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A robust and high-throughput measurement platform for monomer reactivity ratios from surface-initiated polymerization†

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This article describes a robust approach to measure monomer reactivity ratios from surface-initiated copolymerization, by measuring composition of statistical copolymer brush surfaces using X-ray photoelectron spectroscopy. Statistical copolymer brushes were prepared from various monomer feeds by surface-initiated radical copolymerization at room temperature under ultraviolet (UV) irradiation. The copolymer brush composition data were fit to the terminal copolymerization kinetic model resulting in point estimates for the monomer reactivity ratios that are in good agreement with values measured under bulk reaction conditions. Additionally, a high-throughput approach was demonstrated to measure reactivity ratios using a single substrate exhibiting a gradient in copolymer brush composition. This high-throughput approach significantly reduces the time and effort required to generate reliable and reproducible point estimates of reactivity ratios, and these values are in good agreement with values obtained from both the discrete sample surface measurements and classical bulk analytical methods.

Introduction

Free radical copolymerization is a well-established methodology to prepare polymeric materials exhibiting synergistic properties of the constituent monomers for a broad range of applications. The distribution of monomer sequences, as well as compositional heterogeneity along the macromolecular chain plays an influential role in determining the ultimate physical and chemical properties of the copolymer. Knowledge of monomer reactivity ratios provides the necessary insight to control and predict the monomer sequence; however, these kinetic parameters are time-consuming and difficult to accurately measure.[1] Reactivity ratios can be regressed from the copolymer composition (F) in the product as a function of monomer fractions (f) as given by the instantaneous copolymer expression shown in eqn (1).[2] Typically, F values are measured using spectroscopic techniques that are sensitive to the quantity of a specific functional group within

the copolymer structure. Traditionally, nuclear magnetic resonance spectroscopy is used to quantify the copolymer composition following the synthesis and purification of a series of copolymers with a broad range of molar compositions. Other spectroscopic characterization techniques, including Fourier-transform infrared (FTIR)[3] and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry,[4] represent more recent strategies toward the measurement of monomer reactivity ratios.

Recently, we demonstrated a new approach to measure monomer reactivity ratios from surface-initiated copolymerization (SIP) using X-ray photoelectron spectroscopy (XPS).[5] The copolymerization of two monomers from surface-bound initiators yields a statistical copolymer brush surface, where the monomer sequence and distribution within the tethered chains is dictated by monomer reactivities. Such an approach produces a statistical distribution of monomer constituents at the film interface that reflect the distribution along the length of the tethered polymer chains.[6,7] This covalently "trapped" statistical copolymer brush interface provides an ideal platform for determination of surface composition using surface-sensitive spectroscopic techniques such as XPS. Previously, we showed that monomer reactivity ratios for styrene and methyl methacrylate measured by SIP and XPS closely resemble the values measured under bulk conditions by traditional NMR analysis. In this work, we seek to show broader applicability of the statistical copolymer brush measurement platform *via* determination of reactivity ratios for three additional monomer pairs exhibiting a broader range of copolymerization behaviors. Additionally, we present a high-throughput approach enabled by

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microchannel-confined surface-initiated copolymerization to measure reactivity ratios using a single substrate exhibiting a gradient in copolymer brush composition. The high-throughput approach significantly reduces the time and effort required to generate reliable and reproducible point estimates of reactivity ratios.

Experimental

Materials

Reagent chemicals were purchased from Aldrich and used without further purification unless otherwise indicated. Monomers were passed through a column of activated basic alumina to remove the inhibitor and stored at -20 °C prior to use. The asymmetric azo-initiator, modified from the work of Prucker and coworkers,[8] was synthesized as previously reported.[5]

Preparation of initiator functionalized silicon substrates

Silicon wafers were cut into 1.2 cm $\times$ 2 cm pieces and ultrasonically cleaned in acetone, dichloromethane, toluene, and ethanol for 15 min in each solvent. The substrates were dried under a stream of N_2 and treated with UV-ozone for 45 min. The substrates were immediately immersed in a 1 mmol L^{-1} toluene solution of the trichlorosilyl-functionalized initiator containing triethylamine as a catalyst and acid scavenger. The solutions with the substrates were left to stand overnight. The substrates were thoroughly rinsed with toluene, acetone, and ethanol and dried under a stream of N_2. The average thickness of the initiator layer was 2.6 nm $\pm$ 0.13 nm as determined by ellipsometry. Ellipsometric measurements were carried out using a discrete wavelength ellipsometer (EL X-01R, Micro Photonics Inc.) with a 632.8 nm laser at 70° from the normal. Refractive index values of 3.86, 1.45, 1.43 and 1.5 for silicon, oxide layer, photoinitiator monolayer and all polymer layers, respectively, were used to build the layer model and calculate layer thicknesses.[8]

Synthesis of statistical copolymer brush modified substrates

Monomer solutions were prepared with various molar ratios and degassed by bubbling Ar through the solution for 30 min. An initiator-modified silicon substrate was suspended in a reaction tube fitted with a rubber septum and a stir bar. The reaction tube was degassed by three vacuum pump/Ar backfill cycles followed by introduction of the monomer solution *via* a cannula. The reaction tube was then placed on a stir plate and irradiated with UV light (Exfo Novacure 2100) ($\lambda_{max} = 365$ nm) at a distance of 25 cm for an appropriate length of time to obtain the targeted 25 nm brush thickness (specific time varied with monomer composition, *i.e.*, 45 min to 75 min). Light intensity at the substrate surface was approximately 20 mW cm^{-2}. The polymerization reactions were carried out at ambient temperatures. When necessary, the reactions were maintained at ambient temperature through the use a small fan directed at the surface of the reaction vessel. After polymerization, the brush-modified substrate was removed from the reaction tube and rinsed with toluene. The physisorbed polymer was removed by Soxhlet extraction in toluene for a minimum of 24 h. The thickness of the copolymer brush samples averaged 24 nm $\pm$ 3 nm after Soxhlet extraction, as determined by a minimum of three ellipsometry measurements per substrate.

Gradient approach to reactivity ratios

Polymer brush samples exhibiting a stepped copolymer composition gradient were prepared by SIP in a custom built inert atmosphere (nitrogen) box using a microchannel reaction device (fabricated from Norland 81 optical adhesive).[9,10] The initiator-functionalized silicon wafers were placed in a microchannel reaction device approx. 7″ from the UV light source ($\lambda_{max} = 365$ nm, Omnicure Series 1000 with a 5 mm collimating adaptor, light intensity at the surface: 20 mW cm^{-2}). N,N′-dimethylformamide (DMF) served as both a solvent and an internal standard for Raman spectroscopy measurements. Styrene/DMF and MMA/DMF solutions were prepared containing 10% w/w DMF. After purging the reaction chamber and monomer solutions with N_2 for 30 min, the monomer solutions were transferred into glass syringes that were then affixed to separate syringe pumps. A solution gradient was fabricated by stepping the syringe flow rates with respect to one another (*i.e.* styrene flow rate (mL min^{-1}):MMA flow rate (mL min^{-1}) $- 0.27:0.03$, $0.24:0.06$, $0.18:0.12$, $0.15:0.15$, *etc.* with a constant total flow rate of 0.3 mL min^{-1}). Styrene and MMA solutions were passed through a microfluidic passive mixer and into the vertically oriented microchannel holding the initiator-functionalized silicon wafer. The pump time was adjusted such that each step in the solution gradient was approximately 1 cm in height. Comonomer concentration at each step in the solution gradient was measured by Raman spectroscopy using a Raman Systems spectrometer (R3000HR) equipped with a fiber optic probe and 785 nm excitation wavelength laser. The focal point of the laser was adjusted to sit at the midway point within the microchannel between the Si substrate and quartz window. Spectra were normalized to DMF and concentrations were determined using standard calibration procedures. The solution gradient was transferred to the substrate *via* surface-initiated photopolymerization upon exposure to UV light for 45 min. After polymerization, the substrate was removed from the microchannel device, rinsed with toluene, and any physisorbed polymer was removed by Soxhlet extraction in toluene for a minimum of 24 h.

Synthesis of statistical copolymers under bulk conditions

Monomer solutions were prepared with various molar ratios of monomers in septum sealed reaction tubes and degassed by bubbling Ar through the solution for 30 min. The reaction tubes were then immersed in a temperature controlled oil bath at 65 °C $\pm$ 1 °C for 15 min. The polymerizations were quenched by immersion in liquid nitrogen and diluted with tetrahydrofuran. The polymers were purified by precipitation (repeated 3 times) into an excess of non-solvent (*i.e.* methanol) and collected by filtration. Monomer conversion was determined by gravimetric analysis of the recovered polymer after vacuum drying for 3 days. In all cases, monomer conversion was kept well below 10% to avoid compositional drift associated with higher conversions. Copolymer composition was determined by ¹H NMR.

X-ray photoelectron spectroscopy

XPS measurements were performed using a Kratos Axis Ultra Spectrometer (Kratos Analytical, Manchester, UK) with a monochromatic Al K X-ray source (1486.6 eV) operating at 150 W under 1.0×10^{-9} Torr. Measurements were performed in hybrid mode using electrostatic and magnetic lenses, and the pass energy of the analyzer was set at 40 eV for high-resolution spectra and 160 eV for survey scans, with energy resolutions of 0.1 eV and 0.5 eV, respectively. Generally, a total acquisition time of 220 s was used to obtain a single-pass survey spectrum. For a 0° take off angle (angle between sample surface normal and the electron optical axis of the spectrometer), the maximum information depth of the measurements was approximately 8 nm.[11] All XPS spectra were recorded using the Kratos VISION II software; data files were translated to VAMAS format and processed using the CasaXPS software package (v. 2.3.12). Binding energies were calibrated with respect to C 1s at 285 eV. Elemental compositions were determined after subtraction of a universal poly Tougaard background[12,13] and tabulated relative sensitivity factors derived from Scofield cross-sections. This method is estimated to give an accuracy of 10% in the measurement of elemental compositions. High resolution spectra were fitted using mixtures of Gaussian/Lorentzian peaks. The fitting parameters were peak position, full width at half-maximum, intensity, and the Gaussian fraction. Quantification of the surface composition for the statistical copolymer brushes was carried out using a method that considers the elemental O/C (or N/C where appropriate) ratio from the survey spectra. This method was adapted from literature.[14]

Statistical methods[15]

To determine the monomer reactivity ratios we used classical methods to evaluate the data by comparing the copolymer composition to the monomer feed composition (at low monomer conversions) using the instantaneous copolymerization equation:

$$F_1 = G(f_1, r_1, r_2) = \frac{r_1 f_1^2 + f_1(1 - f_1)}{r_1 f_1^2 + 2f_1(1 - f_1) + r_2(1 - f_1)^2} \quad (1)$$

where F_1 is the mole fraction of monomer 1 in the final copolymer, f_1 is the mole fraction of monomer 1 in the feed, and r_1 and r_2 are the reactivity ratios of monomer 1 and 2, respectively. Eqn (1) was fit to the composition data obtained from the XPS and Raman analysis, or known feed composition, using a non-linear least squares method. This method seeks to minimize the difference between the fitting function (eqn (1)) and the real data by iteratively changing the fitting parameters to find the global minimum in the weighted sum of squares error which is defined by:

$$SSE(r_1, r_2) = \sum_{i=1}^{n} \left(\frac{F_{1i} - G(f_{1i}, r_1, r_2)}{\sigma_i} \right)^2 \quad (2)$$

where r_1 and r_2 are the fitting parameters related to the reactivity ratios for the different monomers, F_1 is the mole fraction of monomer 1 in the copolymer as measured by XPS, f_1 is mole fraction of monomer 1 in the feed, σ is the standard deviation of the error distribution in the measured value of F_1, and n is the number of data points. The fitting was carried out using the

DataFit software by Oakdale Engineering. The error bars of the determined reactivity ratios represent one standard deviation in the error associated with the weighted fit.

In order to more accurately represent the error associated with the determination of the reactivity ratios, the 95% unbiased joint confidence interval (JCI) ellipse was evaluated for each set of experiments. The joint confidence region can be expressed using the following inequality:

$$SSE(\theta) \le SSE(\hat{\theta}) \left[1 + \frac{p}{n - p} \cdot F(p, n - p, 1 - \alpha) \right] \quad (3)$$

where θ represents the set of r_1 and r_2 values that minimize the weighted sum of squares error, θ represents a vector array of r_1 and r_2 values centered about the best r_1 and r_2 values, p is the number of fitting parameters, n is the number of data points, α is used to choose the confidence interval (for 95% JCI $\alpha = 0.05$), and $F(p, n - p, 1 - \alpha)$ represents the F-distribution level at the 95% confidence interval. Using the parameters $p = 2$ and $n = 5$, an F-distribution table yielded a value of 9.5521 for $F(p, n - p, 1 - \alpha)$. Using these parameters, the boundary of the joint confidence interval ellipse is described by the values of the $SSE(\theta)$ that satisfy the following condition:

$$SSE(\theta) \le 7.3680 \cdot SSE(\hat{\theta}) \quad (4)$$

The boundary values of the reactivity ratios obtained from eqn (4) were plotted along with the point estimates for the reactivity ratios, therefore outlining the 95% unbiased joint confidence interval ellipse.

Results and discussion

Synthesis and quantification of statistical copolymer polymer brush surfaces

Scheme 1 shows the general route for the synthesis of copolymer brushes *via* surface-initiated photopolymerization. First, silicon
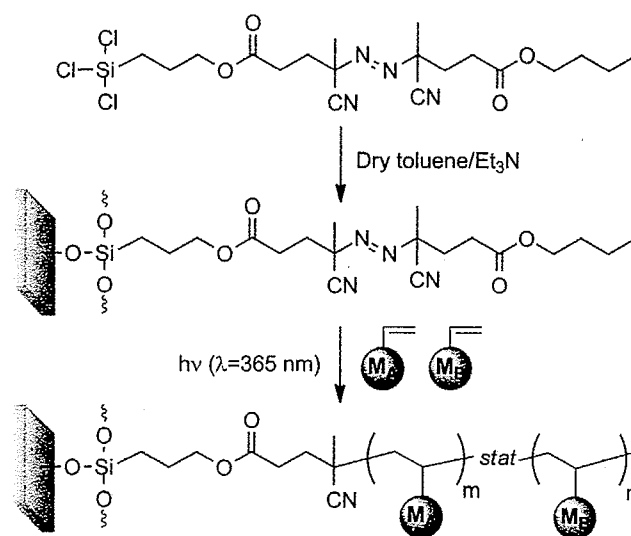
Scheme 1 Synthetic route to statistical copolymer brush surfaces *via* surface-initiated photopolymerization. M_A and M_B represent the vinyl monomer structures used in this work.

wafers were modified with an asymmetric trichlorosilyl-functionalized azo initiator from a dry toluene solution containing triethylamine. The average thickness of the initiator layer (2.6 nm ± 0.13 nm), as measured by ellipsometry, indicates the formation of a monolayer film structure. A minimum copolymer brush thickness of 25 nm was targeted to simplify quantification of the copolymer composition by avoiding spectroscopic contributions from the SiO_x of the initiator layer and the silicon substrate. In all cases of SIP discussed herein, monomer conversion was determined to be less than 1% based on gravimetric analysis of the free polymer formed in solution.

As described in our previous work, XPS was employed to quantify the composition of the statistical copolymer brush surfaces.[5] In the present work, all composition data were calculated from the survey spectra to avoid error associated with polymer degradation under extended X-ray irradiation required to collect high resolution spectra for each constituent element. Thus, the total acquisition time for the survey spectrum for each sample was 180 s during which no statistical change in the elemental percentages were observed. Copolymer compositions were determined by comparing the integrated O and C peak areas, or in some cases the integrated N and C peak areas, from the survey spectra.

Monomer reactivity ratios

Monomer reactivity ratios were determined from SIP reactions using classical methods to evaluate the data by comparing copolymer surface composition (F) to monomer feed composition (f) at low monomer conversions using the instantaneous copolymerization equation (eqn (1)). In all cases, the copolymer composition data was fit to eqn (1) using a nonlinear least squares (NLLS) optimization after van Herk.[15]

The reactivity ratios for all cases explored in the article are summarized in Table 1. It should be noted that due to the homolytic cleavage of the surface-bound azo-initiator, copolymerization occurs both from the surface and in solution. However, due to the low concentration of surface-bound initiator relative to monomer concentration, monomer conversion remains inherently low (less than 1% based on gravimetric analysis of the free polymer formed in solution) and avoids compositional drift associated with depletion of the more reactive monomer with increasing conversion.[26] Consequently, we avoid the necessity of measuring reactivity ratios by either experimentally limiting conversion or accounting for drift with more complex statistical treatments that include functions for conversion.
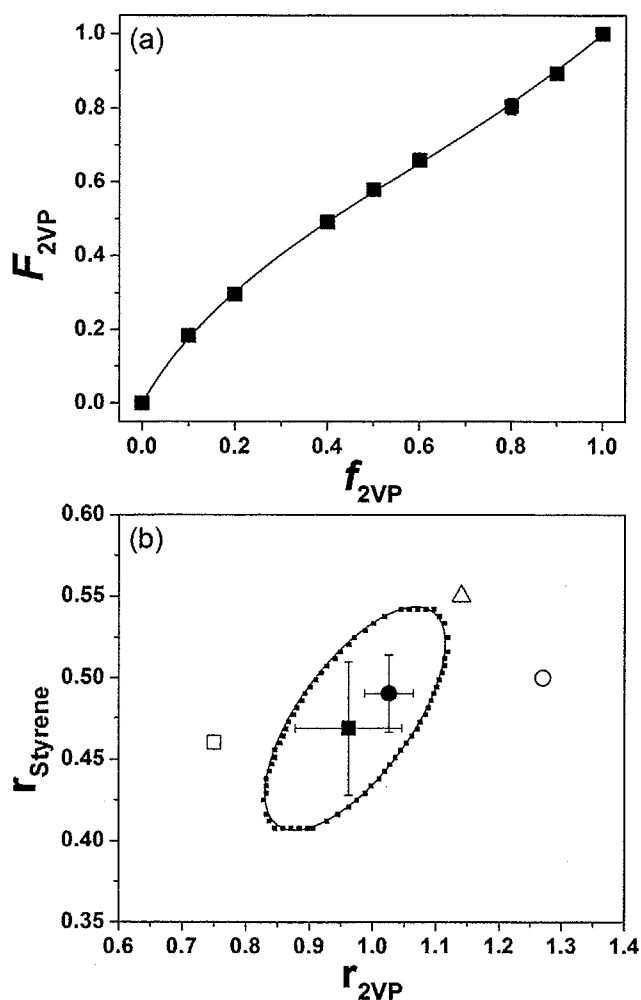

Fig. 1 (a) Mayo-Lewis plots for the styrene/2-vinyl pyridine copolymer brush system as determined by X-ray photoelectron spectroscopy (XPS) (mean ± S.D., replications = 3; error bars lie within the data points). The solid line corresponds to the nonlinear least squares (NLLS) fit for the brush system. (b) Reactivity ratio point estimates (bound by 95% joint confidence interval, error bars correspond to the standard deviation in the NLLS fit) for surface-initiated copolymer obtained by NLLS analysis of the XPS survey (■) and NMR (●) composition data and literature values from bulk polymerization conditions; Tamikado et al.[16] (□), Walling et al.[17] (△), Brown et al.[18] (○). The elliptical line is drawn to guide the reader's eye.

Fig. 1a shows the Mayo-Lewis plot obtained from XPS survey composition data for a styrene/2-vinylpyridine (Sty/2VP) statistical copolymer brush. The composition curve represents the

Table 1 Point estimates of reactivity ratios of various monomers determined under surface-initiated conditions by X-ray photoelectron spectroscopy (XPS) and under bulk conditions by nuclear magnetic resonance spectroscopy (^{1}H NMR)[a]

Method	Sty-MMA[b]		Sty-MMA Gradient[c]		Sty-MA		Sty-2VP		2VP-MA	
	r_1	r_2	r_1	r_2	r_1	r_2	r_1	r_2	r_1	r_2
XPS	0.497	0.459	0.490	0.432	0.797	0.133	0.469	0.962	1.73	0.069
^{1}H NMR	0.495	0.456	N/A	N/A	0.768	0.142	0.490	1.03	1.99	0.073

[a] Abbreviations: styrene (Sty), methyl methacrylate (MMA), methyl acrylate (MA), 2-vinyl pyridine (2VP). [b] Previously published data.[5] [c] Stock monomer solutions prepared at 80% (w/w) in dimethyl formamide. Std. deviations for all data are given in respective point estimate plots.

average of three repetitive runs and exhibits high reproducibility as indicated by the small error bars associated with each copolymer composition (error bars are encompassed by the data point). NLLS evaluation of the composition data yielded a point estimate bound by the 95% joint confidence intervals for the reactivity ratios for the surface-initiated copolymerization of Sty and 2VP. The point estimate values $(0.469_{Sty}, 0.962_{2VP})$ obtained from SIP are in good agreement with the point estimate values $(0.490_{Sty}, 1.03_{2VP})$ obtained from the bulk copolymerization by NMR. For comparison and to show the large variation in reported values, bulk reactivity ratios from several literature sources are also provided. To demonstrate broader applicability, additional monomer pairs were investigated including styrene/ methyl acrylate (Sty/MA) and 2-vinylpryridine/methyl acrylate (2VP/MA). The Mayo-Lewis plot and reactivity ratio point estimates for Sty/MA are shown in Fig. 2a and 2b, respectively. As shown, the reactivity ratio point values obtained by XPS $(0.797_{Sty}, 0.133_{MA})$ and NMR $(0.768_{Sty}, 0.142_{MA})$ are in good agreement, as the 95% joint confidence interval encompassing the XPS value overlaps the value from traditional NMR analysis. Several literature values for the reactivity ratios of Sty/MA are shown for comparison. Similar results were observed for the surface-initiated copolymerization of 2VP and MA as shown in Fig. 3. Again, the NLLS evaluation of composition data obtained by XPS and NMR provide reactivity ratio point estimates (Fig. 3b) that are in reasonable agreement with one another (XPS: $1.73_{2VP}, 0.069_{MA}$ and NMR: $1.99_{2VP}, 0.073_{MA}$). Notably, in all three of the aforementioned examples, the SIP and statistical copolymer brush platform yield reactivity ratios with high reproducibility – likely a direct consequence of not only the inherently low monomer conversion, but also the simplified purification procedures used to obtain the copolymer surface for composition analysis. As previously mentioned, the multistep precipitation and extensive drying steps typically employed to remove excess monomer and solvent are replaced by a straightforward solvent extraction. We believe that with careful control over the accuracy of the initial monomer feed ratios, the SIP and copolymer brush approach to measure reactivity ratios removes much of the variability that arises from differences in lab protocols. However, the tedious process of measuring reactivity ratios – i.e. the synthesis, purification and characterization of multiple individual samples – remains irrespective of the previously described measurement platforms. A high-throughput approach to measure reactivity ratios while maintaining a high degree of reproducibility would be advantageous in terms reducing the time and effort necessary to obtain reliable reactivity ratio values.

We developed a high-throughput approach to measure reactivity ratios based on the previously described platform of surface-initiated copolymerization and XPS analysis, but with implementation of gradient techniques that significantly reduce the time and effort required to produce high quality copolymerization kinetic parameters. Fig. 4 shows the experimental setup designed to fabricate a discretely stepped statistical copolymer brush gradient. The setup employs a vertically-oriented microchannel reactor that holds an initiator-functionalized silicon substrate. Monomer feed solutions were delivered via a syringe pump through a microfluidic passive mixer. A solution gradient was fabricated by stepping the syringe flow
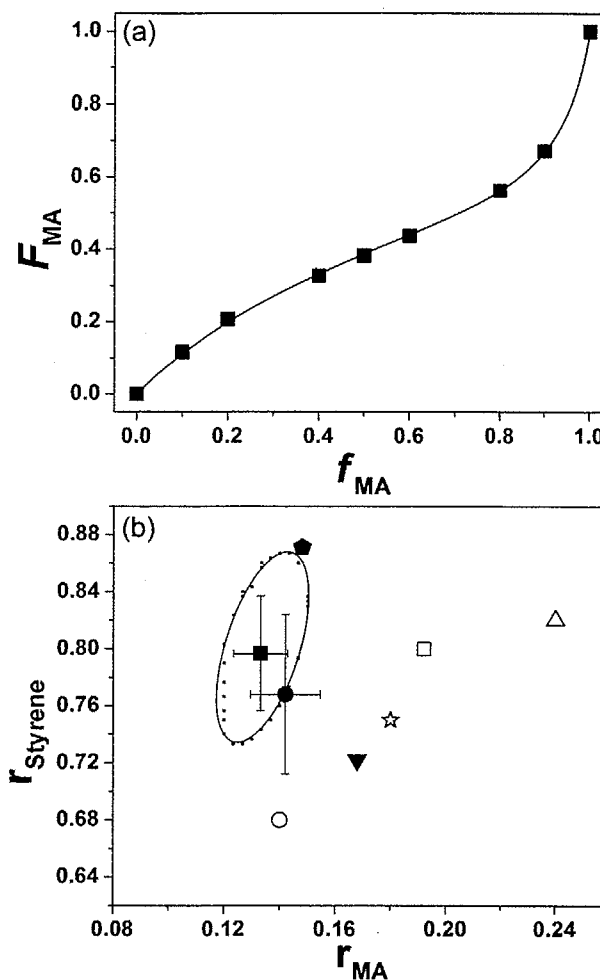

Fig. 2 (a) Mayo-Lewis plots for the styrene/methyl acrylate copolymer brush system as determined by X-ray photoelectron spectroscopy (XPS) (mean ± S.D., replications = 3; error bars lie within the data points). The solid line corresponds to the nonlinear least squares (NLLS) fit for the brush system. (b) Reactivity ratio point estimates (bound by 95% joint confidence intervals, error bars correspond to the standard deviation in the NLLS fit) for surface-initiated copolymer obtained by NLLS analysis of the XPS survey (■) and NMR (●) composition data and literature values from bulk polymerization conditions; Simionescu et al.[19] (◆), Luskin et al.[20] (○), Marvel et al.[21] (▼), Burlant et al.[22] (★), Alfrey et al.[23] (□), Lewis et al.[24] (△). The elliptical lines are drawn to guide the reader's eye.

rates with respect to one another with a constant total flow rate of 0.3 ml min^{-1}, i.e. styrene flow rate (mL min^{-1}):MMA flow rate (mL min^{-1}) was 0.27 : 0.03, 0.24 : 0.06, 0.18 : 0.12, 0.15 : 0.15, etc. The total pump time for each step was adjusted such that the height of each step in the gradient was approximately 1 cm. Although the comonomer feed ratios are known from the pump rates, mixing at the interface of each step in the solution gradient undoubtedly occur. Raman spectroscopy (details provided in the experimental section) was used to measure the actual comonomer concentration at each gradient step prior to SIP. The series of normalized Raman spectra shown in Fig. 5a were used to calculate the feed concentration of styrene and MMA in the center of each step. The solution gradient was then transferred to the substrate using SIP, where the local monomer concentration at each point along the gradient dictates the composition of the
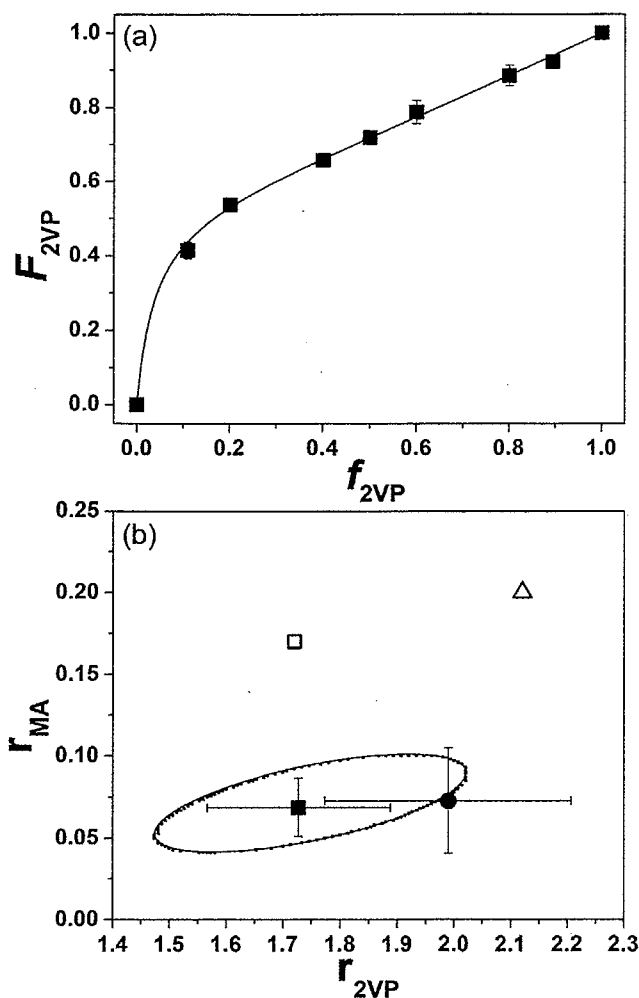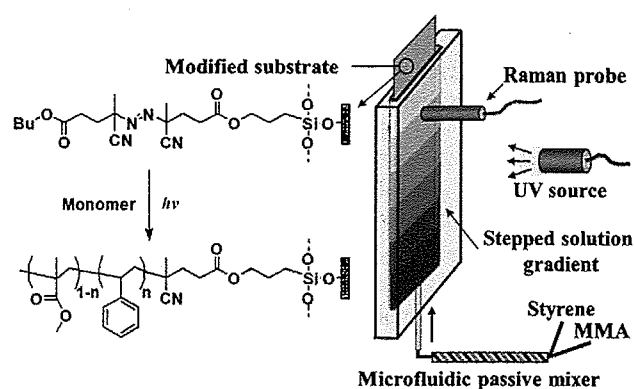
Fig. 4 Experimental setup for preparing stepped monomer gradients within a microchannel device. Monomer concentration is determined by fiber-optic Raman spectroscopy and polymerization is initiated from the surface using ultraviolet light.
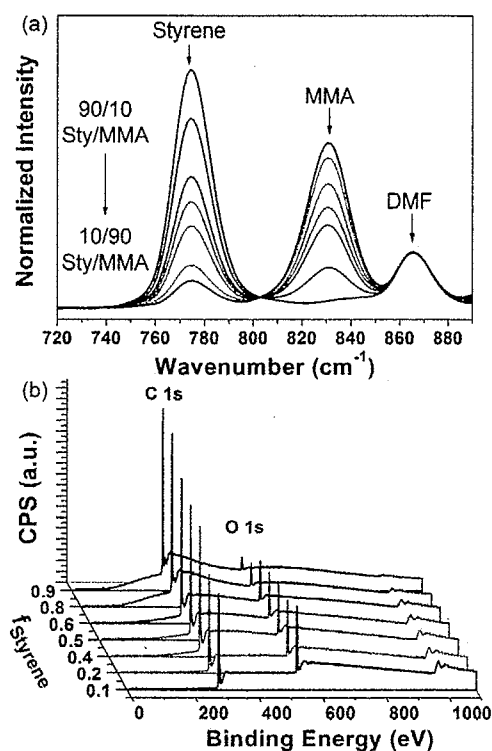

Fig. 3 (a) Mayo-Lewis plots for the 2-vinyl pyridine/methyl acrylate copolymer brush system as determined by X-ray photoelectron spectroscopy (XPS) (mean ± S.D., replications = 3; error bars lie within the data points). The solid line corresponds to the nonlinear least squares (NLLS) fit for the brush system. (b) Reactivity ratio point estimates (bound by 95% joint confidence interval, error bars correspond to the standard deviation in the NLLS fit) for surface-initiated copolymer obtained by NLLS analysis of the XPS survey (■) and NMR (●) composition data and literature values from bulk polymerization conditions; Tamikado *et al.*[16] (□), Natansohn *et al.*[25] (△). The elliptical line is drawn to guide the reader's eye.

Fig. 5 (a) Representative Raman spectra from a styrene/methyl methacrylate stepped solution gradient. Spectra were normalized to DMF and concentrations were determined using standard calibration procedures. (b) Representative X-ray photoelectron spectra obtained from a styrene/methyl methacrylate statistical copolymer brush gradient.

resulting statistical copolymer brush. After extraction, XPS analysis was performed along the gradient at locations corresponding to the locations of the previous Raman spectroscopy measurements of the solution gradient. Fig. 5b shows the series of XPS survey scans taken from each step of the statistical copolymer brush gradient. As expected, the intensity of the C1s peak decreases with decreasing fraction of styrene in the comonomer feed, while the O1s peak intensity increases with increasing fractions of MMA. Quantification of the surface copolymer composition from the XPS survey spectra in Fig. 5b and the comonomer feed from the corresponding Raman spectra in Fig. 5a provides the Mayo-Lewis plot shown in Fig. 6a. Excellent agreement of the gradient composition data points (open squares) with the overlaid discrete composition data points[5] (solid squares) indicates that minimal mixing occurs once

the monomer solution gradient is established within the microchannel and that the solution gradient is stable over the timeframe of SIP. The Sty and MMA reactivity ratios resulting from the NLLS evaluation of the gradient copolymer composition data are shown in Fig. 6b, along with values from our previous publication[5] derived from discrete measurement by XPS and bulk values by NMR. Notably, the reactivity ratios derived from the high-throughput gradient approach are in excellent agreement with our previously reported point estimates from discrete copolymer brush measurements. Furthermore, the 95% joint
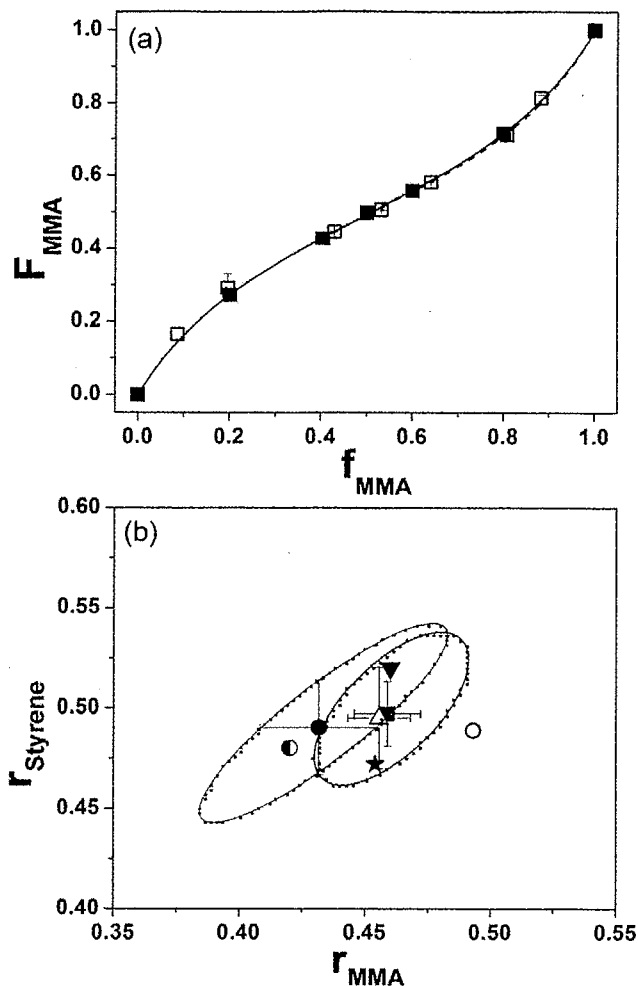
Fig. 6 Comparison of discrete and gradient methods for measurement of reactivity ratios for the styrene/methyl methacrylate brush system. (a) Mayo-Lewis plots for the discrete (■) and gradient (□) styrene/methyl methacrylate copolymer brush system as determined by X-ray photo-electron spectroscopy (XPS), (mean ± S.D., replications = 3; error bars lie within the data points). The solid line and the dotted line correspond to the nonlinear least squares (NLLS) fit for the discrete and the gradient methods, respectively. (b) Reactivity ratio point estimates (bound by 95% joint confidence intervals, error bars correspond to the standard deviation in the NLLS fit) for surface-initiated copolymer obtained by NLLS analysis of the XPS composition data for discrete (■), gradient (●) and NMR (bulk) (△) methods. Literature values from bulk polymerization conditions; Olaj *et al.*[27] (▼), Coote *et al.*[28] (○), van Herk *et al.*[29] (◐), Davis *et al.*[30] (★). The elliptical lines are drawn to guide the reader's eye.

confidence interval from the gradient SIP survey data overlaps the bulk NMR values and many of the previously reported literature values for the Sty/MMA monomer pair. These results demonstrate the utility of high-throughput gradient strategies combined with our SIP approach and enable reproducible measurements of reactivity ratios from a single gradient copolymer brush substrate.

Conclusions

In this article, we have demonstrated a robust approach to measure monomer reactivity ratios using surface-initiated

copolymerization and XPS as a synthesis and characterization toolset. We have shown the broad applicability of the approach to a range of monomer pairs; however, the primary limitation is the requirement of a distinguishable chemical element in one of the constituent monomers, *e.g.* the approach would not be appropriate for determining the reactivity ratios of styrene and α-methylstyrene. For the range of monomer pairs investigated, reactivity ratios obtained from the NLLS evaluation of XPS copolymer composition data are reproducible and are in good agreement with bulk reactivity ratios obtained by traditional NMR analysis. Most notably, we have developed and demonstrated a high-throughput approach to measure reactivity ratios using a single substrate exhibiting a gradient in copolymer brush composition. The high-throughput approach significantly reduces the time and effort required to generate reliable and reproducible point estimates of reactivity ratios, and these values are in good agreement with values obtained from both the discrete statistical copolymer brush and classical bulk analytical methods.

Acknowledgements

Notes and references

1 G. Moad, D. H. Solomon, *The chemistry of radical polymerization*, Elsevier, Amsterdam; Boston, 2006.
2 F. Mayo and F. Lewis, *J. Am. Chem. Soc.*, 1944, **66**, 1594–1601.
3 W. Z. Xu and P. A. Charpentier, *Ind. Eng. Chem. Res.*, 2009, **48**, 1384–1390.
4 K. G. Suddaby, K. H. Hunt and D. M. Haddleton, *Macromolecules*, 1996, **29**, 8642–8649.
5 D. L. Patton, K. A. Page, C. Xu, K. L. Genson, M. J. Fasolka and K. L. Beers, *Macromolecules*, 2007, **40**, 6017–6020.
6 D. Gersappe, M. Fasolka, R. Israels and A. Balazs, *Macromolecules*, 1995, **28**, 4753–4755.
7 C. Xu, S. Barnes, T. Wu, D. Fischer, D. DeLongchamp, J. Batteas and K. L. Beers, *Adv. Mater.*, 2006, **18**, 1427–1430.
8 O. Prucker and J. Ruhe, *Langmuir*, 1998, **14**, 6893–6898.
9 C. Xu, T. Wu, C. M. Drain, J. D. Batteas and K. L. Beers, *Macromolecules*, 2004, **38**, 6–8.
10 R. M. Hensarling, V. A. Doughty, J. W. Chan and D. L. Patton, *J. Am. Chem. Soc.*, 2009, **131**, 14673–14675.
11 M. P. Seah and W. A. Dench, *Surf. Interface Anal.*, 1979, **1**, 2–11.
12 S. Tougaard, *J. Vac. Sci. Technol., A*, 1996, 1415–1423.
13 S. Tougaard, *Surf. Interface Anal.*, 1998, **26**, 249–269.
14 C. Ton-That, A. Shard, D. Teare and R. Bradley, *Polymer*, 2001, **42**, 1121–1129.
15 A. van Herk, *J. Chem. Educ.*, 1995, **72**, 138–140.
16 T. Tamikado, *J. Polym. Sci.*, 1960, **43**, 489.
17 C. Walling, E. R. Briggs and K. B. Wolfstirn, *J. Am. Chem. Soc.*, 1948, **70**, 1543–1544.
18 F. Brown and G. Ham, *J. Polym. Sci., Part A: Gen. Pap.*, 1964, **2**, 3623.
19 C. I. Simionescu, V. Bărboiu, B. C. Simionescu, V. Talmaciu and C. Sava, *J. Polym. Sci., Part A: Polym. Chem.*, 1986, **24**, 851–860.
20 L. Luskin, R. Myers, *Encyclopedia of Polymer Science and Technology*, Interscience Publishers, 1964.
21 C. S. Marvel and R. Schwen, *J. Am. Chem. Soc.*, 1957, **79**, 6003–6005.
22 W. Burlant and D. Green, *J. Polym. Sci.*, 1958, **31**, 227.
23 T. Alfrey, E. Mertz and H. Mark, *J. Polym. Sci.*, 1946, **1**, 37.
24 F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and F. R. Mayo, *J. Am. Chem. Soc.*, 1948, **70**, 1519–1523.
25 A. Natansohn, S. Maxim and D. Feldman, *Polymer*, 1979, **20**, 629.
26 K. Chee and S. Ng, *Macromolecules*, 1986, **19**, 2779–2787.

27 O. Olaj, I. Schnoll-Bitai and P. Kremminger, *Eur. Polym. J.*, 1989, **25**, 535–541.

28 M. Coote, L. Johnston and T. Davis, *Macromolecules*, 1997, **30**, 8191–8204.

29 A. van Herk and T. Droge, *Macromol. Theory Simul.*, 1997, **6**, 1263–1276.

30 T. Davis, K. O'Driscoll, M. Piton and M. Winnik, *J. Polym. Sci., Part C: Polym. Lett.*, 1989, **27**, 181–185.