Solid Phase Synthesis of Polymacromer and Copolymacromer Brushes

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S Supporting Information

ABSTRACT: We report a novel solid phase method for the sequential coupling of heterobifunctional macromonomers to form a new class of polymeric materials that we refer to as polymacromers. Starting from an azide functional substrate, α-azido, ω-protected-alkyne macromonomers are added sequentially by thermally initiated click reactions to form polymacromer brushes wherein macromonomers are linked via triazole groups. After each addition step, the terminal alkyne group can be deprotected to allow addition of the next macromonomer. The use of highly chemoselective click chemistry for the coupling reactions allows virtually any macromonomer to be employed, regardless of its chemical nature. The method is illustrated by formation of two different homopolymacromer brushes: one made by sequentially coupling four polystyrene macromonomers and another by sequentially coupling eight poly(*tert*-butyl acrylate) macromonomers. Two different types of copolymacromer brushes are also prepared: one by alternating sequential coupling of polystyrene macromonomers with poly(methyl methacrylate) macromonomers and another by alternating sequential coupling of polystyrene macromonomers with poly(*tert*-butyl acrylate) macromonomers. The polymacromer brushes are characterized by ellipsometry, contact angle analysis, X-ray photoelectron spectroscopy, and X-ray reflectivity measurements. In all cases the coupling reactions are found to be highly efficient. Analysis of thickness data for the poly(*tert*-butyl acrylate) homopolymacromer brushes indicates that a conversion within the range of 97.5−100% is achieved for each cycle. This solid phase synthesis method is extremely versatile because it can be used to prepare complex sequenced block copolymers from almost any polymers and because the brushes formed can be made to span the entire region of brush behavior between the "grafting from" and grafting to" limits by varying the macromonomer molecular weight.
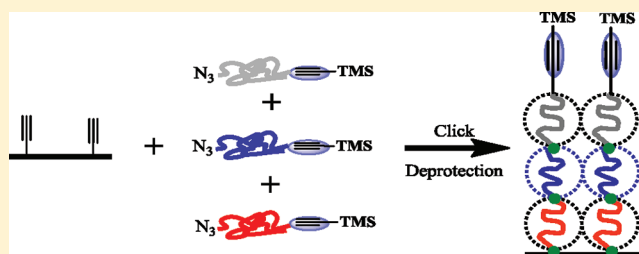
The development of precise techniques for preparing polymers of well-controlled architecture and narrow molecular weight distribution is a major goal of polymer chemistry. We describe herein the general principles of a new modular technique for polymer synthesis wherein a wide variety of preformed molecular building blocks can be simply linked together much like molecular Tinker Toys or Lego building blocks to form complex polymer and copolymer architectures. The new technique is based upon solid phase synthesis (SPS) concepts embodied in the Merrifield synthesis of oligopeptides. Solid phase synthesis techniques are modular in nature, generally involving stepwise addition of heterobifunctional building blocks to an initial reactant that is bound to a solid support. The buildup of specific sequences of the building blocks is controlled by the order of reactant addition mediated by functional group protection−deprotection strategies. Compared to conventional solution synthesis, SPS allows for the construction of nonsymmetric, sequenced structures as well as more facile removal of excess reactants and byproducts because the desired product is covalently bound to the solid substrate. SPS has been used recently in combinatorial chemistry[1−3] and has become an essential route for the preparation of many important biological molecules including peptides,[4−6] DNA,[7−11] and other biopolymers[12,13] for which a certain nonsymmetric predetermined sequence is desirable.

Relatively fewer examples have appeared where solid phase techniques have been used in synthetic polymer synthesis and the majority of these efforts have been restricted to the synthesis of low molecular weight oligomers. Solid phase methods have been used to prepare oligothiophenes,[14] poly(amidoamines),[15] peptide−polymer hybrids,[16] and dendrimers[17] as well as triazole oligomers and their cyclics, the latter from peptide monomers modified to have terminal alkyne and azide groups for coupling by copper(I)-catalyzed azide−alkyne cycloaddition (CuAAC).[18,19] Stepwise protection−deprotection processes have also been applied to prepare a

number of π-conjugated oligomers.[20] An interesting recent variation on the theme of solid phase synthesis is the use of soluble polymer supports (liquid supported synthesis) prepared from initiators that contain the same cleavable p-alkoxybenzyl ester linkers used in solid phase Wang resins.[21] "Molecularly defined" oligomers containing up to 64 ε-caprolactone monomers were synthesized using another liquid supported method (referred to as an iterative divergent−convergent approach), in which a substrate was avoided by clever use of two separate, orthogonal protection strategies to promote nonsymmetric monomer addition.[22] A similar liquid phase dual protection approach was coupled with CuAAC to prepare monodisperse oligomers and macrocycles of ethylene oxide, its dimers, and its trimers.[23] The few investigations that have used solid phase and similar liquid-supported methods for polymer synthesis have produced inspiring results but have only begun to tap the tremendous potential of supported polymer synthesis methods.

In this first paper, we apply SPS principles to develop a modular method for the synthesis of a new class of polymers we term "polymacromers". Polymacromers (PM) are multiblock polymers of a defined sequence produced by coupling heterobifunctional macromonomer building blocks. As prepared, they take the form of a polymer brush because they are bound to a solid substrate but can in principle be isolated by incorporating a cleavable linker at the substrate interface. In conventional polymer synthesis, multiple monomers are joined to form a "polymer", where the term "polymer" is derived by taking the word "monomer" that describes the repeating unit, adding to it the syllable poly, meaning many, and dropping the syllable mono. If we apply the same logic to our new class of materials, that is, by adding poly and dropping mono from the word "macromonomer", the result is the term polymacromer, which we believe is a suitable and accurate descriptor for the new materials. It follows that homopolymacromers are prepared by multiple addition cycles using a single macromonomer while segmented block copolymacromers of a desired sequence are prepared using different macromonomers in each cycle. Azide−alkyne click chemistry[24,25] via the Hüisgen 1,3-dipolar cycloaddition mechanism is used as the coupling chemistry because the alkyne group can be readily protected and subsequently deprotected using relatively mild conditions. This click reaction can be initiated at room temperature with a copper catalyst (CuAAC)[26] or thermally[27] at temperatures as low as 70 °C without catalyst. The high chemoselectivity of the reaction enables the coupling of virtually any macromonomer, regardless of its chemical nature and the required heterobifunctional macromonomers, comprising one azide end group and a second protected alkyne end group, are readily prepared by atom transfer radical polymerization (ATRP).[28]

■ RESULTS AND DISCUSSION

The procedure for preparing polymacromer brushes by SPS is described schematically in Figure 1. The critical requirement that enables this strategy is an ability to synthesize heterobifunctional building blocks, heterobifunctional macromonomers (HetBi), that are terminated at one end with an azide group (N$_3$) and on the other end with a trimethylsilane protected alkyne group (TMS−≡) as depicted in the figure. HetBi functional macromonomers of this nature can be prepared by atom transfer radical polymerization (ATRP),[28] a controlled radical polymerization technique, using a functional initiator as described in the Supporting Information. The SPS
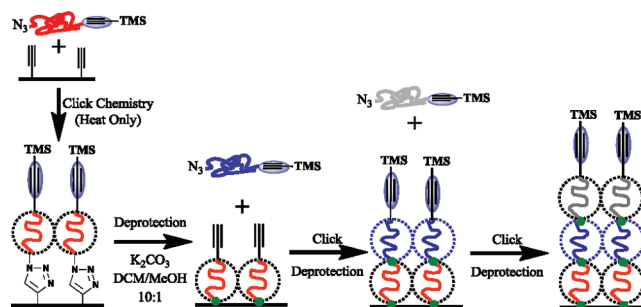

Figure 1. Schematic representation of the SPS process for preparing sequenced copolymacromer brushes. The green circles denote triazole linkages.

method begins with functionalization of the substrate with surface alkyne groups (≡), accomplished by self-assembly of alkyne-functional phosphonate esters[29] (metal oxide substrates), alkyne-functional thiols (gold substrates),[30] alkyne-functional silanes (glass substrates and silicon wafers),[31] or alkyne-functional block copolymers[32,33] (glass and polymeric substrates).

Covalent attachment of the first macromonomer (red chain in Figure 1) involves a "click" reaction (i.e., 1,3-cyclopolar addition) between the azide terminus on the red macromonomer and an alkyne group on the functionalized substrate surface, coupling the macromonomer to the surface via a triazole linkage. The result is a substrate coated with a covalently bound brush of red polymer that presents trimethylsilane-protected alkyne groups (TMS−≡) at the surface. An alkyne functional surface (≡) is subsequently regenerated by deprotection of the TMS-protected alkyne groups. After surface alkyne groups are regenerated, a second macromonomer (blue chain in Figure 1), not necessarily the same as the first macromonomer, is attached by another click reaction. The coupling/deprotection process may be applied multiple times to prepare a desired copolymacromer sequence (the preparation of three distinct segments is illustrated in Figure 1). Because click coupling reactions are highly chemoselective, the chemical nature of the macromonomer blocks is only limited by our ability to synthesize appropriate heterobifunctional building blocks. While the coupling of macromonomers is illustrated herein, our SPS method is quite flexible, and a versatile toolkit of molecular building blocks can be imagined including monomers, branching units, or molecules that furnish specific functions such as sites for cleavage or for subsequent attachment of receptors or ligands. Two simple steps are required to add each building block: click coupling of the building block and subsequent deprotection to regenerate surface alkyne groups.

Three HetBi macromonomers were synthesized to illustrate the new method for preparing polymacromer brushes: α-alkyne-trimethylsilane-ω-azide-poly(styrene) (TMS-alkyne-PS-N$_3$) and α-alkyne-trimethylsilane-ω-azide-poly(tert-butyl acrylate) (TMS-alkyne-PtBA-N$_3$) and α-alkyne-trimethylsilane-ω-azide-poly(methyl methacrylate) (TMS-alkyne-PMMA-N$_3$). These polymers were synthesized by ATRP using a trimethylsilane protected alkyne-functional ATRP initiator,[34] followed by conversion of the resultant terminal bromine groups to azides by the addition of sodium azide[35] (see Supporting Information for details). Molecular characteristics of the macromonomers are presented in Table 1, and their chemical structures are shown in Scheme 1.

Table 1. Number-Average Molecular Weights (M_n), Weight-Average Molecular Weights (M_w), and Polydispersity Indices (PDI) of the Polystyrene, Poly(tert-butyl acrylate), and Poly(methyl methacrylate) HetBi Macromonomers Determined by Gel Permeation Chromatography (GPC)[a]

polymer code	M_n [Da]	M_w [Da]	PDI	$M_{n,adjusted}$ [Da]
TMS-alkyne-PS-N$_3$	21 500	24 000	1.12	21 500
TMS-alkyne-PtBA-N$_3$	17 000	20 000	1.17	22 170
TMS-alkyne-PMMA-N$_3$	12 000	20 000	1.67	14 600

[a]Adjusted M_n values employ a universal calibration based upon literature values of Mark–Houwink–Sakurada parameters[42] to correct the GPC molecular weight for hydrodynamic volume effects.

Scheme 1. Chemical Structures of HetBi Macromonomers: TMS-Alkyne-PS-N$_3$ (top); TMS-Alkyne-PtBA-N$_3$ (middle); TMS-Alkyne-PMMA-N$_3$ (bottom)
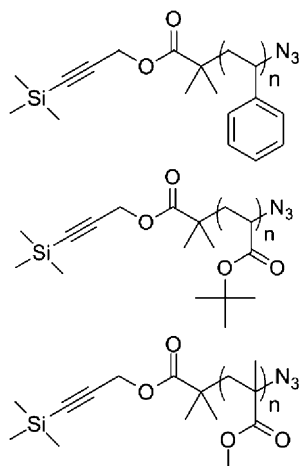
The initial step in SPS brush synthesis was to functionalize the substrate with alkyne groups. For glass and silicon wafers, the substrates used herein, this was accomplished by forming a self-assembled monolayer (SAM)[36–39] of an alkyne functional silane on the substrate surface. The thickness of the SAM, determined by angle-dependent X-ray photoelectron spectroscopy analysis, was 1.8 ± 0.3 nm, while that measured by ellipsometry was 1.7 ± 0.2 nm. From the structure of the silane, the thickness is expected to be about 1.1 nm. Similar silanes with 4–7 methylene units have a reported thickness of 1.5–2.3 nm.[40] The finding that these SAMs were thicker than expected is consistent with previous studies of other silanes that reported their polymerization to form multilayers.[41] The water contact angle of the alkyne-functionalized substrate was 61.8 ± 1°, compared to <10 ± 2° for the bare glass substrate, as expected for the more hydrophobic silane monolayer.

After functionalizing the substrate with alkyne groups, HetBi macromonomers were coupled to the surface by a click reaction between terminal azide groups of the macromonomers and surface alkynes. Each HetBi macromonomer was dissolved in toluene and spin-coated onto the surface, after which the coated substrates were placed in a vacuum oven and heated to 100–115 °C for 3–12 h to effect a thermally initiated "click" reaction (in the melt state) between substrate-bound alkyne groups and the azide termini of the polymers.[43] After the reaction period, excess polymer was removed by extensive washing with solvent (DCM) for 1–24 h. Click reactions proceed to very high conversion under mild conditions with no

side reactions or byproducts, and the resulting aromatic triazole is extremely stable.[44] In addition, click reactions are highly chemoselective such that virtually any polymer backbone may be used in the SPS process without interfering with the click reactions used to bond adjacent macromonomers.

The thermal stability of the TMS protecting groups was verified by a control experiment in which we attempted to couple a macromonomer onto a polymer-modified surface that was not subject to the deprotection step. The thickness did not change when the deprotection step was omitted, indicating that no reaction occurred and that the TMS protecting groups are stable under the conditions used for the thermal click reaction.

Substrate bound alkyne groups were regenerated after macromonomer addition by deprotection of the terminal TMS–alkyne groups, accomplished by dipping the substrate into a KCO$_3$-saturated solution of 10:1 DCM/MeOH. The regenerated alkyne surface was then used to couple additional macromonomers by repeating the two-step addition cycle with other HetBi macromonomers.

The first validation of the SPS method was homopoly-macromer formation by multiple addition of TMS-alkyne-PS-N$_3$. Successful sequential addition of multiple macromonomers is indicated by the thickness data in Figure 2. (Details of the
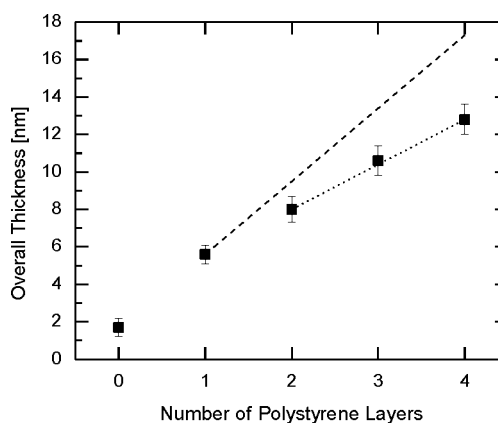

Figure 2. Ellipsometric thicknesses for SPS films prepared from TMS-alkyne-PS-N$_3$. The dashed line shows predictions for complete conversion based upon the areal density of the brush comprising one macromonomer layer, and the dotted line shows predictions based upon the areal density of brushes comprising two macromonomers.

ellipsometry analysis are provided in the Supporting Information.) When the first macromonomer is added to the alkyne–silane functionalized substrate, surface alkyne groups are in excess and a PS brush with a thickness of about 4 nm is formed. If each macromonomer is assumed to form a cube with the density of bulk PS (note, the coupling is performed in the melt), the expected thickness of a monomolecular layer would be about 3.24 nm. Polystyrene chains in the first layer therefore assume somewhat extended configurations, consistent with the results of previous studies of polystyrene brushes prepared by end-grafting from the melt.[45] The thicknesses for the second through fourth addition cycles are linearly dependent on the number of macromonomers added, with each addition cycle adding about 2 nm to the overall film thickness.

The fact that the thickness increase is the same for each macromonomer addition cycle is an important result because it suggests that the conversion of the interfacial click reactions is effectively complete for each macromonomer addition cycle. In

other words, when a macromonomer adds to the growing brush on the substrate, the areal density of peripheral alkyne groups remains constant, each chain adding exactly one macromonomer in true step-growth fashion. If the conversion were less than complete, the areal density of alkyne groups and consequently the areal density and thickness of PS chains added would decrease each time a macromonomer was added. It is quite remarkable that complete conversion is apparently achieved for brushes prepared in a sequential "grafting to" fashion as is done herein. Certain attributes of the method are conducive to this result. First of all, the alkyne group is one of few reactive functional groups that has a low surface tension (estimated to be 26 mN/m by group contribution methods) and is therefore expected to segregate preferentially to the surface of most polymers.[46] Second, the molecular weight of macromonomer added is identical in each cycle so that the occupied volume and functional group density of each are also the same. Third, because each cycle comprises the same PS macromonomer, there can be significant interpenetration between the brush and the macromonomer reacting to it. Interpenetration across the interface increases the effective volume for the reaction since complementary functional groups can only meet within the zone of interpenetration.

Completion of the reaction for each layer can be verified by calculating the areal density of functional groups at the surface of the first PS layer and using this value to predict the thickness of subsequent layers. The areal density of functional groups for a tethered polymer brush layer can be calculated from the measured thickness, molecular weight, and density according to

$$\Sigma = \rho A t / M_{\mathrm{n}} \qquad (1)$$

where ρ, t, and M_{n} are the homopolymer density, thickness, and macromonomer molecular weight, respectively, and A is Avogadro's number. If the conversion is complete, the areal density of each layer will be the same, allowing for a prediction of the thickness, t_i, of any subsequent layer i from the relation

$$t_i = \sum M_{\mathrm{n},i} / \rho_i A \qquad (2)$$

The dashed line in Figure 2 shows the results of thickness predictions based upon the areal density after addition of the first PS macromonomer. As can be seen, the data fall below this line, indicating that the conversion for adding the second macromonomer is less than complete. This result arises from the fact that PS chains in the first macromonomer brush layer were found to be extended while chains in the spin-coated layer deposited to couple the second macromonomer are in an unperturbed melt. The lateral dimensions in the melt must exceed those of the extended polymer brush so that the areal density of azide groups in the spin-coated layer will be less than the areal density of alkyne groups in the initial brush layer. This situation alters the reaction stoichiometry so that complete conversion is not possible when the second macromonomer is coupled to the initial macromonomer brush.

The dotted line in the figure shows the thickness predictions based upon the areal density achieved after addition of the second PS macromonomer. This prediction is in excellent agreement with the thickness of the third and fourth macromonomers, suggesting that complete conversion is achieved for all subsequent addition cycles after addition of the second macromonomer, a logical result because these reactions all involve coupling a macromonomer in the unperturbed melt state. Therefore, we can quantitatively

predict the thickness change for subsequent macromonomer addition cycles from the known macromonomer molecular weight and the measured areal density of functional groups after addition of the second layer (determinable from a thickness measurement).

Thickness data for homopolymacromer brushes prepared by multiple SPS addition cycles of the TMS-alkyne-PtBA-N$_3$ macromonomer are shown in Figure 3. The dashed line
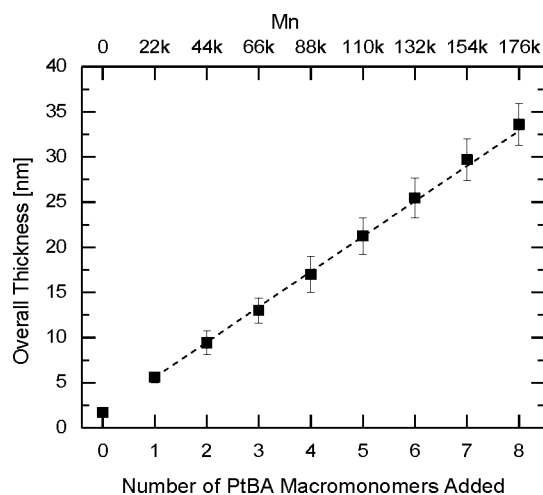

Figure 3. Ellipsometric thicknesses for films prepared from TMS-alkyne-PtBA-N$_3$.

shows predictions assuming complete conversion based upon the areal density of the brush comprising one macromonomer. The thickness scales linearly with the number of macromonomer addition cycles up to 8 cycles and within error agrees with the predicted thickness for complete conversion (dashed line in figure), for all layers. If we assume that the increase in thickness is directly proportional to the conversion, a statistical analysis of the data provides a 95% confidence limit that the conversion for each addition falls within the range of 97.5–100%. Ellipsometry is of course an indirect measurement, and we would need to perform direct molecular weight measurements on cleaved polymers to validate this initial observation.

In contrast to the results for PS, the thickness added by coupling the first and second macromonomer is identical for the PtBA brushes. One difference between the two macromonomers can be found in their propensity to wet the substrate. The surface tension of PS is reported to be about 40 mN/m,[47] whereas the surface tension of PtBA is about 30 mN/m.[48] The tendency for the first PS layer to be somewhat extended may therefore be related to its difficulty to wet the substrate. PtBA, on the other hand, should readily wet the substrate so that the initial macromonomer brush formed can assume an unextended configuration after grafting, matching that in the reacting melt of the second macromonomer.

The accuracy of ellipsometric thickness data was validated by X-ray reflectivity (XR) measurements on PtBA brushes prepared independently on large silicon wafers using a slightly different alkyne silane as described in the Supporting Information. The ellipsometric and XR thickness data in Table 2 are in excellent agreement for four PtBA macromonomer addition cycles, illustrating the remarkable robustness, reproducibility, and quantitative nature of the SPS method for preparing homopolymacromer brushes. Details regarding

Table 2. Comparison of Thicknesses Determined by Ellipsometry and X-ray Reflectivity for P*t*BA Brushes Prepared by SPS on Silicon Substrates

	thickness [nm]	
P*t*BA macromonomers added	ellipsometry	X-ray reflectivity
1	5.5	5.4
2	7.5	7.7
3	9.5	9.6
4	11.5	11.9

the XR measurements can be found in the Supporting Information.

The solid phase synthesis of copolymacromer brushes was also investigated. In general, the linear thickness behavior observed for SPS of homopolymacromer brushes by multiple addition of the same macromonomer is not expected for brushes comprising different macromonomers or for that matter for brushes prepared from macromonomers of the same type but differing in molecular weight (i.e., molecular volume). Asymmetry in molecular weight (i.e., molecular volume) causes a mismatch in areal density of the two complementary functional groups that must react across the interface, as depicted in Figure 4. For example, when a higher molecular
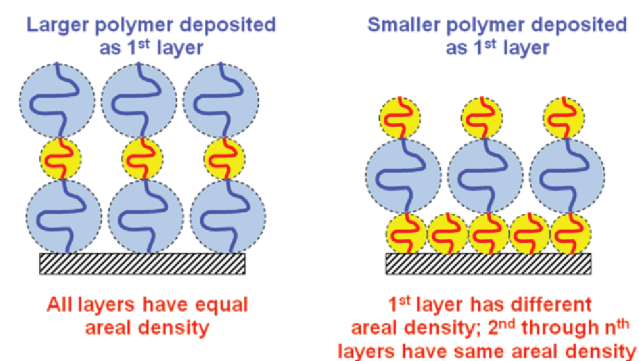

Figure 4. Brush growth for macromonomers of different size.

weight polymer is added to a layer created from a lower molecular weight polymer, functional groups on the substrate (i.e., lower molecular weight layer) are in excess, and the higher molecular weight polymer can readily add. The conversion for functional groups on the substrate is less than complete, yet a full monolayer of the reacting macromonomer can form. However, if the inverse is true, that is, a higher molecular weight macromonomer is followed by a lower molecular weight macromonomer, functional groups on the substrate are the limiting reactants and functional groups on the lower molecular weight macromonomer to be added are in excess. In this latter case, a full monolayer of the lower molecular weight reacting macromonomer cannot form, but the conversion of surface functional groups can go to completion.

In most cases, a brush will be immiscible with a chemically distinct macromonomer that is added to it. The width of the interphase between immiscible polymers, which dictates the volume in which the interfacial reaction can occur, depends on the nature of thermodynamic interactions between the two different macromonomers[49] and may influence the reaction conversion.

The effects of asymmetry in molecular size and chemical nature were studied for copolymacromer films prepared by

alternating addition of TMS-alkyne-PS-N$_3$ and TMS-alkyne-P*t*BA-N$_3$. The deposition of each successive macromonomer was confirmed by contact angle, X-ray photoelectron spectroscopy (XPS), and ellipsometry measurements. The results of XPS characterization of the copolymacromer brushes are shown in Figure 5. The photoelectrons detected have distinct binding
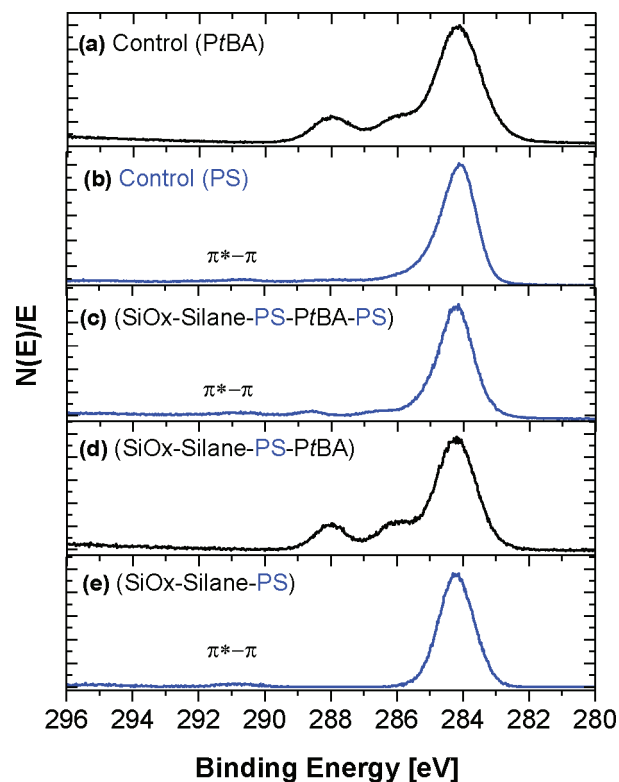

Figure 5. XPS high-resolution C 1s spectra of base polymer controls (a, b) and brushes (c–e) (15° takeoff angle).

energies associated with the atomic composition of the material being interrogated. The photoelectron spectra associated with carbon 1s orbitals are different for films of pure P*t*BA and PS due to chemical shifts induced by the presence of oxygen in the P*t*BA. The peak at 284.6 eV is the unshifted C 1s signal arising from carbon atoms bonded to only hydrogen or other carbon atoms. This signal is found in both the PS and P*t*BA control spectra. In P*t*BA, the signals associated with carbons bonded to oxygen undergo chemical shifts: the peak centered at 288.8 eV arises from the carbonyl carbon (O–$\underline{C}$=O) in P*t*BA, and the peak near 287.2 eV originates from the ester carbon ($\underline{C}$–O) in P*t*BA. The $\pi^*-\pi$ transition for pure PS is also apparent at ca. 291 eV. An O 1s signal from P*t*BA is also found at 531 eV (O 1s spectrum not shown).

The spectrum for the substrate coated with a covalently bound PS brush (Figure 5e) is identical to that of the pure PS control (Figure 5b), including the $\pi^*-\pi$ shakeup satellite, confirming successful coupling of the PS macromonomer. After the P*t*BA macromonomer is added, the XPS spectrum (Figure 5d) is found to closely resemble that of pure P*t*BA (Figure 5a). When another PS macromonomer is added, the spectrum (Figure 5c) reflects the presence of PS but also shows signals from P*t*BA. P*t*BA is detected in this case because the thickness of the deposited PS monomolecular layer is not thick enough to screen photoelectrons emanating from the underlying P*t*BA layer. The contact angle data shown in Figure 6 confirm that
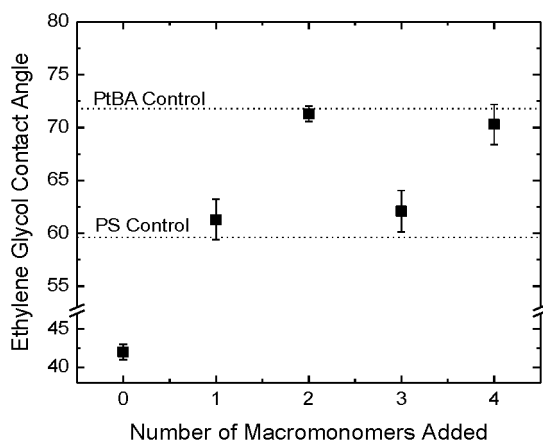
Figure 6. Ethylene glycol contact angles for copolymacromer brushes consisting of alternating TMS-alkyne-PS-N$_3$ (additions 1 and 3) and TMS-alkyne-PtBA-N$_3$ (additions 2 and 4) macromonomers. The dashed lines indicate the contact angles for pure PtBA and PS, respectively.

copolymacromer brushes have been built up by successive addition of alternating TMS-alkyne-PS-N$_3$ and TMS-alkyne-PtBA-N$_3$ macromonomers. Brushes terminated with PtBA and PS macromonomers exhibit ethylene glycol contact angles that are similar to those of the corresponding homopolymer controls.

Figure 7 presents thickness data for the PtBA-PS alternating copolymacromer brushes. Once the first brush layer is
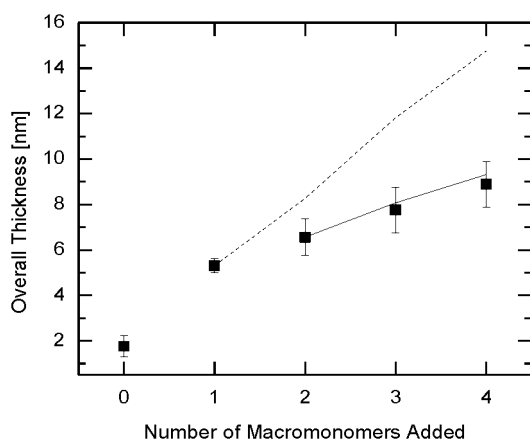

Figure 7. Ellipsometric thicknesses for alternating copolymacromer brushes: TMS-alkyne-PS-N$_3$ (additions 1 and 3) and TMS-alkyne-PtBA-N$_3$ (additions 2 and 4). The dashed line shows predictions based upon the areal density of functional groups in the first PS brush; the solid line is the prediction based upon the areal density after addition of the first PtBA macromonomer.

deposited onto the functional substrate, subsequent macromonomer additions yield a linear increase in thickness as the number of layers is increased. The resultant thin films are dense, segmented block copolymer brushes consisting of alternating sequences of PS and PtBA.

The dashed line in Figure 7 shows the thicknesses predicted from the areal density of functional groups in the first PS brush based upon application of eqs 1 and 2; the solid line illustrates predictions based upon the areal density of functional groups after addition of the first PtBA macromonomer. As was seen for the PS homopolymacromer brushes, the conversion of the

second layer is not complete, but we are able to predict the thicknesses of subsequent layers from the known molecular weight of the macromonomer and the areal density of the preceding layer. This observation indicates that after deposition of the second macromonomer the conversion of the interfacial reactions for subsequent macromonomer additions appears to be complete.

The ellipsometric thicknesses for alternating copolymacromer films of TMS-alkyne-PMMA-N$_3$ and TMS-alkyne-PS-N$_3$ are shown in Figure 8. The same general behavior is
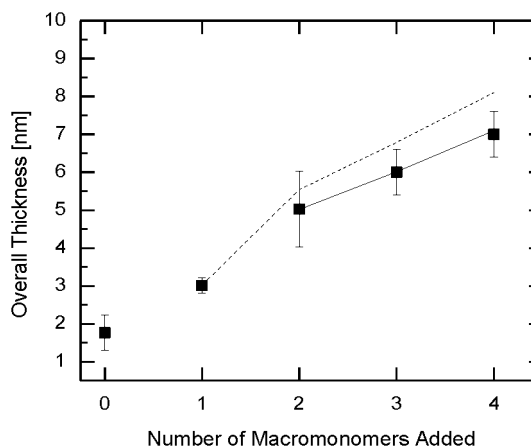

Figure 8. Ellipsometric thicknesses for alternating copolymacromer brushes: TMS-alkyne-PMMA-N$_3$ (additions 1 and 3) and TMS-alkyne-PS-N$_3$ (additions 2 and 4). The dashed line shows predictions based upon the areal density of functional groups after addition of the first macromonomer, and the solid line is the prediction based upon the areal density of functional groups after addition of the second macromonomer.

again realized. Alternating macromonomers can be successfully added, but the conversion upon addition of the second macromonomer is again less than complete. The thickness of the brush comprising three macromonomers, however, can again be predicted quantitatively from the known polymer molecular weight and the areal density of the preceding brush comprising two macromonomers calculated according to eqs 1 and 2, assuming that the interfacial reaction goes to completion.

Implications for Future Development of the Solid Phase Synthesis Method. The SPS process for polymer brush synthesis is both extremely simple and versatile. Two steps are involved with each deposition cycle: an interfacial click reaction and deprotection of the silane protected alkyne end group. The materials produced are technically poly-(triazoles) by nature of the triazole linkage formed when macromonomers are coupled. We have chosen to employ a new nomenclature, that is, polymacromers, to describe the novel materials prepared by the SPS method for a number of reasons. First and foremost, the IUPAC nomenclature is cumbersome. For example, if two HetBi polystyrene macromonomers were joined, we believe that the IUPAC name for this material would be, neglecting the end groups, bis{poly(1-phenylethylene)triazoleoxy[1,2oxodimethylmethylene]}. Second, materials of this nature have not been prepared before and would be difficult to prepare by other means, meriting in our opinion a unique name for a unique material. For example, alternating block copolymers of PMMA and PtBA are difficult to prepare directly by ATRP because the reactivity decreases after PtBA addition, making crossover back to PMMA

problematic. Polymacromers constitute a unique type of polymer brush that can be characterized as both "grafting to" and "grafting from". Normally, "grafting from" refers to the addition of a monomer while "grafting to" denotes addition of a preformed polymer. The coupling of multiple macromonomers clearly has attributes of both. In contrast to conventional brushes, the areal density and total molecular weight of polymacromer brushes can be controlled independently by selection of the macromonomer molecular weight and the number of addition cycles. Polymacromer brushes therefore smoothly span the limits between what currently is referred to as "grafting to" and "grafting from"; SPS of macromonomers is capable of preparing any brush that falls between these two extremes. Another interesting aspect of polymer brushes prepared by SPS is that the polydispersity is predicted to decrease with the number of macromonomers added because these are end-linking reactions.[50] We are currently working on the development of cleavable linkers to the substrate so that the reaction conversions and polydispersity may be measured directly by size exclusion chromatography.

We have opted to use thermal initiation in the present work because of its simplicity; however, we are also examining synthesis by copper-catalyzed solution phase click reactions. Coupling (i.e., reaction) from solution, however, is complicated by the effect of the solvent on polymer chain dimensions and density as well as the propensity for the reacting polymer to physisorb at the surface.[51−53] For example, it has been shown that the rates of interfacial reactions can increase by several orders of magnitude when the polymer in solution physisorbs at the surface.[54] Click reaction in the melt state is not subject to solvent effects; the thin film or reactive polymer can be deposited by a simple spin-coating process.

Because the interfacial click reaction is orthogonal to other chemistries, virtually any type of polymer backbone (e.g., charged or functional) can be employed. While the method was illustrated herein for PS, PtBA, and PMMA layers, ATRP is capable of producing HetBi polymers from a wide variety of monomers, and any of these could be employed. The number of other building blocks that could be employed in this scheme is only limited by imagination. For example, appropriate HetBi monomers can be synthesized, and we have prepared heterotrifunctional molecules that can be used to impart chain branching which will be reported in future communications. SPS in principle provides a rich toolkit for the synthesis of nonsymmetric sequenced polymers of almost any structure and architecture.

The most important limitation of SPS is that asymmetry in molecular weight can reduce the conversion of the interfacial reaction due to steric hindrance, not unlike the difficulty in preparing higher generation dendrimers. This complication can be circumvented, however, by the use of nonlinear functional materials to increase the areal density of functional groups at an interface of interest. For example, if the areal density of surface functional groups is insufficient to attach a subsequent layer, it can be increased by addition of a layer of click functional dendrimers. Gaining a detailed understanding of the effects of factors such as molecular weight asymmetry and surface curvature on the SPS of polymer structures will be the subject of future investigations. Finally, we describe only one version of SPS based upon azide−alkyne click chemistry. A number of other orthogonal chemistries can also be employed in SPS, some of which may not require a protection step.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Synthesis and characterization procedures; Schemes S1−S3; Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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