

Supporting Information

Measurement of Reactivity Ratios in Surface-Initiated Radical Copolymerization**

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Experimental Section

Materials. Reagent chemicals were purchased from Aldrich and used without further purification unless otherwise indicated. Styrene (99+%) and methyl methacrylate (99+%) were passed through a column of activated basic alumina to remove the inhibitor and stored at -20 °C prior to use.

Synthesis of Asymmetric Azo-Initiator (Figure S1). 4,4'-azobis(4-cyanovaleric acid) (3.0 g, 11 mmol), dimethylaminopyridine (DMAP) (80 mg, 0.65 mmol) and butanol (0.815 g, 11 mmol) were dissolved in tetrahydrofuran (THF) (25 mL) in a 250 mL round bottom flask under an Ar atmosphere. The solution was cooled to 0 °C and dicyclohexylcarbodiimide (DCC) (2.2 g, 11 mmol) in 20 mL of THF was added dropwise with vigorous stirring. The reaction mixture was stirred at 0 °C for 5 min and then allowed to warm to room temperature overnight. Precipitated dicyclohexylurea (DCU) was removed by filtration and 100 mL of dichloromethane (CH_2Cl_2) was added. The crude mixture was washed with water (25 mL x 2) and dried over magnesium

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sulfate (MgSO₄). The solids were removed by filtration and the CH₂Cl₂ was removed by rotary evaporation at 30 °C. (The crude residue is used in the next step without further purification)

The crude mixture (**2**), allyl alcohol (0.65 g, 11.2 mmol) and DMAP (80 mg, 0.65 mmol) were dissolved in 25 mL of CH₂Cl₂ and cooled to 0 °C. DCC (2.2 g, 11 mmol) in 25 mL of CH₂Cl₂ was added dropwise via syringe. The reaction was kept at 0 °C for 5 minutes and then allowed to warm to room temperature overnight. The solids were removed by filtration and the filtrate was washed with saturated sodium bicarbonate (25 mL x 2), water (25 mL x 2) and dried over MgSO₄. The solids were removed by filtration and the solvent was removed by rotary evaporation. The residue was passed through a short plug of silica gel using CH₂Cl₂ as an eluent. After removal of solvent, the final product (**3**) was obtained as a yellow oil that solidified upon standing at -4 °C. ¹H NMR (270 MHz, CDCl₃) δ: 0.918 (t, 3H); 1.12-1.85 (m, 10H); 2.21-2.65 (m, 8H); 4.00-4.15 (m, 2H); 5.42-4.64 (m, 2H); 5.18-5.38 (m, 2H); 5.80-5.95 (m, 1H). The allyl product was converted to the trichlorosilane derivative (**4**) using conditions reported in literature.¹

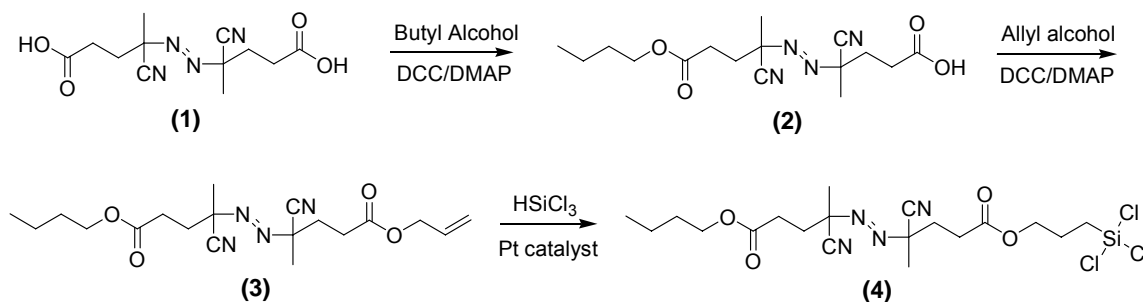


Figure S1. Reaction scheme for the asymmetric azo-initiator.

Preparation of Initiator Functionalized Silicon Substrates. Silicon wafers were cut into 1.2 cm × 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 N₂ and treated

with UV-ozone for 45 min. The substrates were immediately immersed in a 1 mmol/L toluene solution of (**4**) 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 N₂. The average thickness of the initiator layer was 2.6 nm ± 0.13 nm as determined by ellipsometry. This thickness indicates the formation of a “multi-layer” film structure.

Synthesis of PS-PMMA Statistical Copolymer Brush Modified Substrates. Monomer solutions were prepared with various molar ratios of sty and MMA and degassed by bubbling Ar through the solution for 30 min. An initiator-modified silicon substrate was suspended in a reaction tube fit with a rubber septum and a stir bar. The reaction tube was degassed by three vacuum pump/Ar refill 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) ($\lambda_{\text{max}} = 365 \text{ nm}$) 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 reaction 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 ± 3 nm after Soxhlet extraction.

Synthesis of PS-PMMA Statistical Copolymer Under Bulk Conditions. Monomer solutions were prepared with various molar ratios of styrene and MMA 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 $65\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$ 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 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.

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, total acquisition times of 180 s and 440 s were used to obtain high resolution and survey spectra, respectively. 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.² 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^{3,4} 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. High resolution spectra were fitted using a multiple region optimization of the C 1s and O 1s envelopes to maintain the correct stoichiometry for the PMMA component. Initial estimates for binding energy peak locations were based on homopolymer spectra found in the literature.⁵

Quantification of the surface composition for the statistical copolymer brushes was carried out using two methods: (i) a method that considers the elemental O/C ratio from the survey spectra, and (ii) a method that considers the relative contribution of the carbonyl carbon from PMMA to the C 1s envelope after cross-correlation of the C and O envelopes. These methods were adapted from literature.⁶

Statistical Methods.⁷ 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:

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

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.

Equation 1 was fit to the composition data obtained from the XPS analysis using a non-linear least squares method. This method seeks to minimize the difference between the fitting function (**Equation 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:

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

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

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

where $\hat{\theta}$ represent 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:

$$SSE(\theta) \leq 7.3680 \cdot SSE(\hat{\theta}) \quad \text{Equation 4}$$

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

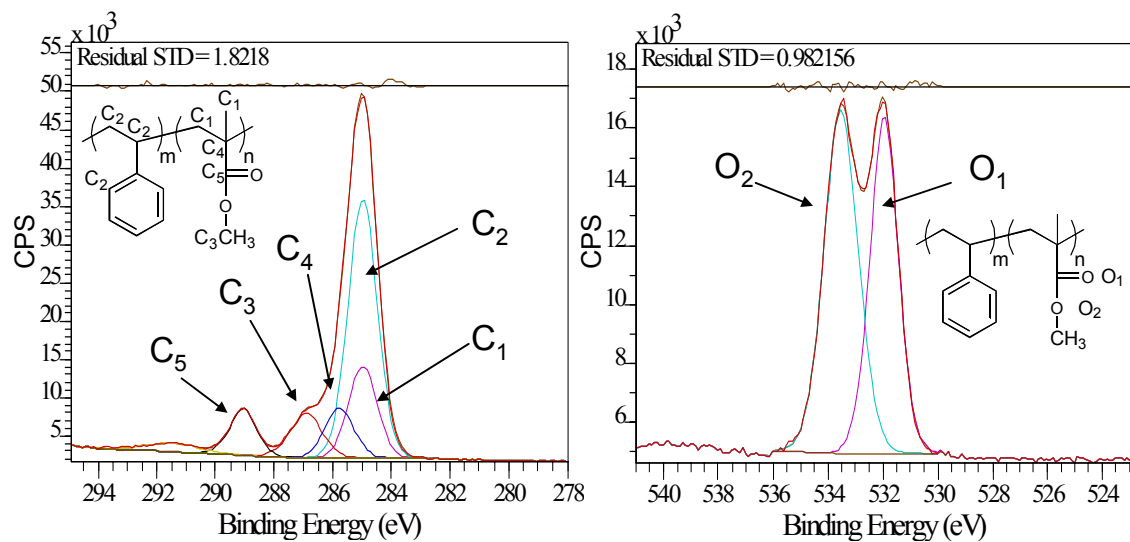


Figure S2. Representative high resolution C 1s and O 1s envelopes showing the cross-correlated peak fit analysis. The peak labels correspond to data in Table S1. The inset structures show the corresponding chemical assignments.

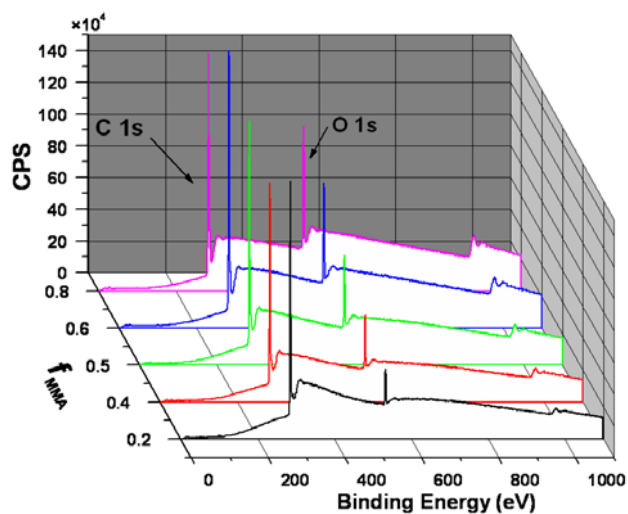


Figure S3. Survey spectra of the Styrene-methyl methacrylate (Sty-MMA) copolymer brush samples as a function of MMA in the monomer feed.

Table S1. Brush and bulk copolymer composition and peak parameters from XPS analysis (corresponds to Figure 3 in the manuscript). The chemical assignments (C₁, C₂,...) for the high resolution (HR) peak components correspond to the structures shown in Figure S2.

Bulk Comp. ^a		Brush Composition ^a		Survey ^b	HR Component % Concentration ^{b,c}						
f_{MMA}	$F_{\text{MMA}, \text{NMR}}^a$	$F_{\text{MMA}, \text{Survey}}^a$	$F_{\text{MMA}, \text{HR}}^a$	O/C	C ₁	C ₂	C ₃	C ₄	C ₅	O ₁	O ₂
0.2	0.269±0.02	0.272±0.012	0.285±0.004	0.080	7.83	72.2	4.51	4.34	3.71	3.71	3.71
0.4	0.426±0.006	0.429±0.010	0.432±0.006	0.132	12.3	56.4	7.06	6.8	5.81	5.81	5.81
0.5	0.494±0.005	0.498±0.011	0.495±0.006	0.158	14.1	50.1	8.10	7.80	6.67	6.67	6.67
0.6	0.563±0.006	0.558±0.010	0.555±0.002	0.181	15.8	43.8	9.10	8.77	7.49	7.49	7.49
0.8	0.715±0.003	0.716±0.009	0.703±0.006	0.250	20.2	28.1	11.7	11.2	9.61	9.61	9.61

^a Mean ± S.D., n = 3 ^b Representative values from a single experiment. ^c % concentration extracted from the high resolution cross-correlated peak fit.

Table S2. Comparison of copolymer composition determined from XPS and ¹H NMR for bulk copolymers of the same batch

Feed	Copolymer Composition			
f_{MMA}	$F_{\text{MMA}, \text{Survey}} (\text{spin-cast})$	$F_{\text{MMA}, \text{HR}} (\text{spin-cast})$	$F_{\text{MMA}, ^1\text{H NMR}}$	
0.2	0.276	0.264	0.277	
0.4	0.419	0.413	0.425	
0.5	0.496	0.476	0.490	
0.6	0.570	0.540	0.564	
0.8	0.713	0.686	0.717	

Table S3. Initial estimates for 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	
	r_{MMA}^c	r_{Sty}^c	r_{MMA}^c	r_{Sty}^c	r_{MMA}^c	r_{Sty}^c
FR ^a	0.457±0.029	0.490±0.034	0.408±0.024	0.450±0.038	0.455±0.017	0.498±0.057
KT ^b	0.460±0.028	0.494±0.035	0.407±0.011	0.451±0.024	0.466±0.021	0.514±0.066

^aFineman-Ross, ^bKelen-Tudos, ^cMean ± S.D., replications = 3

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