sup> pieces and cleaned using successive washing with deionized water, acetone and isopropyl alcohol. The samples were then immersed in Nanostrip 2X solution for 30 minutes at 80°C and then rinsed with deionized water and dried under nitrogen.

Statistical Copolymer Grafting. Statistical copolymer brushes were grafted by spin coating films of P(MMA-*ran*-St*ran*-HEMA) solution onto the cleaned wafers. Spin coating from a 1.5 wt% solution in toluene at 4000 rpm gave 40-45 nm thick films. The samples were then annealed in a vacuum oven at 150°C for 18 hours. The samples were sonicated twice at 50°C in toluene for 10 minutes to remove any unbound copolymers. The final brush thickness was found to be between 10-15 nm by ellipsometry.

**Copolymer Deposition.** The copolymers were deposited on the grafted substrate by spinning at either 3000 or 4000 RPM from a 1 wt% or 1.5 wt% solution. Film thickness varied from 44 to 67 nm.

**Rapid Thermal Annealing.** Rapid thermal annealing was performed in a Jipelec JetFirst 200 system. The samples were first placed in the chamber, the chamber was then evacuated and finally backfilled with nitrogen. The heating ramp was set to 19 °C s<sup>-1</sup>. The samples were annealed at 220°C for 3 minutes and subsequently cooled to room temperature.

**Analysis.** <sup>1</sup>H NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer in deuterated chloroform (CDCl<sub>3</sub>) with tetramethyl silane (TMS) as an internal standard. For MMA/St copolymers: ( $\delta$ ) 7.2-6.9 (m, 5 H, aromatic, -CH-), 3.6-3.4 (s, 3 H, -O-CH<sub>3</sub>), 2.3-1.0 (m, 5 H, -CH-CH<sub>2</sub>-, -CH<sub>2</sub>-C), 0.9-0.7 (s, 3 H, -C-CH<sub>3</sub>). For HEMA/MMA/St terpolymer: ( $\delta$ ) 7.2-6.9 (aromatic, -CH-), 4.3 (m, 2 H, -O-*CH*<sub>2</sub>-CH<sub>2</sub>-OH), 3.8 (m, 2 H, -O-*CH*<sub>2</sub>-CH<sub>2</sub>-OH), 3.6-3.4 (s, 3 H, -O-CH<sub>3</sub>), 3.0-1.5 (m, 7 H, -CH-CH<sub>2</sub>-, -CH<sub>2</sub>-C, -CH<sub>2</sub>-C), 1.5-0.5 (m, 6 H, -C-CH<sub>3</sub>).

Diffusion Ordered Spectroscopy (DOSY) was performed on a Varian Mercury 500 MHz spectrometer in CDCl<sub>3</sub> with TMS as an internal standard. The recorded spectra were processed using a Bayesian DOSY transform.

Molecular weights and dispersity (Đ) were determined using gel permeation chromatography (GPC) (Waters Breeze) equipped with three Waters Styragel HF columns (molecular weight ranges: HR1:  $10^2 - 5 \times 10^3$  g mol<sup>-1</sup>, HR2:  $5 \times 10^2 - 2 \times 10^4$  g mol<sup>-1</sup>, HR3:  $5 \times 10^3 - 6 \times 10^5$  g mol<sup>-1</sup>) and a guard column was used. The results obtained were from the Waters 2410 refractive index (RI) detector using tetrahydrofuran (THF) as the eluent at 40°C and a flow rate of 0.3 ml min<sup>-1</sup>. Poly(methyl methacrylate) (PMMA) standards were used for calibration.

The thicknesses of the polymer films were measured using a Sopra GES-5E spectroscopic ellipsometer at a 75° incident angle, with WinElli II analysis software. The software used the Levenberg Marquard approach to calculate the film thickness and error.

The characterization of the GCP morphology was done using a Tescan XM scanning electron microscope (SEM) at an accelerating voltage of 3.5 kV. In order to improve image contrast, the PMMA domains were selectively removed by reactive ion etching (RIE). Samples were exposed to a 30 W oxygen plasma at 20 mTorr for 30 seconds. The samples were then coated with a thin layer of chromium or titanium to reduce charging effects. Image analysis to determine average feature sizes was performed using ImageJ.

#### Results

## Polymerization Characteristics

Two brush terpolymers were synthesized to manipulate the surface wetting of the subsequently deposited copolymers. The statistical terpolymer, H1, had a final molecular weight of 39 000 g mol<sup>-1</sup> and  $F_{st} = 0.53$ , sufficient to induce vertical

orientation of the lamellar copolymer films. A second statistical terpolymer, H2, with a molecular weight of 42 000 g mol<sup>-1</sup> and a F<sub>st</sub> of 0.63, was used to induce vertical orientation of cylindrical copolymer films.(22) The BCP, B1, used in this work had a total molecular weight of 58 000 g mol<sup>-1</sup>, D = 1.37 and F<sub>st</sub> = 0.76 and served as a comparative to the various gradient copolymers.

P(MMA-grad-St) copolymers were synthesized in one of two ways in order to produce the desired composition and transition length. For the blocky gradients, characterized by higher average homopolymer sequence length, the polymerization time before and after the addition of St was varied to produce differing final compositions. The results are summarized in Table 1.

In the case of the smooth GCPs, the injection rate was varied to produce a different transition length and average monomer sequence lengths. Additionally, the temperature was steadily increased from the initial set point of 90°C to the final set point of 110°C over the course of the injection. This was due to the lower propagation rate of St compared to MMA at 90°C and thus the higher temperature was used when the copolymerization monomer mixture was richer in St. The results are summarized in Table 2.

Yields were low due to the bulk synthesis approach, which required excess monomer to prevent the reaction mixture from becoming too viscous. Upon precipitation in methanol, short oligomeric chains were removed along with any homopolymer contamination, as confirmed by diffusion ordered NMR spectroscopy.

Figure 1 shows the instantaneous styrene fraction as a function of chain length for the blocky and smooth copolymers as calculated by the penultimate model using reactivity ratios of  $r_{st} = 0.523$ ,  $r_{MMA} = 0.46$ .(35–37)

#### **Copolymer Self-Assembly**

To determine whether the copolymers would successfully selfassemble, they were spin coated onto substrates with a neutral brush to promote vertical orientation of the domains. Figure 2 and Figure 3 below indicate that self-assembly was successful in all cases. The average diameter, spacing and standard deviation for all polymers are reported in Table 3.

Table 1 Properties of Blocky Poly(methyl methacrylate-grad-styrene) Gradient Copolymers.

Polymer	Injection	Mn (g	Đª	Fst <sup>b</sup>	$N_{n,St}^{d}$	$N_{n,MMA}^{d}$
	Time	mol⁻¹)				
	(min)	а				
G1 <sup>c</sup>	90	94	1.59	0.76	3.3	3.7
		000				
G2 <sup>c</sup>	120	64	1.35	0.69	3.9	3.2
		000				

a. Molecular weight distribution (Mn, dispersity) were estimated by GPC relative to linear PMMA standards in THF at 40  $^{\rm o}C$ 

b. F<sub>st</sub> indicates the molar fraction of styrene as determined by <sup>1</sup>H NMR.

c. Total reaction time: 270min

d. Average sequence length of MMA and St units are  $N_{n,MMA}$  and  $N_{n,St}$ .

Table 2 Properties of Smooth Poly(methyl methacrylate-grad-styrene) Gradient Copolymers

Polym	Injectio	Injecti	Т	Mn	Ъ	Fst <sup>b</sup>	Nn,	N <sub>n,M</sub>
er	n	on	ram	(g			St	MA
	Durati	Rate	р	mo				
	on	(ml	rate	⁻¹) ª				
	(min)	min⁻¹)	(°C					
			min					
			<sup>1</sup> )					
G3 <sup>c</sup>	120	0.206	0.17	64	1.4	0.7	2.4	1.7
				00	4	1		
				0				
G4 <sup>d</sup>	360	0.0688	0.05	62	1.4	0.8	3.7	1.6
			6	00	3	1		
				0				

a. Molecular weight distribution (M\_n, dispersity) were estimated by GPC relative to linear PMMA standards in THF at 40  $^{\rm o}C$ 

b.  $F_{st}$  indicates the mole fraction of styrene in the polymer.

c. Reaction proceeded over 210 minutes, pump started after 30 min.

d. Reaction proceeded over 390 minutes, pump started after 30 min.



Figure 1 Instantaneous polymer composition as a function of chain length. a) Blocky GCPs. b) Smooth GCPs.

Table 3 Copolymer Feature Size from Self-Assembly

Polymer	Film Thickness	Feature Size	Center-to-Center		
	(nm)	(nm)	Spacing (nm)		
B1 <sup>a</sup>	41 ± 0.4	31 ± 9	58 ± 7		
G1ª	67 ± 0.3	36 ±12	59 ± 7		
G2 <sup>b</sup>	67 ± 0.1	23 ± 4	-		
G3ª	45 ± 0.2	16 ± 8	46 ± 23		
G4ª	66 ± 0.6	16 ± 7	41 ± 16		

a. Cylindrical domains, feature size indicates the diameter.

b. Lamellar domains, feature size indicates the width.





Figure 2 SEM images of blocky gradient copolymers on silicon substrates: a) B1 on H2, b) G1 on H2, c) G2 on H1.



Figure 3 SEM images of smooth gradient copolymers on silicon substrates modified with H2. a) G3, b) G4.

# Discussion

In this work, the self-assembly of block and gradient copolymers produced equilibrium microstructures driven by thermodynamics in agreement with previous work. They lacked any long-range order, as expected.(10,11) We first

investigated the limits to which a nitroxide-mediated, continuously made GCP (i.e. no intermediate purification and – re-initiation step) can self-assemble in a thin film.

Although this work discusses the effect of the gradient on - self-assembly, previous work has shown that self-assembly behaviour of BCPs has a strong dependence on both the film thickness and the wetting behaviour of the blocks.(38,39) These defects are the result of a combination of surface energy and film thickness effects. The film thickness for all of - the polymers used in this study ( $t \approx 42-66$  nm) was larger than the average feature size. Controlling the thickness so that it is slightly smaller than the average feature size would result in more consistent vertical orientation of the domains.(39,40) We confirmed that there was negligible homopolymer impurities using 2D DOSY in all of the block and gradient copolymers studied, and thus any effect of homopolymers on self-assembly (eg. swelling) could be ignored.

#### Effect of Gradients on Self-Assembly

The presence of the gradient increases the compatibility of the blocks, leading to increased mixing at the domain interface, thereby lowering the effective enthalpic interaction parameter,  $\chi$ .(27,41) Figure 2 and Figure 3 clearly demonstrate that the nature of the GCPs influences self-assembly. Figure 2.a shows block copolymer B1. The observed morphology is vertically aligned cylinders which matches the morphology predicted by theory.(10) Figure 2.b,c show gradient or tapered block copolymers where the second monomer (St) was added nearly instantaneously after a certain period of time to the PMMA-rich chains. Figure 3 demonstrates the final case studied where the second monomer was added gradually over a period of time. If we were to compare the results seen in Figure 2 and Figure 3 to block copolymers with compositions and molecular weights identical to each GCP, we would see that cylindrical domains would form in all cases except for G2, which would self-assemble into lamellar domains.(42) In general, we see that the GCP morphologies match those predicted for their equivalent BCPs, however the defect density observed in the gradients G3 and G4 is quite high.

Despite their similarity to the blocky single injection gradients G1 and G2 in terms of molecular weight and composition, the two smooth GCPs synthesized in this study exhibit poorer self-assembly compared to the blocky gradients. Both smooth gradients were found to have smaller feature sizes but larger variation in the overall size. By employing kinetic simulations, Wang and Broadbelt were able to look beyond the composition profiles of GCPs and examine the individual monomer sequence lengths along a GCP.(43) They found that monomer feed composition has a large effect on sequence lengths for polymers with reactivity ratios less than one, as is the case with MMA/St copolymers ( $r_{St}$  = 0.523,  $r_{MMA}$  = 0.46).(35,43–45) Polymers G4 and G5 were synthesized in such a way that they both have an MMA-rich initial segment, like gradients G1 and G2. However, due to the slow addition of St and temperature increase (from 90 to 110 °C) to polymerize the styrene more effectively (i.e. increase its polymerization

rate, due to its lower propagation rate constant),(46,47) the homopolymer sequence lengths differ greatly from gradients G1 and G2.



Figure 4 The change in homopolymer sequence length from head to tail of each gradient copolymer. Solid line represents the St sequence length, dashed line represents the MMA sequence length. a) G1, b) G2, c) G3, d) G4.

Figure 4 demonstrates the homopolymer sequence lengths as determined using the penultimate model developed by Merz et al.(48) From this figure, we see that the blocky gradients exhibit a sharp change in the homopolymer sequence lengths. The MMA sequence length for both G1 and G2 begins at 6 near the head of the chains and ends at 1 near the tail. However, the St sequence length differs slightly between G1 and G2, with G1 ending at 6 and G2 ending at 7. This can be attributed to the different injection times of the second batch of monomer, allowing G2 to consume more of the MMA before the remaining St was added, meaning less MMA was incorporated after the injection time. Additionally, the location of the crossover point from longer MMA sequence lengths to longer St sequence lengths differs from G1 to G2. In the case of the cylinder-forming G1, the crossover point happens nearer to the beginning of the chains. For the lamellar-forming G2, the crossover point happens near the middle of the chains.

In contrast, polymers G3 and G4 exhibit lower initial MMA sequence lengths of 4 and much more gradual changes in sequence lengths. G3 in particular has the lowest starting sequence length of MMA and ending sequence length St at 4 and 3.5 respectively, which should result in the lowest  $\chi$  of all the polymers studied. This outcome is in good agreement with the poor self-assembly performance seen in Figure 3.a. In contrast to G3, G4 was polymerized for a much longer time, allowing for more St to be incorporated at the end of the reaction as the St sequence length grew to 8, the longest of

any GCP studied, resulting in better self-assembly than G3. However, like G3, the middle of the chains are composed of short homopolymer sequence lengths, increasing the compatibility of the blocks and decreasing the effective  $\chi$ .

In all cases, the result should be a decrease in domain spacing as a direct consequence of the decrease in  $\chi$ . However, the results summarized in Table 4 indicate that the observed D was actually larger than an equivalent BCP for all gradients studied. The reason for this will be discussed in the next section.

#### Effect of Dispersity on Self-Assembly

All of the GCPs possess relatively broad molecular weight distributions (D = 1.35-1.59) compared to typical anionically synthesized copolymers (D < 1.1). The influence of D is well-catalogued with one result being increases in D leading to increase in size of the domain spacing as a result of the decrease in  $\chi$ .(49,50) For the lamellar-forming G2, the comparison was made to results obtained by Anastasiadis et al. who determined a scaling law for lamellar forming monodisperse BCPs.(51) The GCP domain period was found to be nearly twice as large as a monodisperse BCP with identical molecular weight and composition. Using the domain scaling developed by Semenov,(52) and Matsen and Bates(42) for BCPs in the strong-segregation regime, the domain spacing of cylindrical BCPs ( $D \propto N^{2/3}$ ) were estimated. This method provides a spacing of 37.6 nm for a BCP with a molecular

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weight of 67 kg mol<sup>-1</sup> which is in good agreement with experimental results found by Stuen et al.(53) The effect of dispersity on domain spacing is summarized in Table 4 below. Here we can see that in all cases the domain spacing is larger than expected for a monodisperse BCP. The cylindrical GCPs tend to have a relatively small increase in dispersity, ranging from 15% to 27%, while the lamellar forming GCP, G2, has a much larger increase of 49%. Notably, BCP B1 has an increase in expected domain spacing of 70%. This result is expected since the domain spacing scales with both  $\chi$  and N. The presence of the gradient decreases the overall  $\chi$ , offsetting the increase in D due to dispersity.

Table 4 Effect of Dispersity on Domain Spacing

Polymer	Domain	Monodisperse	% Increase	
	Spacing	Domain	in D	
	(nm)	Spacing (nm)		
B1ª	58 ± 7	34	70	
G1ª	59 ± 7	47	25	
G2 <sup>b</sup>	46 ± 8	31	49	
G3ª	46 ± 23	37	26	
G4ª	41 ± 16	36	15	

a. Calculated according to Matsen and Bates(42)

b. Calculated according to Anastasiadis et al.(51)

In this study, we show that NMP can be used to make block and gradient PMMA-PSt copolymers with fairly broad molecular weight distributions. Despite this, self-assembly into microstructures that are similar to that expected for neat block copolymers was observed. Only in cases where the interface was very diffuse due to short homopolymer sequence lengths (i.e. smooth gradients) did the self-assembly become interrupted and poorly ordered domains resulted.

# Conclusions

In this study, GCPs were synthesized in semi-batch mode by NMP, allowing for a single reaction compared to the two steps required for a BCP. The blocky GCPs were able to selfassemble into both vertically aligned cylindrical and lamellar morphologies with feature sizes comparable to BCPs with identical properties. However, the smooth GCPs had very poor self-assembly due to their long transition length and statistical copolymer-like structure in the transition from the MMA-rich to St-rich domains. By further refining the surface wetting and film thickness, in combination with applying patterning from ebeam lithography, it should be possible to produce selfassembled gradient copolymer films with very low defect densities and long-range order.

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## Author Information

#### **Corresponding Author**

\*To whom correspondence should be addressed. E-mail: milan.maric@mcgill.ca.

#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Self-Assembly of Gradient Copolymers Synthesized in Semi-Batch Mode by Nitroxide Mediated Polymerization

# lan Bennett, Kevin Wylie, Milan Maric\*

