"Click-functional Block Copolymers Provide Precise Surface Functionality via Spin Coating" by Hernán R. Rengifo, Lu Chen, Cristian Grigoras, Jingyue Ju and Jeffrey T. Koberstein

Supplemental Information

Synthesis of a Protected Alkyne-Functional Initiator-(TMS-Br). Unless otherwise noted, all chemicals were purchased from Aldrich and used as received. In a 100 mL round bottom flask, 3-(trimethylsilyl)propargyl alcohol (5 g, 38.98 mmol), triethylamine (Et_3N 3.93 g, 38.98 mmol) and 50 mL of dry Et_2O were added and stirred in an ice-water bath for 20 min. Bromoisobutyryl bromide (7.8 g, 33.90 mmol) dissolved in 15 mL of dry Et_2O was added drop-wise. After the addition was complete, the reaction was allowed to warm-up to 23 ^{o}C and stirring was continued for 24 h. The reaction mixture was poured into ice-water and the organic product was extracted with CH_2Cl_2. The organic phase was washed with 100 mL H_2O (2x) and 100 mL brine (2x), and then dried over anhydrous Na_2SO_4. The solvent was distilled at 30 ^{o}C under reduced pressure on a rotary evaporator to yield a slightly yellow liquid that was purified by vacuum distillation to yield 5.3 g of final product (54 %), propanoic acid, 2-bromo-2-methyl-, 3-(trimethylsilyl)-2-propynyl ester), or TMS-Br, a protected alkyne-functional initiator for atom transfer radical polymerization (ATRP). ^{1}H-NMR δ 4.78 (s, 2H, CH_2), 1.94 (s. 6H, CH_3), 0.08 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR δ 171.77 (CC(O)O), 90.03 (Si-C≡C), 98.55 (C≡C-Si), 55.88 (OCC(O)), 54.56 (C(CH$_3$)$_2$), 31.01 (CH$_3$), -0.83 (CH$_3$Si)[S1].

Synthesis of the First Block Copolymer Sequence-(TMS-P*t*BA-Br). The first monomer, *tert*-butylacrylate (*t*BA) (99+ % purity), was passed through a basic Al_2O_3 chromatographic column (flash) to remove inhibitor. Monomer (*t*BA, 2.5 g, 19.53 mmol), solvent (toluene, Acros ,99.8 %, 1.5 mL), initiator ((TMS-Br, 13.5 mg, 0.046 mmol),

catalyst (CuBr, 8 mg, 0.051 mmol) and *N, N, N', N', N"* – pentamethyldiethylenetriamine (99 % purity) ligand (PMDETA, 11.1 mg, 0.062 mmol) were weighed directly in a 25-mL Schlenk tube. After three freeze-pump-thaw cycles, the tube was filled with argon, and the reaction mixture was heated to 70 $^{\circ}$C in an oil bath. The side arm of the tube was purged with argon for at least 5 minutes before it was opened for samples to be removed at predetermined times with an airtight syringe. Samples were dissolved in CDCl$_3$, and the conversion was measured by ^{1}H-NMR spectroscopy Bruker DRX400 NMR. A part of the solution was injected into a Shimazu LC-10AT gel permeation chromatograph (GPC) with refractive index detector to measure the number-average and weight-average molecular weights relative to PS standards. Once the desired conversion was achieved, the Schlenk tube was removed from the oil bath, allowed to reach room temperature and the polymerization mixture diluted with CH$_2$Cl$_2$. This solution was passed through a basic alumina flash column, the catalyst-free mixture was collected and solvent was removed under reduced pressure using a rotary evaporator. Polymer was recovered by filtration after precipitation of a concentrated polymer solution in CH$_2$Cl$_2$ with a MeOH/H$_2$O mixture (7:3 v/v). The number average molecular weight determined via GPC was $M_n = 14,322$, and the polydispersity index was $M_w/M_n = 1.34$.

Addition of Second Block Copolymer Sequence (TMS-P*t*BA-PMMA-Br). The second monomer, methyl methacrylate (MMA) (99+ % purity), was passed through a basic Al$_2$O$_3$ chromatographic column (flash) to remove inhibitor. Monomer (MMA, 0.88 g, 8.7 mmol), solvent (toluene, 1.5 mL), initiator (TMS-P*t*BA-Br) polymer, 0.5 g, 0.035 mmol), catalyst (CuBr, 8 mg, 0.052 mmol) and ligand (PMDETA, 22.0 mg, 0.122 mmol) were weighed directly in a 25-mL Schlenk tube. After three freeze-pump-thaw cycles, the

tube was filled with argon, and the reaction mixture was heated in an oil bath thermostated at 90 $^{\circ}$C ± 2. The side arm of the tube was purged with argon for at least 5 minutes before it was opened for samples to be removed at predetermined times with an airtight syringe. Samples were dissolved in CDCl$_3$, and the conversion was measured by ^{1}H-NMR spectroscopy. A part of the solution was injected into the GPC, to measure the number-average and weight-average molecular weights relative to PS standards. Once the desired conversion was achieved, the Schlenk tube was removed from the oil bath, allowed to reach room temperature and the polymerization mixture diluted with CH$_2$Cl$_2$. This solution was passed through a basic alumina flash column and the catalyst-free mixture was collected and solvent was removed under reduced pressure, using a rotary evaporator. Polymer was recovered by filtration after precipitation of a concentrated polymer solution in CH$_2$Cl$_2$ by hexane addition. The number average molecular weight of the block copolymer determined via GPC was M_n = 24,477 and the polydispersity of the block copolymer was $M_{w/}$ M_n = 1.42. The average number molecular of the block copolymer calculated from 1H-NMR analysis was 23,281 ($M_n^{NMR} = M_w^{Initiator} + DP^{PtBA}$ x $M_w^{tBA} + DP^{PMMA}$ x M_w^{MMA}), where DP is the degree of polymerization[S2].

Deprotection of the Protected Alkyne Groups. In a 50 mL round bottom flask, TMS-PtBA-PMMA-Br block copolymer was dissolved in 10 ml CH$_2$Cl$_2$ and 2 mL methanol and 0.23 g of K$_2$CO$_3$ were added. The flask was immersed in an oil bath thermostated at 50 $^{\circ}$C ± 2 and the suspension was stirred under Ar overnight. The suspension was filtered and the organic mixture was extracted with CH$_2$Cl$_2$. The organic phase was washed with 100 mL H$_2$O (2x) and 100 mL brine (2x) then dried over anhydrous Na$_2$SO$_4$. The solvent was distilled at 30 $^{\circ}$C under reduced pressure on a rotary

evaporator to yield a viscous slightly yellow mass. The α-alkyne-ω-Br-P(tBA-b-MMA) diblock copolymer was recovered via filtration after precipitation of concentrated polymer solution (CH_2Cl_2) in a cooled $MeOH/H_2O$ mixture (7:3 v/v).

AFM Measurements. Noncontact mode atomic force microscopy measurements using the AutoProbe CP Research probe head (Veeco Instruments) were performed to study the topography of spin-coated films. Silicon cantilevers (dLevers[TM]) with a spring constant of 2.2 N/m were employed and the analysis was carried out under air-ambient condition. AFM images of a typical MMA28-tBA28 diblock copolymer film before and after the click reaction with azide-functional fluorescein are shown in Figure S1. The surfaces are basically featureless and have a surface roughness of less than 0.3nm, indicating that they are sufficiently smooth to apply x-ray photoelectron spectroscopy to characterize the specimens.
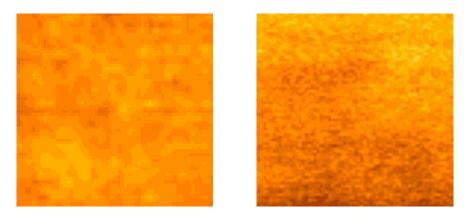

Figure S1 Left: 2D AFM height image (1 μm x 1 μm) of MMA28-tBA28 block copolymer film (coated from 0.5% solution; RMS roughness is less 0.2 nm). Right: 2D AFM height image (1 μm x 1 μm) of MMA28-tBA28 block copolymer film (coated from 0.5% solution; RMS roughness is 0.3 nm) after click reaction with azide- fluorescein.

ADXPS Measurements. Typical high-resolution carbon (i.e., C1s) and oxygen (i.e., O1s) XPS spectra for a block copolymer monolayer on a silicon oxide substrate are

shown in Figures S2 and S3. Different chemical shifts in the BEs are observed due to carbon and oxygen atoms existing in different chemical environments. Most spectral features are common to both P*t*BA and PMMA. The C1s peak assignments are as
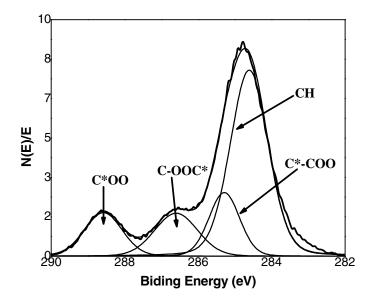

Figure S2. Deconvolution results for the ADXPS high resolution C1s spectrum of MMA28-*t*BA28 spin coated onto a silicon wafer from a 0.4% w/w solution showing the contribution of each carbon type (TOA=15°).

follows: the peak centered at 288.8 eV arises from the carbonyl carbon (C*OO), the peak near 286.3 eV is ascribed to the ester carbon (COO–C*), the peak centered at 285.4 eV is associated with the carbon adjacent to the carbonyl group (C*–COO) and the unshifted C1s peak appears at 284.6 eV. The fraction of the two monomers at the surface can, however, be differentiated because the ratio of the unshifted C 1s peak to the shifted C1s peaks is significantly different for each polymer due to differences in the ester group (the ratios C:C*OO:COO–C*:C*–COO are 4:1:1:1 for P*t*BA and 2:1:1:1 for PMMA). The O1s peak assignments are as follows: the peak centered at 533.4 eV arises from carbonyl

oxygen (C=O*–O) in the ester group, while the unshifted oxygen at 531.3 eV is the ester oxygen (C=O–O*). Atomic percentages were determined as a function of the photoelectron takeoff angle for all components of the C1s and O1s spectra by resolving composite spectra into contributions from each carbon and oxygen type. The data taken at the lowest takeoff angle reflects the composition of the shallowest probe depth.
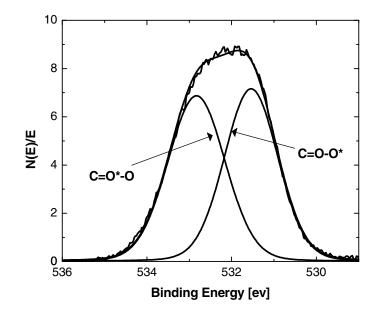

Figure S3. Deconvolution results for ADXPS high resolution O1s spectrum (TOA=15$^{\text{o}}$) of MMA28-tBA28 spin coated onto a silicon wafer from a 0.4% w/w solution showing the contribution of each oxygen type.

The surface molar composition of PtBA, $\Phi_{S,PtBA}$, is calculated from the ratio of the average intensity of the unshifted C 1s signal, $I(\theta,\ C\ 1s\text{-}unshifted)$ to the total C 1s signal, $I(\theta,\ C1s\text{-}total)$.

$$\frac{I(\theta, C1s - unshifted)}{I(\theta, C1s - total)} = \frac{4\phi_{PtBA} + 2(1 - \phi_{PtBA})}{(7\phi_{PtbA} + 5(1 - \phi_{PtBA}))} = \frac{2(1 + \phi_{PtBA})}{5 + 2\phi_{PtbA}} \qquad \text{(ES1)}$$

This relationship is simply a mass balance where the first term in the denominator represents the contribution of the seven carbons from the PtBA repeat unit and the second term represents the contribution from the five carbons in the PMMA repeat unit. The surface compositions determined from (ES1) represent averages over the sampling depth and are presented in Table S1.

Table S1. ADXPS derived elemental and surface compositions for MMA28-tBA28 spin coated onto silicon wafers from 0.4% wt/wt solutions.

Takeoff Angle (∘)	Integral Depth	% Unshifted C 1s	$\phi_{S,PtBA}$[a]
15	2.4	57.1	0.99
30	4.7	56.8	0.97
45	6.6	55.8	0.89
60	8.1	55.6	0.88

[a] Assumes an electron mean free path of 3.1 nm

ADXPS was also applied to quantitatively determine the thickness of the PtBA layer and to confirm the formation of a bilayer structure. ADXPS is an integral technique for which the signal from a particular atomic species is given by[S3]

$$I_i(\theta) = \kappa \int_0^{\infty} n_i(x) \exp(\frac{-x}{\lambda \sin(\theta)}) dx \qquad \text{(ES2)}$$

where k is an instrumental factor. For the bilayer model, the ratio of the magnitude of the C 1s signal from the binding-energy-unshifted carbons to that from all carbons can be expressed as

$$\frac{I(\theta, C1s - unshifted)}{I(\theta, C1s - total)} = \frac{\frac{4}{7}\rho_{tBA}\int_0^d \exp\left(\frac{-x}{\lambda \sin\theta}\right)dx + \frac{2}{5}\rho_{MMA}\int_d^{\infty}\exp\left(\frac{-x}{\lambda \sin\theta}\right)dx}{\rho_{tBA}\int_0^d \exp\left(\frac{-x}{\lambda \sin\theta}\right)dx + \rho_{MMA}\int_d^{\infty}\exp\left(\frac{-x}{\lambda \sin\theta}\right)dx} \qquad \text{(ES3)}$$

Here d is the thickness of the PtBA surface layer, ρ_{tBA} is the total carbon atomic density in the PtBA layer, and ρ_{MMA} is the total carbon atomic density in the underling PMMA layer. Rearrangement of ES3 yields a relationship (ES4) that can be graphically analyzed to estimate the thickness, d, of the PtBA surface layer

$$R(\theta) = \ln\left[\frac{1 - \dfrac{4}{7}\dfrac{(\theta, C1s - total)}{(\theta, C1s - unshifted)}}{\dfrac{2}{5}\dfrac{\rho_{MMA}}{\rho_{tBA}}\dfrac{(\theta, C1s - total)}{(\theta, C1s - unshitted)} - \dfrac{4}{7}\dfrac{(\theta, C1s - total)}{(\theta, C1s - unshifted)} - \left(1 - \dfrac{\rho_{MMA}}{\rho_{tBA}}\right)}\right] = \frac{-d}{\lambda \sin\theta} \qquad (ES4)$$

If the surface is layered, a plot of R(θ) against 1/sin θ should be linear with a slope of $-d/\lambda$. An example of a typical plot of this nature is shown in Figure S4. The data shows a linear relationship, consistent with the expectations of the bilayer model.
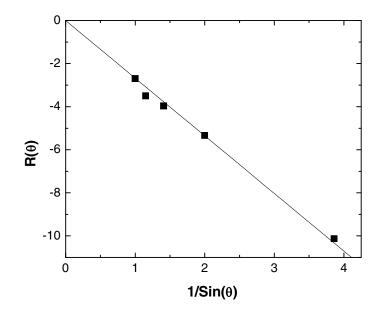

Figure S4. ADXPS estimation of the PtBA surface layer thickness according to the substrate-overlayer model (ES4)[S4] for MMA28-tBA28 spin coated onto a silicon wafer from a 0.4% wt/wt solution.

Incompatibility of Copolymer Blocks. A crucial parameter in all theories of block copolymers segregation is the interaction parameter χ_{AB} (Flory-Huggins) that provides the driving force for the phase separation or the formation of bilayer structure. Where χ_{AB} segment-segment interaction parameter describe the free energy cost per monomer of conduct between A and B monomeric units and is given by: $\chi_{AB}=(Z/k_B)[\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2]$, where ε_{AB} is the energy per monomer unit between A and B monomer and Z is the number of the nears neighbors monomer to a copolymer configuration cell. Another parameter strongly influence the block copolymer behavior is the total degree of polymerization N. For large N, the loss of combinatorial and configuration entropy leads to the reduction of the A-B monomer contacts and thus the local ordering. Since the entropic and enthalpic contributions to the free energy scale as N^{-1} and χ_{AB} respectively, it is the product that is of interest in the block copolymer phase state. The critical $\chi_{AB}N$ is 10.5 for microphase separation of block copolymer in the bulk. The strong segregation limit corresponds to the situation where $\chi N > 100$. In this regime narrow interfaces are formed depending on the χ_{AB} parameter which was used for our calculations[S5].

$$\chi = \frac{V_{REF}(\delta_{PtBA} - \delta_{PMMMA})^2}{RT}$$

Where;

$\delta_{PtBA} = 19.3\ (J/cm^3)^{1/2}$

$\delta_{PMMA} = (18.6(J/cm^3)^{1/2} + 26.4(J/cm^3)^{1/2})/2 = 22.5\ (J/cm^3)^{1/2}$

$$\chi = \frac{95.02\frac{cm^3}{mol}\left[19.3\left(\frac{J}{cm^3}\right)^{1/2} - 22.5\left(\frac{J}{cm^3}\right)^{1/2}\right]^2}{8.134\frac{J}{mol*K}*298K} = 0.4$$

$N_{nT} > 100/0.4 > 250$

$N_{nT} > \frac{1}{2}(N_A + N_B) > 250$

$N_A = N_B > 130$ (symetric blocks)

$M_{nPtBA} > 128$ g/mol * 125 > 16,000 g/mol

$M_{nPMMA} > 100$ g/mol * 125 > 12,500 g/mol

$M_{nT} > 28,500$ g/moL

According to the theoretical calculation the total molecular weight (M_{nT}) must be at least 29,000 g/mol to be in the strong segregation limit. Therefore, MMA14-*t*BA9 with a Mn$_T$ 23,000 is too close the critical point for microphase separation.

Supplementary References

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