

Statistical Copolymer Brush Composition Gradients via Microchannel Confined Surface-Initiated Photopolymerization

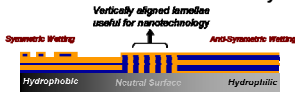


Motivation

The design of new combinatorial libraries of surface-grafted polymers that express systematic gradients in complex chemistries and molecular architecture are of interest for development of two basic measurement platforms:

- 1) Measurement of reactivities and kinetic parameters which are key to developing viable applications of surface-initiated polymerization (SIP), and
- 2) Combination with nano- and micro-scale patterning for high-throughput characterization of surface and interfacial effects key to nanotechnology and nanometrology

Surface Directed Self-Assembly

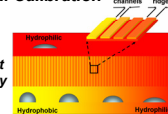


Macromolecules 1998, 31, 7641.
Macromol. Rapid Com. 2003, 24, 131.

Applications Areas

- Surface functionalization
- Stationary phase modification for affinity chromatography
- Friction management in MEMS
- Adhesion management
- Particle functionalization

SPM Calibration

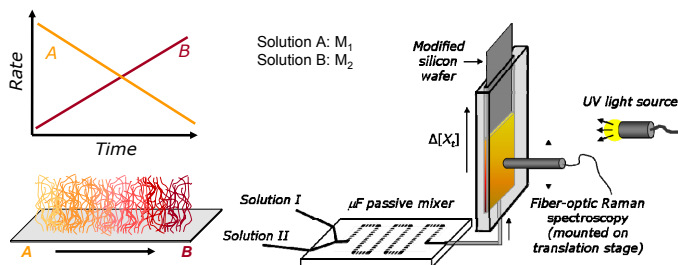


Calibrated Gradient Micropattern Library

Nanoletters, 2005, 5, 1535.

Approach

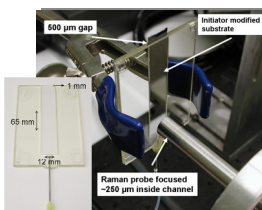
Statistical Copolymer Brush Gradients



A solution gradient is created within the microchannel by systematically varying the relative infusion rates of two monomer solutions as the channel is filled. The solution gradient stability is then measured using Raman spectroscopy and transferred to the substrate at room temperature by surface-initiated ATRP or photopolymerization.

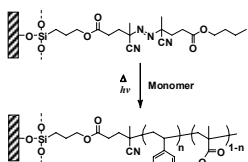
For previous work on statistical copolymer gradients see Adv. Mater. 2006, 18, 1427.

Experimental Setup



- The microchannel device is designed and fabricated using rapid prototyping technology (frontal photopolymerization of thiolene chemistry) Langmuir 2005, 21, 3629.
- A 500 μm gap is obtained by inserting an initiator modified substrate into the microchannel device

Substrate Modification



Surface-Initiated Photopolymerization

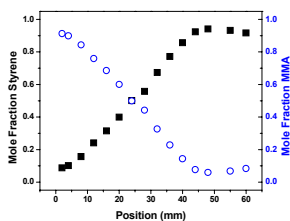
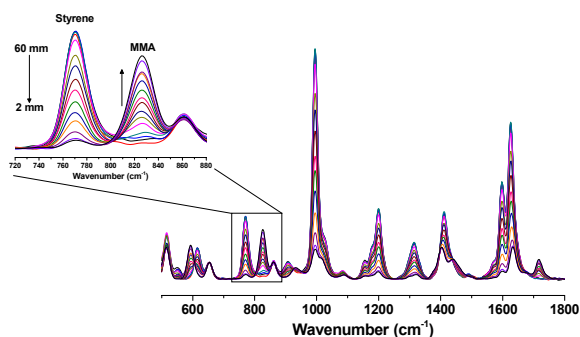
- Polymer brush is grown from substrates modified with an AIBN derivative
- Initiation is induced by exposure to UV irradiation ($\lambda_{max} = 365 \text{ nm}$)
- Room temperature reaction condition is a key requirement for stabilization of the solution gradient
- Wide range of monomer types

Macromolecules 1998, 31, 592.
Adv. Polym. Sci. 2006, 197, 47.

Results

Solution Gradients: Styrene/MMA

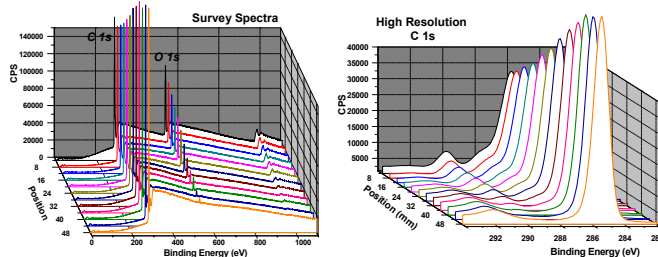
- The solution gradient inside the channel was established by manipulating the relative infusion rates of the two monomer solutions (0.2 mL min^{-1}), and designed to be 40 mm in length with a step height of 4 mm
- Composition of the solution gradient was mapped using Raman spectroscopy by taking spectra at 4 mm intervals along the channel. A series of reference spectra were obtained from solutions of known concentration for calibration purposes
- Spectra were normalized to a band specific to DMF after background and baseline correction



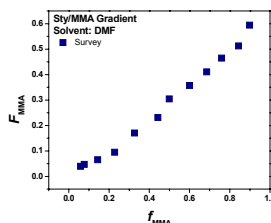
- A plot of monomer concentration vs. position confirms the presence of a composition gradient from ~9 mol % styrene to ~94 mol % styrene
- Excess styrene (15 mm) was incorporated into the gradient to account for evaporation

Statistical Copolymer Brush Gradients: PS/PMMA

- X-ray photoelectron spectroscopy (XPS) was used to map the surface composition of the statistical copolymer brush gradients
- Spectra were collected at 4 mm intervals along the gradient substrate allowing correlation between monomer feed and copolymer brush composition



- A gradient in copolymer composition was confirmed by XPS analysis
- Survey spectra of the gradient surface shows a gradual decrease in the O 1s peak from the PMMA rich region to the PS rich region
- The corresponding C 1s and O 1s high resolution spectra show a linear decrease in the PMMA content as a function of position



- The instantaneous copolymer composition diagram (left) correlates the monomer feed data (obtained from Raman) to the copolymer brush composition data (obtained from XPS survey data)
- The diagram for the gradient Sty/MMA system shows a composition ranging from ~0.04 to 0.59 mole fraction MMA indicating an enrichment of the styrene component in the copolymer brush

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Results (cont.)

Quantitative Analysis of Surface Composition

- Quantitative analysis of the copolymer brush surface composition was evaluated using two methods: (1) Elemental O/C ratio from the survey spectra and (2) relative ester contribution to the C 1s envelope
- High resolution spectra were fitted with a unified model across the C 1s and O 1s envelopes using constraints from the known stoichiometry to separate the various contributions

Survey Method

$$F_{MMA} = \frac{8(O/C)_{exp}}{3(O/C)_{exp} + 2}$$

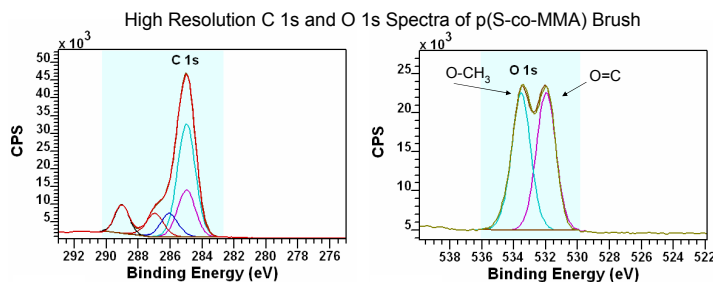
where $(O/C)_{exp}$ is the O/C ratio obtained from XPS

Ton-That et al. *Polymer* 2001, 42, 1121.

High Resolution Method

$$F_{MMA} = \frac{8(I_{O=C}/I_C)_{exp}}{3(I_{O=C}/I_C)_{exp} + 1}$$

where $(I_{O=C}/I_C)$ is the ratio of the carbonyl C to the total C

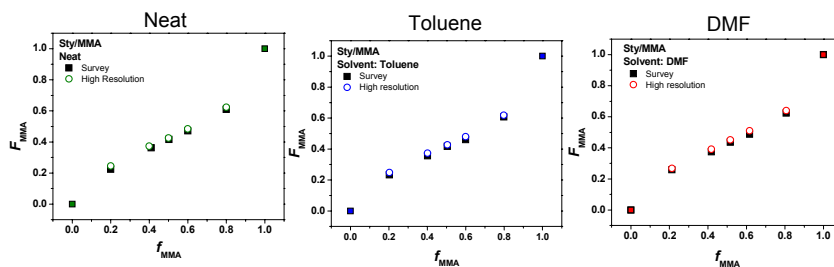


- The C 1s spectrum of PS consists of a main hydrocarbon peak at a binding energy (BE) of 285.0 eV and $\pi - \pi^*$ shake-up satellites at 6 – 8 eV higher in BE
- The C 1s envelope of PMMA can be resolved into four components: hydrocarbon (C-C/C-H) at a BE of 285.7 eV, β -shifted carbon at 285.7 eV, methoxy carbon at 286.8 eV, and the carbonyl carbon at 289.1 eV

Discrete Samples: Reactivity Ratios from Surface-Grafted Polymer Systems

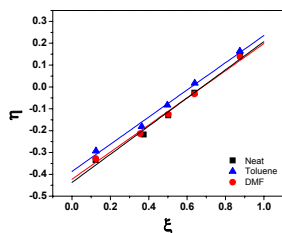
- Discrete statistical copolymer brush samples were prepared from known monomer feeds under various solvent conditions to evaluate the effect of reaction conditions on the resulting brush composition and to explore the feasibility of obtaining reactivity ratios from a surface grafted polymer system
- Monomer feeds included 80/20, 60/40, 50/50, 40/60, and 20/80 mole ratios of neat Sty/MMA and the corresponding toluene and DMF solutions
- Copolymer composition was obtained from XPS analysis of survey and high resolution spectra

Instantaneous Copolymer Composition Diagrams for Sty/MMA



Methods for Evaluating Reactivity Ratios

- Initial reactivity ratios from the Sty/MMA surface grafted system were first estimated by graphical analysis according to Fineman-Ross and Kelen-Tüdös methods
- Reactivity ratios were determined by a linear least-squares fit of the experimental data



- Kelen-Tüdös diagram for Sty-MMA brush system evaluated from the high resolution XPS data. ξ and η are mathematical functions of the mole ratios of monomers in the feed and in the copolymer brush

J. Polym. Sci., Polym. Chem 1950, 5, 259.
J. Macromol. Sci. Chem. A, 1975, 9, 1.

- No significant dependence of brush composition on the various reaction conditions was observed for the discrete copolymer brush samples
- The instantaneous copolymer composition diagrams for the PS-PMMA brush system resemble that obtained from bulk reaction conditions, yet the PMMA content is lower than expected as the MMA content in the monomer feed increases

Copolymers	Method	XPS Survey			XPS High Resolution		
		$r_{1,MMA}$	$r_{2,Sty}$	$r_{1}r_{2}$	$r_{1,MMA}$	$r_{2,Sty}$	$r_{1}r_{2}$
Sty-MMA (neat)	Fineman-Ross	0.207	0.694	0.144	0.229	0.634	0.145
	Kelen-Tüdös	0.198	0.675	0.134	0.208	0.597	0.124
Sty-MMA (toluene)	Fineman-Ross	0.206	0.706	0.145	0.219	0.618	0.135
	Kelen-Tüdös	0.179	0.654	0.117	0.199	0.581	0.116
Sty-MMA (DMF)	Fineman-Ross	0.217	0.629	0.136	0.244	0.557	0.136
	Kelen-Tüdös	0.196	0.588	0.115	0.236	0.543	0.128
Commonly accept literature values for bulk polymerization of Sty-MMA							
Sty-MMA (neat)		0.46	0.52	<i>Macromolecules</i> 1989, 22, 1145.			
Sty-MMA (toluene)		0.39	0.53				

- It is our intention to further evaluate the kinetic data using a non-linear error in variables model (EVM) method

Conclusions and Future Work

- Statistical copolymers can be prepared with a gradient in chemical composition across the surface utilizing surface-initiated photopolymerization
- Demonstrated a novel approach for evaluating monomer reactivity ratios using surface-grafted statistical copolymer systems as a measurement platform

Future Work:

- Develop a combinatorial approach to map block copolymer self-assembly using the statistical copolymer brush gradients
- Combine the surface grafted gradients with patterned surfaces for SPM calibration and templating applications
- Continue the development of our approach to reactivity ratio measurements with other monomer pairs to better understand the influence of surface-initiated polymerizations on the fundamental reactivities and kinetic parameters

Contributors

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