

Communications to the Editor

Measurement of Reactivity Ratios in Surface-Initiated Radical Copolymerization[†]

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Free radical copolymerization is a valuable tool for tailoring the properties of polymeric materials for a broad range of applications. For statistical copolymers, the monomer sequence distribution and compositional heterogeneity in and among the copolymer chains have a profound influence on the behavior and physical properties of the material.¹ Measurement of monomer reactivity ratios, the key synthetic parameters for designing tailored copolymers, provides insight necessary to control monomer sequence; however, these parameters are time-consuming and difficult to measure.² The standard method for measuring monomer reactivity ratios requires the synthesis and purification of a series of copolymers with a broad range of molar compositions followed by characterization (typically nuclear magnetic resonance (NMR) spectroscopy). Often, the necessity to “artificially” limit conversion and extensive purification protocols result in intrinsic errors and poor reproducibility in the obtained kinetic parameters.

Analogous to their bulk counterparts, statistical copolymer brushes result from the copolymerization of two monomers from surface-bound initiators, where the arrangement of monomers within the tethered chains is dictated by monomer reactivities.

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[†] Certain equipment and instruments or materials are identified in the paper to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that the materials are necessarily the best available for the purpose. Error bars, unless otherwise stated, represent one standard deviation from the mean of triplicate experiments and are the estimates of the standard uncertainty for the measurement.

Because of the lack of segmental rearrangement (as observed in, e.g., block copolymers³), these copolymer brush surfaces enable the expression of a statistical distribution of monomer constituents at the interface which reflect the distribution along the length of the tethered chains.^{4,5} Consequently, statistical copolymer brushes provide a platform for covalently “trapping” the copolymer composition on a surface and thus allowing determination of surface chemistry by spectroscopic methods such as near-edge X-ray absorption fine structure spectroscopy (NEXAFS)⁴ or X-ray photoelectron spectroscopy (XPS). Knowledge of the surface chemistry expressed from a given monomer feed may provide a straightforward assessment of the kinetic parameters that dictate copolymer composition.

In this communication, we describe a new approach to measure monomer reactivity ratios from surface-initiated copolymerization (SIP) using X-ray photoelectron spectroscopy (XPS). Using styrene/methyl methacrylate (Sty/MMA) as an illustrative monomer pair, we show that the reactivity ratios of statistical copolymer brushes via SIP closely resemble the values measured under bulk reaction conditions. This method eliminates several of the experimental complications of solution polymerizations as previously discussed. Furthermore, these experiments elucidate the behavior of reactions at interfaces and represent one of the few methods reported for quantifying polymerization behavior from a surface.

Polymer brushes have been synthesized using numerous polymerization mechanisms including free radical,⁶ ionic,^{7,8} and various controlled radical techniques such as nitroxide-mediated⁹ and atom transfer radical polymerization.^{10,11} Here, we employ conventional free radical photopolymerization because it is a simple, flexible, and well-studied case. The basic synthetic strategy shown in Figure 1 was adapted from the work of Prucker et al.¹² First, an asymmetric trichlorosilyl-functionalized azo initiator was attached to an –OH-terminated silicon substrate. The average thickness of the initiator layer, (2.6 ± 0.13 nm) as measured by ellipsometry, indicated the formation of a multilayer film structure. The azo-functionalized substrates were immersed into monomer solutions containing known molar

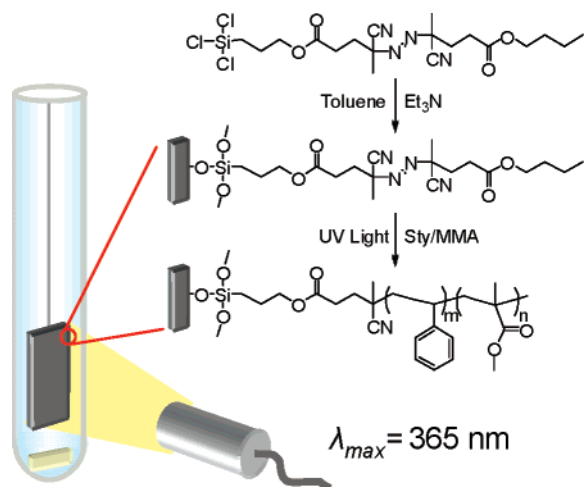


Figure 1. Reaction scheme and experimental setup for the preparation of statistical copolymer brushes.

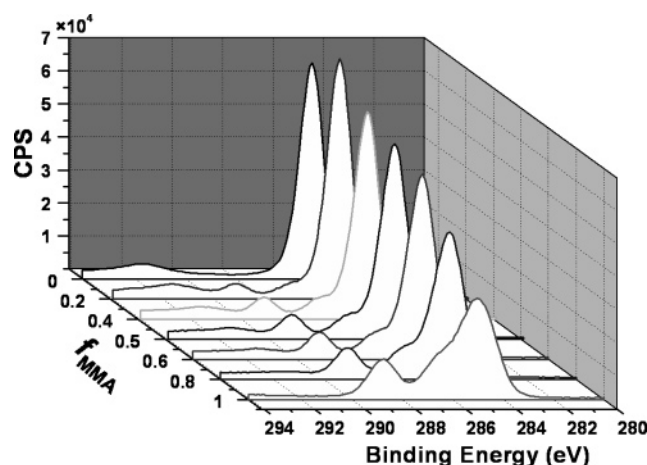


Figure 2. High-resolution C 1s spectra of the statistical styrene/methyl methacrylate (Sty/MMA) copolymer brushes as a function of mole fraction MMA in the feed.

ratios of Sty/MMA and irradiated with UV light (365 nm) for ~1 h with magnetic stirring (see Supporting Information).

The thickness of the copolymer brush samples averaged 24 ± 3 nm as measured by ellipsometry after Soxhlet extraction. A target thickness of 25 nm was chosen to simplify quantification of the composition by avoiding spectroscopic contributions from the substrate. Compositions of the statistical copolymer brush specimens were measured by XPS. Figure 2 shows the C 1s envelope for a series of brush samples prepared from various monomer feeds. The carbonyl peak ($\text{C}=\text{O}$) at 289.1 eV and the methoxy peak (CH_3-O) at 287.0 eV, both characteristic of PMMA,¹³ gradually appear with increasing mole fraction of MMA in the monomer feed. Quantitative brush compositions can be determined by comparing the integrated O and C peak areas from survey spectra or by considering the relative contribution of the PMMA carbonyl peak to the total high-resolution C 1s envelope after cross-correlating the C and O envelopes.¹⁴ These complementary methods agree well, with average discrepancies of less than 2% (see Supporting Information).

To determine monomer reactivity ratios in SIP, we used classical methods to evaluate the data by comparing copolymer composition, F (determined by XPS), to the monomer feed

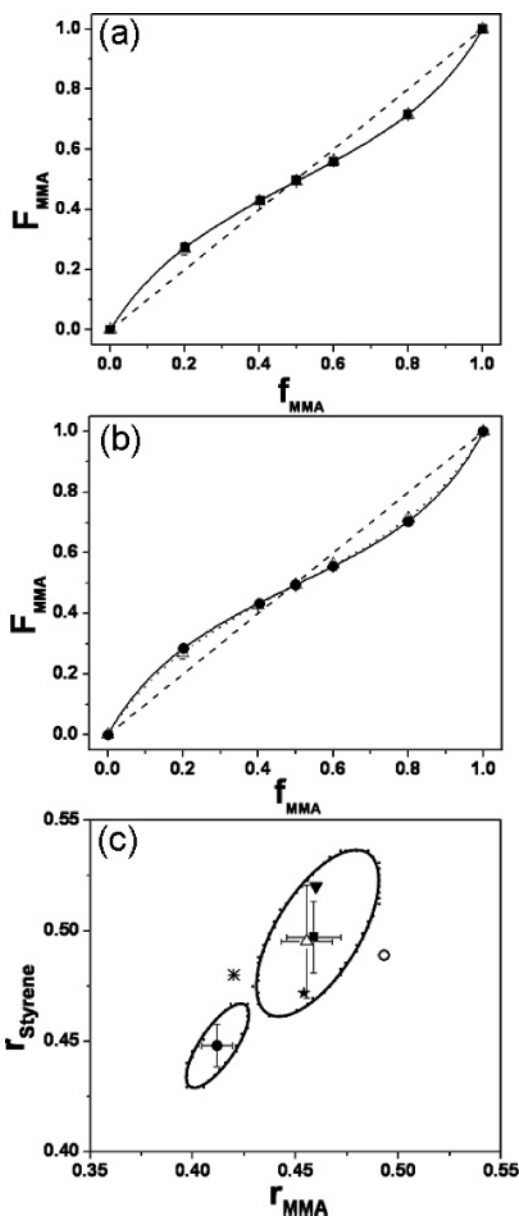


Figure 3. Mayo-Lewis plots for the styrene/methyl methacrylate copolymer brush system as determined by X-ray photoelectron spectroscopy (XPS) (a) survey (■), (b) high resolution (●), and the bulk copolymer system as determined by nuclear magnetic resonance spectroscopy (NMR) (Δ) (mean \pm SD, replications = 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 brush system and the bulk system, respectively. Dashed line shows the ideal case of random monomer addition. (c) 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 (■), high resolution (●), and NMR (bulk) (Δ) composition data and literature values from bulk polymerization conditions; Olaj et al.²⁰ (▼), Coote et al.²¹ (○), van Herk et al.²² (*), Davis et al.²³ (★). The elliptical lines are drawn to guide the reader's eye.

composition, f , at low monomer conversions using the instantaneous copolymerization equation.¹⁵

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

Because of the low concentration of initiator on the surface relative to solution monomer concentrations, surface-initiated

Table 1. Reactivity Ratios (*r*) of Styrene (Sty) and Methyl Methacrylate (MMA) Determined under Surface-Initiated Conditions Using X-ray Photoelectron Spectroscopy (XPS) and Comparative Bulk Data from NMR

method	XPS survey		XPS high resolution		¹ H NMR	
	<i>r</i> _{MMA} ^b	<i>r</i> _{Sty} ^b	<i>r</i> _{MMA} ^b	<i>r</i> _{Sty} ^b	<i>r</i> _{MMA} ^b	<i>r</i> _{Sty} ^b
NLLS ^a	0.459 ± 0.013	0.497 ± 0.016	0.412 ± 0.008	0.448 ± 0.010	0.456 ± 0.012	0.495 ± 0.025

^a Nonlinear least squares. ^b Mean ± SD, replications = 3.

polymerizations remain at low monomer conversions for the time scale of the reaction. Our estimated monomer conversion was 0.56 ± 0.05% based on gravimetric analysis of the free polymer formed in solution, which results from homolytic cleavage of the surface-bound initiator. SIP addresses a key issue for the measurement of monomer reactivity ratios by avoiding compositional drift associated with depletion of the more reactive monomer as conversion increases. Therefore, we avoid the necessity of measuring reactivity ratios by either limiting conversion experimentally or accounting for drift with more complex statistical treatments that include functions for conversion.¹⁶ Parts a and b of Figure 3 show the Mayo–Lewis plots generated from the survey and high-resolution XPS composition data, respectively, for the Sty/MMA copolymer brush. For comparison, analogous data extracted from ¹H NMR analysis of the copolymerization of Sty/MMA under *bulk* conditions is also shown. The excellent agreement between the composition of the copolymer brushes and the composition of the bulk copolymers indicates a similar copolymerization behavior exists under surface-initiated and bulk conditions. Control experiments were performed to validate the agreement between the XPS and NMR measurements by spin-casting the bulk copolymers for XPS analysis (see Supporting Information). Generally, quantification of the high-resolution data showed a tendency to underestimate the MMA concentration compared with the survey method and NMR for the same copolymers. This underestimation can be attributed to degradation of the PMMA constituent of the copolymer which is known to occur under X-ray irradiation.¹³ The effects of degradation are manifested in the high-resolution data since it is acquired after the longest exposure times, thereby reducing the O/C ratio. In all cases, the composition data was fit to eq 1 with a nonlinear least-squares (NLLS) optimization after van Herk¹⁷ (see Supporting Information). Initial fitting parameters for the NLLS optimization were obtained by linearization of the experimental data using the Fineman–Ross¹⁸ and Kelen–Tüdös¹⁹ methods (see Supporting Information).

Figure 3c shows the results of the NLLS evaluation of the XPS composition data yielding point estimates for the reactivity ratios bound by 95% joint confidence intervals (JCI) for the SIP of styrene and MMA (also summarized in Table 1). Point estimates were determined from both the survey and the high-resolution XPS data. The variation in the reactivity ratios obtained from the two quantification methods can be attributed to the degradation effects previously discussed. The bulk reactivity ratios we measured along with several reported literature values are also shown in Figure 3c. The reactivity ratios measured for the SIP of Sty/MMA agree well with the values reported under bulk reaction conditions. The 95% JCI obtained from the SIP survey data overlaps several of the bulk literature values, further validating this new approach as a viable method for estimating bulk reactivity ratios using surface-initiated copolymerization. It should be noted that in certain cases specific interactions between the monomers and the substrate surface may affect the local monomer concentration at the reaction interface, resulting in apparent reactivity ratios.

We have demonstrated a new approach to measure monomer reactivity ratios using surface-initiated copolymerization and XPS as a synthesis/characterization toolset. The ratios obtained for Sty and MMA using this method are in close agreement with values measured under bulk reaction conditions. The utility of XPS in this approach is dependent on the presence of distinguishable chemical species of the constituent monomers. This work illustrates the significance and opportunity in understanding the fundamental aspects of reactions at interfaces and how that knowledge may be correlated to bulk reaction conditions. Furthermore, our work suggests that we can use a combinatorial gradient approach to measure reactivity ratios on grafted copolymer libraries.⁴ Currently, we are examining the broader applicability of this method to other monomer pairs and pursuing the development of a combinatorial approach for measuring monomer reactivity ratios.

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Supporting Information Available: Details of synthesis and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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