Thermoresponsive Behavior of Semifluorinated Polymer Brushes

Anthony M. Granville,[†] **Stephen G. Boyes,**[‡] **Bulent Akgun,**[†] **Mark D. Foster,**[†] **and William J. Brittain**[*,†]

Department of Polymer Science, University of Akron, 170 University Ave., Akron, Ohio 44325, and School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

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ABSTRACT: The surface rearrangement of polymer brushes composed of diblock copolymer chains with fluoropolymer blocks has been shown to be readily induced using thermal annealing. Changes in surface composition accomplished by the rearrangement were demonstrated by tensiometry and atomic force microscopy (AFM). Most of the research focused on brushes consisting of a hydrocarbon inner block [either poly(methyl acrylate) or polystyrene] and a fluoropolymer outer block [poly(pentafluorostyrene), poly-(heptadecafluorodecyl acrylate), poly(pentafluoropropyl acrylate), or poly(trifluoroethyl acrylate)]. The diblock copolymer brushes were first treated with a block selective solvent for the hydrocarbon block. Rearrangement was complete for all brushes except those in which poly(heptadecafluorodecyl acrylate) was the outer block. Subsequentially, the surfaces were then thermally treated to allow the fluoropolymer to migrate to the surface. The optimal temperature and exposure time for thermal treatment were found to vary with the glass transition temperatures (T_g). The poly(methyl acrylate)-*b*-poly(pentafluoropropyl acrylate) brush exhibited the most complete surface rearrangement upon solvent treatment and the fastest rearrangement upon thermal treatment. The thermal rearrangement of a poly(2-hydroxyethyl methacrylate)-*b*-poly(methyl acrylate) brush that was reacted with heptafluorobutyryl chloride via an acylation reaction was also studied. Fluoropolymer-rich surfaces created by thermal rearrangement were rougher than those created by solvent rearrangement.

Introduction

In an earlier paper, we reported the synthesis and solvent-switching of semifluorinated polymers brushes.[1] We refer the reader to that previous publication for an introduction to the field of polymer brushes and the properties of fluoropolymers. This paper extends the previous work by using temperature as a switching stimulus. We also describe the synthesis of a new diblock system with the fluorine-rich block adjacent to the substrate interface.

Fluoropolymers are known to exhibit an affinity for the air interface in polymeric materials.[2] This migration of fluorine moieties to the polymer−air interface should also extend to diblock copolymer brushes and would constitute a novel surface rearrangement mechanism. In this report, we investigate and characterize the thermally induced surface rearrangement of semifluorinated diblock copolymer brushes. Diblock copolymers containing a hydrocarbon polymer inner block and a fluoropolymer outer block were solvent treated to form a polymer brush layer where the surface properties were similar to those of the hydrocarbon polymer block. The diblock brushes were then thermally treated to increase the mobility of the tethered polymer chains and allow the fluoropolymer block to migrate to the brush−air interface. A similar thermal rearrangement study was extended to a semifluorinated diblock copolymer brush where the fluoropolymer segment was the inner block of the brush. This sample was synthesized by performing an acylation reaction on a poly(2-hydroxyethyl methacrylate)-*b*-poly(methyl acrylate) diblock copolymer brush. Acylation of poly(2-hydroxyethyl methacrylate) homopolymer brushes has been performed by other research groups recently to develop various hydrocarbon[3] and fluorocarbon[4] polymer derivatives. The intent of considering the brush with the fluorinated inner block was to probe how the rearrangement behavior might differ with the location of the fluorinated block, whether it was the inner or the outer block.

Experimental Section

Materials. See ref 1 for description of materials used in the preparation of semifluorinated polymer brushes. Heptafluorobutyryl chloride (98%) and *N,N*-dimethylformamide (DMF, HPLC grade 99.9%) were obtained from Aldrich and used without further purification. 2-Hydroxyethyl methacrylate (HEMA) was obtained from Aldrich and passed through a column of activated basic alumina (~150 mesh) prior to use. Polystyrene (PS)-based (Si/SiO$_2$//PS-*b*-PPFS, Si/SiO$_2$//PS-*b*-PHFA, Si/SiO$_2$//PS-*b*-PPFA, Si/SiO$_2$//PS-*b*-PTFA) and poly-(methyl acrylate) (PMA)-based (Si/SiO$_2$//PMA-*b*-PPFS, Si/SiO$_2$//PMA-*b*-PHFA, Si/SiO$_2$//PMA-*b*-PPFA, Si/SiO$_2$//PMA-*b*-PTFA) brushes were synthesized as previously reported;[1] PPFS = poly(2,3,4,5,6-pentafluorostyrene), PHFA = poly(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate), PPFA = poly(1*H*,1*H*-pentafluoropropyl acrylate), PTFA = poly(1*H*,1*H*-trifluoroethyl acrylate).

Si/SiO$_2$//PHEMA-*b*-PMA Diblock Copolymer Brush Synthesis. This synthesis followed the diblock synthesis procedure described in ref 1. Final concentrations and conditions for the HEMA brush were [CuBr]$_0$ = 41 mM, [HEMA]$_0$ = 4.2 M, [*N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA)]$_0$ = 83 mM, [CuBr$_2$]$_0$ = 4.1 mM, and [ethyl 2-bromoisobutyrate (E2BriB)]$_0$ = 41 mM; methanol was used as solvent, and the polymerization was run for 1.5 h at 22 °C. Because of the limited solubility of PHEMA chains, the reaction solvent for methyl acrylate was DMF. Final concentrations and conditions for the PMA brush were [CuBr]$_0$ = 16 mM, [methyl acrylate]$_0$ = 3.7 M, [PMDETA]$_0$ = 30 mM, and [E2BriB]$_0$ = 15 mM; the polymerization was run for 3.0 h at 90 °C.

[†] University of Akron.
[‡] University of Southern Mississippi.
[*] To whom all correspondence should be addressed: Fax (330) 972-5290; e-mail wjbritt@uakron.edu.

Acylation of Si/SiO₂//PHEMA-*b*-PMA with Heptafluorobutyryl Chloride. Si/SiO₂//PHEMA-*b*-PMA samples were placed in a round-bottom flask and then filled with 30 mL of DMF solvent. Heptafluorobutyryl chloride (0.36 mL, 80 mM) was added to the flask along with pyridine (0.24 mL, 0.1 M). The reaction flask was closed, and the reaction proceeded at room temperature for 6 h. After acylation, the samples were removed and were sonicated three times in fresh THF for 30 min. The samples were then characterized using ATR-FTIR, ellipsometry, and tensiometry.

Selective Solvent Treatment of Diblock Surfaces. Surfaces were treated with different solvents in order to induce a surface rearrangement. The block-selective solvent was a poor solvent for the outer fluoropolymer block and a good solvent for the inner hydrocarbon polymer block. For the surface samples where PS was the inner block, cyclohexane was used as the selective solvent. For the samples where PMA was the inner block two different selective solvents were used. Acetone was used as a selective solvent for the PPFS-based brush while ethyl acetate was used for the poly(fluoroalkyl acrylate)-based brushes. All solvent exposures were performed at 60 °C for 1 h. After solvent exposures, the samples were removed and dried using an air stream before being tested via tensiometry and AFM.

Thermal Treatment of Diblock Surfaces. The rearranged brush samples were placed in an oven at temperature for 40 min. After thermal treatment, contact angle measurements were performed to measure the extent of surface rearrangement. This process of solvent exposure and thermal switching was repeated several times, at various temperatures, to obtain the dependence of contact angle (θ_a) on temperature for each diblock system.

The temperature at which the maximum contact angle change occurred was then used for exposure time optimization experiments. As before, the samples were first exposed to a solvent selective for the lower hydrocarbon block. The solvent-treated samples were then placed in the oven and annealed at a set temperature for a given time duration and the contact angles of the treated samples were measured. This procedure was repeated, and the time duration varied, until a maximum contact angle change was observed, thereby yielding an optimized thermal switching condition.

Characterization Methods. See ref 1 for a description of our characterization techniques. For the thickness layer calculations, a refractive index of $n = 1.5$ was used for PHEMA.[5]

Results and Discussion

Selective Solvent Treatment of Semifluorinated Diblock Copolymer Brushes. We previously reported the synthesis of semifluorinated diblock copolymer brushes by surface-initiated polymerization (SIP) using atom transfer radical polymerization (ATRP).[1] These samples were generated from silica surfaces utilizing a suitable immobilized ATRP initiator, which had a trichlorosilane anchoring group and a bromoisobutyrate initiating moiety. From this initiator, sequential polymerization of a hydrocarbon monomer (styrene or methyl acrylate) and a semifluorinated monomer (HFA, PFA, TFA, or PFS) was performed to generate the desired diblock copolymer brushes.

These diblock samples were treated with a selective solvent at 60 °C for 1 h to induce a surface rearrangement. The solvent was a good solvent for the lower hydrocarbon block and a poor solvent for the outer fluoropolymer block. We speculate that the lower hydrocarbon polymer block, in an attempt to increase the favorable polymer−solvent interactions, extended toward the polymer brush−air interface layer. This solvent-induced rearrangement was probed by water contact angles (Table 1). In every diblock copolymer brush system except those where PHFA was the outer

Table 1. Block-Selective Solvent Treatment of Semifluorinated Diblock Copolymer Brushes

brush structure[a]	solvent exposure[b]	water contact angle (deg)[c]	
		θ_a	θ_r
Si/SiO₂//PS-*b*-PPFS	cyclohexane	101	85
Si/SiO₂//PS-*b*-PHFA	cyclohexane	110	92
Si/SiO₂//PS-*b*-PPFA	cyclohexane	97	78
Si/SiO₂//PS-*b*-PTFA	cyclohexane	95	81
Si/SiO₂//PMA-*b*-PPFS	acetone	79	67
Si/SiO₂//PMA-*b*-PHFA	ethyl acetate	110	90
Si/SiO₂//PMA-*b*-PPFA	ethyl acetate	80	66
Si/SiO₂//PMA-*b*-PTFA	ethyl acetate	74	62

[a] PS = polystyrene, PMA = poly(methyl acrylate), PPFS = poly(2,3,4,5,6-pentafluorostyrene), PHFA = poly(1*H*,1*H*,2*H*,2*H*-hexadecafluorodecyl acrylate), PPFA = poly(1*H*,1*H*-pentafluoropropyl acrylate), and PTFA = poly(1*H*,1*H*-trifluoroethyl acrylate). [b] Solvent exposure at 60 °C for 1 h. [c] The standard deviation of contact angles was <2°.

fluoropolymer block, the contact angles were characteristic of the lower hydrocarbon block. This is consistent with a surface rearrangement. The samples containing PHFA as the fluorinated outer block showed incomplete rearrangement as evidenced by the higher than expected contact angles exhibited after solvent treatment.

It is remarkable that the solvent-induced rearrangement of the diblock brushes with PMA inner blocks is stable at room temperature. Since the bulk T_g of PMA is 10 °C, one might expect the PMA-containing diblocks exposed to solvent to rapidly return to a state with the fluoropolymer at the surface upon being removed from the solvent; however, they do not. This suggests that the mobility of the PMA block must be substantially less than that characteristic of bulk PMA at room temperature. This point is addressed in greater detail below in the discussion of thermal rearrangement.

Thermal Treatment of Diblock Copolymer Surfaces. Previous studies of untethered semifluorinated diblock copolymer cast films have shown that the fluorinated blocks have an affinity to reside at the polymer−air interface.[2,5−7] In particular, Li et al.[7] were able to show that the fluoropolymer block surface migration was enhanced upon annealing of the diblock copolymer cast film. They speculated that the driving forces for the surface enhancement were the unfavorable enthalpic interactions between the fluoropolymer and the hydrocarbon polymer and the favorable reduction in free energy attained by replacing higher surface energy hydrocarbon polymer with fluoropolymer at the surface. Therefore, extending this annealing process to the solvent-treated tethered polymer brush surfaces should cause the brush layer to extend and allow the fluoropolymer block to "bloom" to the surface. To obtain sufficient mobility of the tethered diblock copolymers to allow for thermal rearrangement and migration of the fluoropolymer block to the polymer−air interface, the annealing temperature should be at or above the T_g value for the block with the highest T_g. Table 2 lists the T_g values for the polymers used in this study.

The initial step in the thermal rearrangement study of the tethered surfaces was the generation of a fluorine-deficient layer. The semifluorinated diblock copolymer brushes were first treated with a block-selective solvent (poor solvent for the fluoropolymer block and a good solvent for the hydrocarbon polymer brush) to induce a surface rearrangement. All of the diblock copolymer brush samples, including the poorly rearranged PHFA-based samples, were annealed at a given temperature

Table 2. Glass Transition Temperatures of Polymers Used in This Study

polymer block	T_g (°C)[a]
polystyrene	100
poly(methyl acrylate)	10
poly(pentafluorostyrene)	105
poly(trifluoroethyl acrylate)	−10
poly(pentafluoropropyl acrylate)	−26
poly(heptadecafluorodecyl acrylate)	−5

[a] Experimental data taken from *Polymer Handbook*.[8]
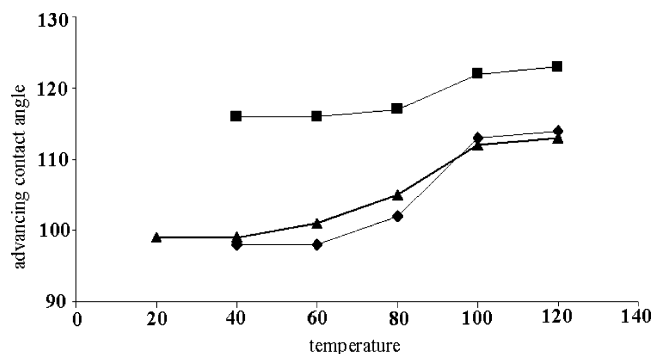
Figure 1. Dependence of the advancing water contact angle on annealing temperature for PS-based diblock copolymer brush layers: (■) Si/SiO₂//PS-*b*-PHFA, (▲) Si/SiO₂//PS-*b*-PPFA, (◆) Si/SiO₂//PS-*b*-PPFS. Lines added as guides for the eye.
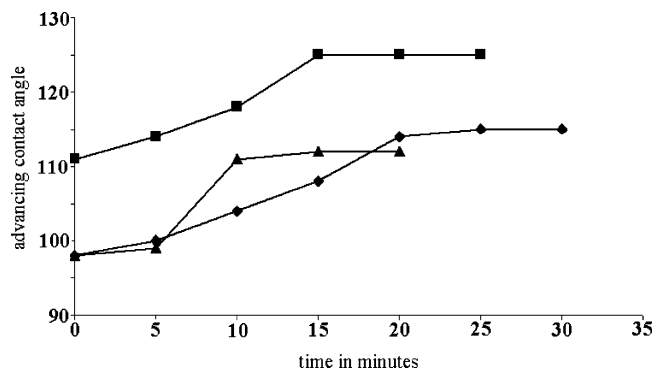
Figure 2. Dependence of the advancing water contact angle for PS-based diblock copolymer brush layers on annealing time for annealing at 100 °C: (■) Si/SiO₂//PS-*b*-PHFA, (▲) Si/SiO₂//PS-*b*-PPFA, (◆) Si/SiO₂//PS-*b*-PPFS. Lines added as guides for the eye.

for 40 min. After thermal treatment, the samples were removed and water contact angles were measured to probe the change in surface properties. The samples were then treated again with the appropriate selective solvent for the bottom block, and the process was repeated, for various temperatures, until a maximum contact angle change was obtained. This temperature of highest, optimum contact angle (indicative of a fluorine-rich surface) was used to determine the time interval needed to induce a thermal surface rearrangement. The samples were annealed at the optimum temperature for various time intervals, and the surfaces were tested via tensiometry.

Figures 1 and 2 depict the contact angle changes as a function of temperature and time for the semifluorinated diblock copolymer brushes having PS as the inner block. The Si/SiO₂//PS-*b*-PTFA brush sample was not analyzed using this annealing technique due to the relatively small difference between contact angles for the individual diblocks (θ_a for PS = 98° and for PTFA = 102°). As can be seen in Figure 1, regardless of the nature of the fluoropolymer block (whether a fluoroalkyl
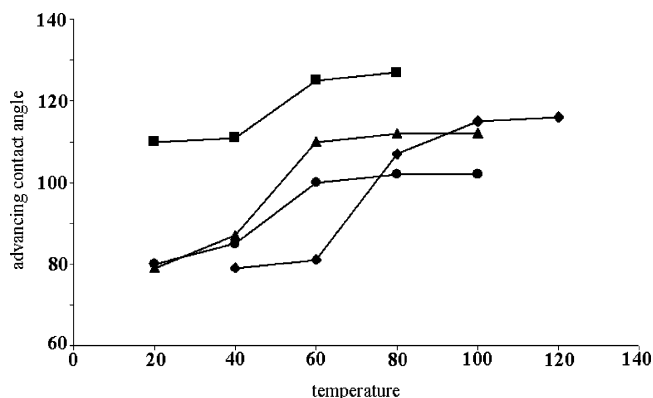
Figure 3. Dependence of the advancing water contact angle on annealing temperature for PMA-based diblock copolymer brush layers: (■) Si/SiO₂//PMA-*b*-PHFA, (▲) Si/SiO₂//PMA-*b*-PPFA, (●) Si/SiO₂//PMA-*b*-PTFA, (◆) Si/SiO₂//PMA-*b*-PPFS. Lines added as guides for the eye.

acrylate or a fluorostyrene) the surface rearranges partially at temperatures below 100 °C, but maximum rearrangement to yield fluoropolymer surface properties requires annealing at 100 °C. The Si/SiO₂//PS-*b*-PPFS diblock brush was slower to rearrange than the fluoroalkyl acrylate tethered diblocks, as evident from Figure 2. The time required for the tethered surface to fully rearrange and yield properties similar to those of PPFS was approximately 20 min. The time required to obtain full rearrangement to fluoropolymer surface properties decreased when a fluoroalkyl acrylate comprised the outer block. The Si/SiO₂//PS-*b*-PHFA diblock copolymer brush rearranged in roughly 15 min, but the surface present at the beginning of the annealing already had a contact angle that was higher (ca. 111°) than would be expected for a PS-rich surface, suggesting that the brush had not fully rearranged with solvent treatment. In contrast, the Si/SiO₂//PS-*b*-PPFA brush had exhibited a complete solvent-induced rearrangement based on contact angle measurements and, upon thermal treatment, reverted to a fluorine-rich surface in 10 min. We attribute these time decreases in time needed to rearrange under thermal stimulation to the higher mobility of the fluoroalkyl acrylate polymer segments as compared to the PPFS block segment, based on the T_g values in Table 2. However, one must consider other factors than T_g values alone, especially in the case of the PHFA brushes. The melting point of PHFA is 74 °C[10] and should be considered when evaluating these data.

The same thermal rearrangement testing was performed on samples where the inner hydrocarbon polymer block was PMA rather than PS. For these samples, the semifluorinated outer polymer block was varied among PPFS, PHFA, PPFA, and PTFA. For the Si/SiO₂//PMA-*b*-PPFS sample, the thermal rearrangement required an annealing temperature of 100 °C (Figure 3). The observed annealing temperature of 100 °C is consistent with the argument that the block with the highest T_g would determine the annealing temperature. This temperature to induce surface rearrangement is the same as that for the Si/SiO₂//PS-*b*-PPFS brush. However, unlike the Si/SiO₂//PS-*b*-PPFS polymer brush that took 20 min to rearrange, the Si/SiO₂//PMA-*b*-PPFS brush needed only 5 min to rearrange (Figure 4). Again, we attribute this difference in rearrangement time to the greater mobility of PMA as compared to PS due to its much lower T_g (10 °C).
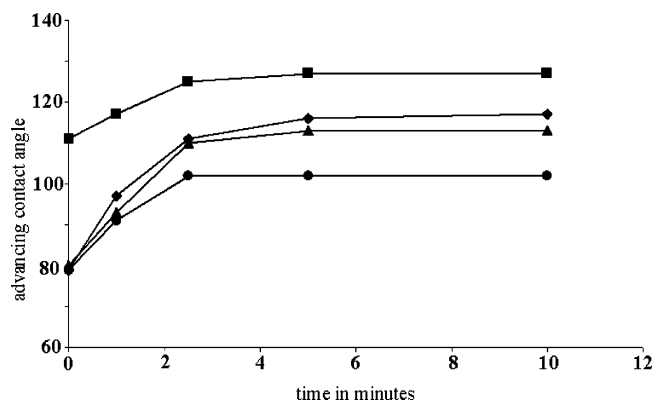
Figure 4. Dependence of the advancing water contact angle for PMA-based diblock copolymer brush layers on annealing time: (■) Si/SiO$_2$//PMA-*b*-PHFA annealed at 60 °C, (▲) Si/SiO$_2$//PMA-*b*-PPFA annealed at 60 °C, (●) Si/SiO$_2$//PMA-*b*-PTFA annealed at 60 °C, (◆) Si/SiO$_2$//PMA-*b*-PPFS annealed at 100 °C. Lines added as guides for the eye.

When the fluorinated outer block is a fluoroalkyl acrylate, the lower PMA block possesses the higher T_g as evident from Table 2. Each of the fluoroalkyl acrylates (HFA, PFA, and TFA) possesses a T_g at least 15 °C lower than that of PMA. According to our hypothesis of thermal rearrangement occurring at a temperature near the temperature for the higher T_g block, we would expect the diblock copolymer brushes to rearrange at room temperature. However, for all of the fluoroalkyl acrylate diblock systems shown in Figure 3, the surface continues to exhibit a contact angle characteristic of PMA after days at room temperature. This indicates that the thermal rearrangement is impeded at room temperature. One way of attempting to describe this would be to say that the brushes exhibit a behavior consistent with an elevation of the apparent T_g of the PMA block above that characteristic of bulk T_g. The annealing times used here are sufficiently long that the value of a genuine T_g should be able to manifest itself. It is possible that the preparation of the sample could induce a structure in the sample that would affect its apparent T_g. In this case, to see the true "T_g" the structure must relax over the length scales pertinent to the collective motions involved in the glass transition.[11] If the T_g of the PMA block were equal to that of bulk PMA, 40 min at 60 °C would be more than sufficient to anneal away sample history effects that could make the T_g of that block look abnormally high. Thus, the lack of mobility observed is not simply an artifact of sample history. We recognize, however, that the measurements done here, while reflecting the mobility of the chains, do no constitute an actual measurement of T_g,[11] and therefore we must be circumspect in placing an exact value on the amount by which T_g may have been elevated.

Literature reports pertinent to the question of whether elevation of the brush glass transition temperature above that of the corresponding bulk material is possible are mixed. We consider first what has been reported for thin films in general. Forrest and Dalnoki-Veress[11] have critically reviewed the state of understanding of the glass transition in thin polymer films as of 2001. They conclude that a consensus among several studies exists that in PS films the value of T_g decreases with film thickness for films thinner than about 100 nm. They refer to both the work of Keddie et al.[12] and Prucker et al.[13] in arguing that this decrease with thickness occurs

whether the chains in the film are free or grafted. The value of T_g has been seen to increase with decreasing thickness in cases where there are recognized favorable interactions between the polymer and the substrate. In particular, T_g was seen to increase at sufficiently small thicknesses for PMMA films on silica surfaces.[14] Work by Porter and co-workers[15] suggests, on the basis of NMR measurements, that when PMMA chains are adsorbed on silica at sufficiently low density that appreciable portions of individual chains are in contact with the surface, the mobility of the chains is reduced. The thickest layer they studied was only 2 nm thick. They do not attempt to assign a value of T_g for these layers. Lin and co-workers[16] have also considered the mobility of PMA adsorbed to silica surfaces. Again, the results suggest that in the case that substantial fractions of the individual chains contact the silica surface (i.e., for low coverage and low chain molecular weight) chain mobility is sharply curtailed up to a temperature of about 50 or 40 °C above the bulk T_g of PMA. Apparently PMA segments closer to the air surface, which do not contact the substrate, are more mobile. The grafting densities of the brushes in the present work are sufficiently high that it seems unlikely that many of the segments from a given PMA chain would be directly adsorbed to the substrate. However, the chains are tethered to the substrate, and this confinement could potentially cause a decrease in mobility.

Reports in the literature comparing the T_g's of polymer brushes with those of corresponding bulk polymer offer varying appraisals of the effect of this confinement. Lemieux et al.[17] argue that the T_g of a densely grafted brush of poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) is the same as that in the bulk. They also consider the mechanical properties of a densely grafted 50 nm PMA brush and, while they do not report a value of T_g for the PMA brush, find that it has mechanical properties at room temperature characteristic of a rubbery material, not of a glass. Prucker and co-workers[13] find the T_g's of free radical polymerized PMMA polymer brushes decrease as the brush thickness decreases from 200 to 3 nm. Molecular dynamics of grafted layers of PDMS by Hartmann et al.[18] suggest that a lowering of T_g should be expected in brushes of thickness less than 40 nm.

Data from two other papers in the literature suggest that the value of T_g in the brush is higher than that in the bulk. For the case of PS brushes on silica substrates, where there is no special interaction with the substrate, Tate and co-workers[19] find that the value of T_g elevation is roughly 25 °C for a 40 nm thick brush. The brushes considered in our work are about half that thickness, and one may anticipate favorable interactions between PMA and the silica substrates similar to those observed for PMMA films on silica. Yamamoto et al.[14] have reported that 15−25 nm densely grafted PMMA brushes exhibit a value of T_g roughly 20 °C above that of bulk PMMA. In summary, prior work by others seems to allow for the possibility that in sufficiently thin diblock brushes in which the inner block is strongly attracted to the substrate an elevation of T_g could be possible.

In the present work the annealing temperature required to obtain rearrangement of the brushes with PMA inner blocks and poly(fluoroalkyl acrylate) outer blocks is roughly 60 or 50 °C above the bulk T_g of PMA. There is some slight difference in mobility among the three brushes with PHFA, PTFA, and PPFA blocks. The

Scheme 1. Synthesis of Si/SiO₂//PHEMA-*b*-PMA Brush on a Silicon Substrate and Subsequent Fluorination via Acylation Reaction
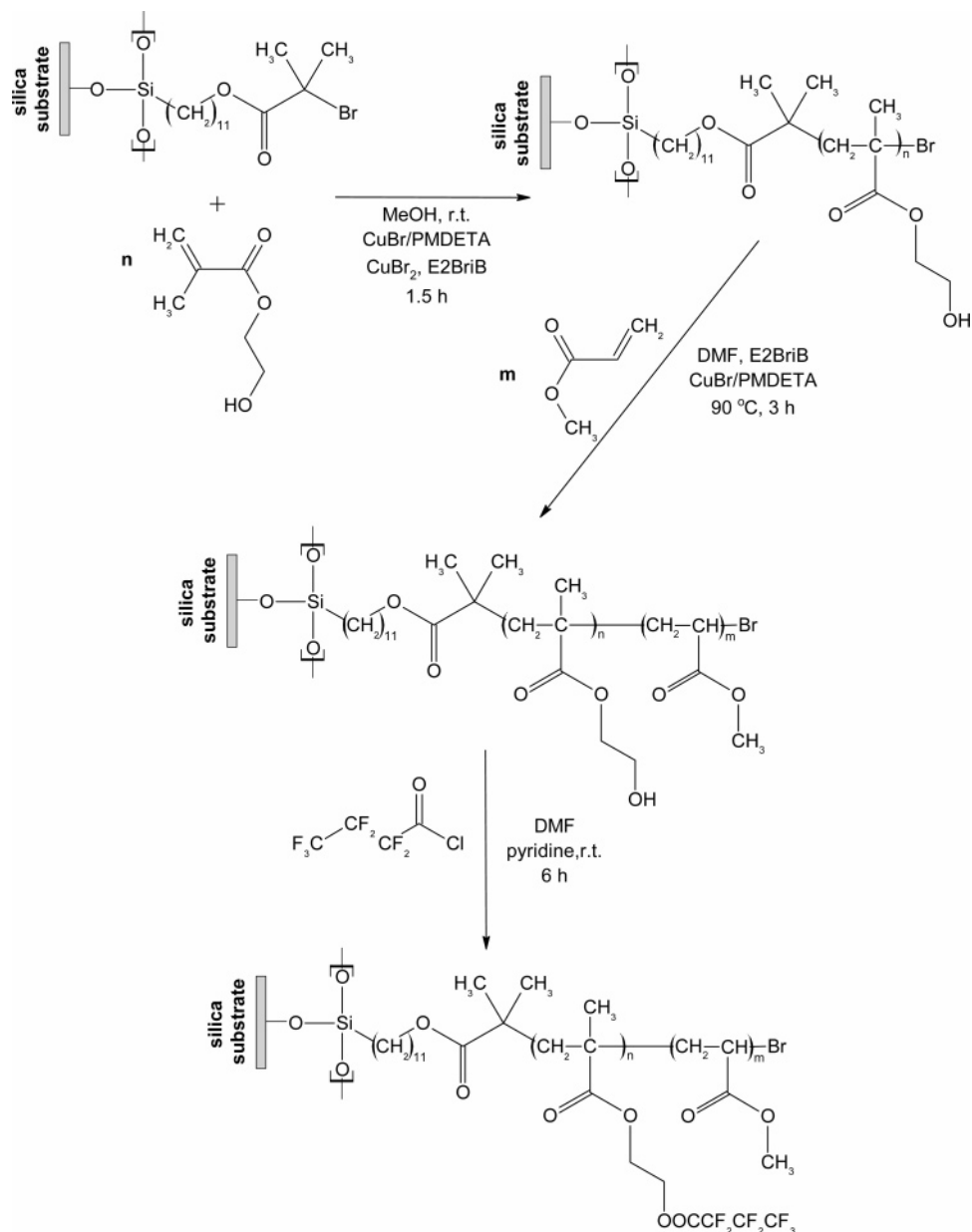
brush with the PPFA outer block shows some change at 40 °C, and PPFA has the lowest T_g (−26 °C) of the three fluoroalkyl acrylate blocks. PTFA has the next lowest T_g (−10 °C), and the brush with this block also shows some mobility at 40 °C, but less than seen for PPFA. Finally, the brush with fluoroalkyl acrylate block (PHFA) having the highest T_g (−5 °C) shows no change at 40 °C but does rearrange at 60 °C. All these observations suggest that the mobility of the outer block contributes some in determining the rearrangement of the brushes with fluoroalkyl acrylate outer blocks, but the dominant feature remains the strong influence of the PMA on the rearrangement temperature. When the outer block is switched to PPFS, the behavior of the PMA no longer dictates the overall behavior. Apparently the PPFS block has a T_g higher than even that of the confined PMA, since the Si/SiO₂//PMA-*b*-PPFS brush rearranges substantially already at 80 °C, about 25 °C below the bulk T_g of PPFS. This suggests that for the PPFS outer block there is no restriction of mobility by confinement due to tethering. It may even be that the

mobility is slightly enhanced as compared to that in bulk PPFS due to the chains' proximity to the surface. However, the observations made here are insufficient to discuss in detail the possibility of enhanced mobility near the surface. Not only did the PMA-based, fluoroalkyl acrylate outer block brushes rearrange at annealing temperatures lower than those needed for brushes containing PS inner blocks, they also rearranged rapidly, in 2.5 min. Both the annealing temperature decrease and dramatic reduction in time to rearrange give evidence that the greater mobility of the PMA block, as compared to that of the PS block, greatly affects the thermal surface rearrangement characteristics of the semifluorinated polymer brush systems.

Since in all of the brushes considered to this point the fluoropolymer blocks were used as the outer block of the diblock copolymer brush, it is possible that thermal treatment is merely allowing for extension of the polymer brush to alleviate strain rather than permitting favorable migration of fluorine to the polymer−air interface. To address the question of how the
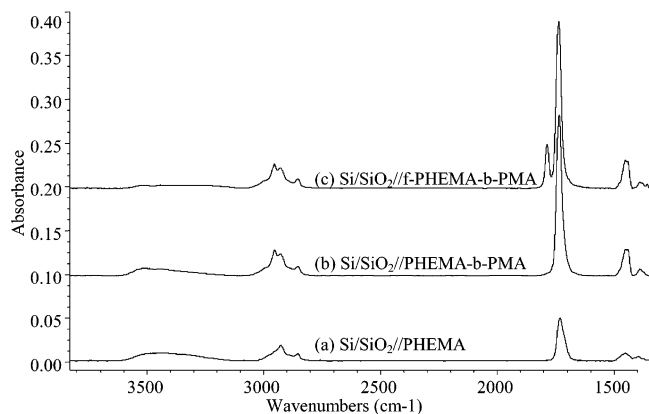
Figure 5. ATR-FTIR spectra for samples at various stages of brush synthesis: (a) Si/SiO$_2$//PHEMA, (b) Si/SiO$_2$//PHEMA-*b*-PMA, (c) Si/SiO$_2$//f-PHEMA-*b*-PMA.

Table 3. Surface Analysis of Si/SiO$_2$//f-PHEMA-*b*-PMA Brush Synthesis

| | contact angle (deg)[a] | | thickness[b] |
brush structure	θ_a	θ_r	(nm)
Si/SiO$_2$//PHEMA	53	38	9
Si/SiO$_2$//PHEMA-*b*-PMA	78	64	7
Si/SiO$_2$//f-PHEMA-*b*-PMA	77	64	5[c]

[a] The standard deviation of contact angles was <2°. [b] Thickness determined by ellipsometry and representative of the outer block only. [c] Thickness increase of PMA block due to acylation reaction.

location of the fluorinated block in the tethered polymer affects the ability to rearrange the surface, a brush with the fluoropolymer block as the inner block was studied. Attempts were first made to directly synthesize a semifluorinated diblock; however, reinitiation of the dormant fluoropolymer brush chain ends in the presence of styrene or methyl acrylate proved unsuccessful. Therefore, a Si/SiO$_2$//PHEMA-*b*-PMA brush was synthesized and then fluorinated via an acylation reaction of the PHEMA units with heptafluorobutyryl chloride (Scheme 1). This generated the desired fluoropolymer block as the inner block of the diblock copolymer brush system (Si/SiO$_2$//f-PHEMA-*b*-PMA), as shown by ATR-FTIR spectroscopy (Figure 5). In addition to ATR-FTIR analysis, the polymer brush was subjected to ellipsometry and tensiometry analysis after each polymerization and acylation reaction (Table 3). Acylation of the PHEMA segment to introduce fluorination resulted in an increase of the diblock brush thickness by 5 nm. As well as a thickness increase, attributed to increased elongation of the brush chain to incorporate the longer fluoroalkyl side chain as seen by other research groups,[3,4] acylation also results in the loss of the broad hydroxyl peak between 3600 and 3200 cm^{-1} and the formation of a new carbonyl peak at 1790 cm^{-1} (Figure 5c).

The Si/SiO$_2$//f-PHEMA-*b*-PMA brush was treated with DMF to extend the brush, yielding surface characteristics similar to those of PMA ($\theta_a = 75°$). The brush was annealed at 60 °C, the same temperature at which all the other acrylate diblock copolymer brushes were annealed. However, this brush system required 6 min to yield a fluoropolymer surface ($\theta_a = 114°$) rather than the 2.5–3 min observed when the outer block was the fluoropolymer. Even though twice as long is required for surface rearrangement when the fluoropolymer is the inner block, thermal treatment clearly allows for migration of the fluoropolymer to the polymer–air
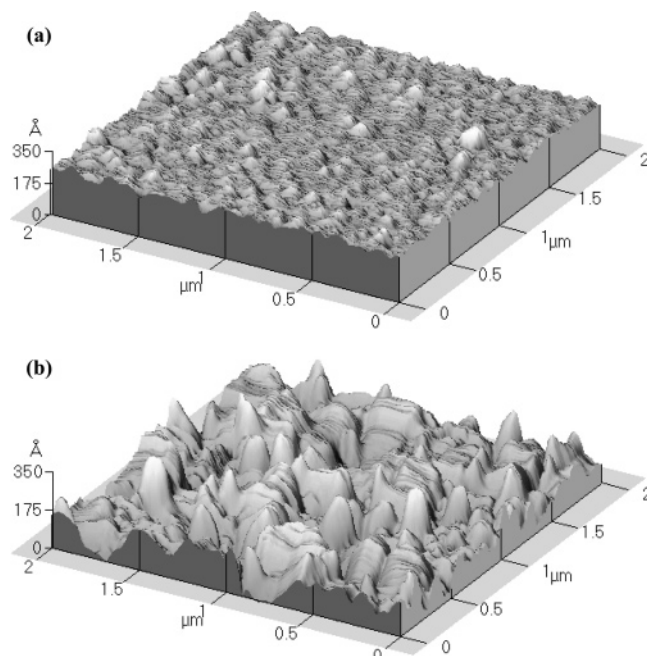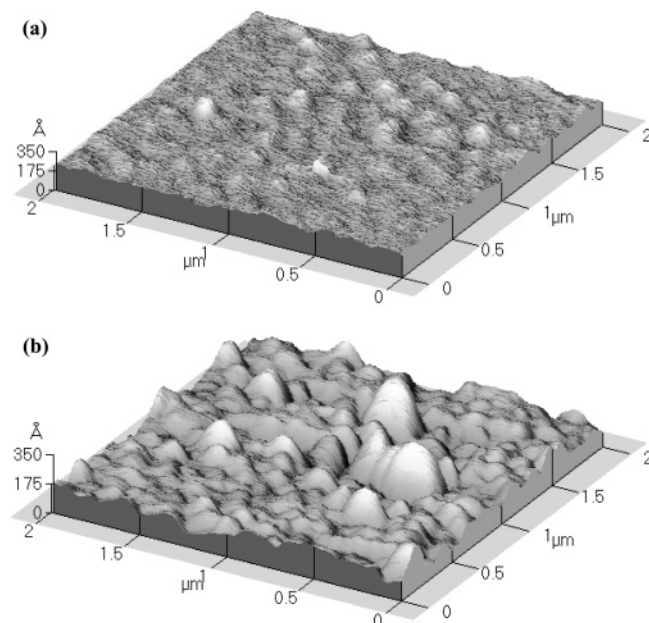

Figure 6. AFM images of Si/SiO$_2$//PS-*b*-PPFS sample after (a) fluorobenzene treatment and (b) annealing at 100 °C for 20 min.

interface, whether the fluoropolymer is in the inner or outer block.

AFM Analysis of Tethered Diblock Copolymer Brushes. To further investigate the surface rearrangement properties of these diblock copolymer samples, AFM was used to determine the surface morphology. We previously used this technique to illustrate the change in surface morphology of the tethered diblock copolymer brushes upon solvent treatment.[1] Upon treatment with a nonselective solvent, the surface was relatively smooth. After annealing the diblock copolymer brushes in this study, the measured water contact angles were similar to those observed when the brush was treated with a good solvent, both exhibiting a surface rich in fluoropolymer. However, the surface morphologies of the samples treated with a good solvent and those that were thermally treated are not the same, though one might expect them to be the same from the tensiometry results. Figure 6a depicts the surface morphology of a Si/SiO$_2$//PS-*b*-PPFS brush treated with fluorobenzene to extend the polymer brush chains. The surface roughness, defined as the root-mean-square of the height deviations taken from the mean data plane, was 1.4 nm over a 2 μm × 2 μm scan. To rationalize the magnitude of this roughness and compare it to that of the thermally annealed sample, it is helpful to note carefully the trajectory leading to this structure. When the sample is swollen with fluorobenzene, the effective exchange interaction between the two blocks, χ, is strongly reduced by the solvent.[20] When χ is small, the two blocks mix readily and the internal structure of the swollen brush will be dictated by a balance between the free energy reduction gained by mixing with solvent and the free energy penalty due to stretching. The cost of contacts between block segments will be unimportant. When the sample is pulled from the solvent, the brush will simultaneously collapse and vitrify as solvent is rapidly removed from the brush. Over the length scale of the AFM image it may be anticipated that this collapse will be laterally uniform. The magnitude of roughness that is seen in the vitrified surface (1.4 nm)

Figure 7. AFM images of Si/SiO₂//PMA-*b*-PPFA sample after (a) trifluorotoluene treatment and (b) annealing at 60 °C for 5 min.

Table 4. Calculated δ Based on Group Contribution Values Compared to Experimental Values[a]

monomer	calcd δ (J/cm³)$^{1/2}$	exptl δ (J/cm³)$^{1/2}$
methyl acrylate	19.86	19.9−21.3
methyl methacrylate	19.02	18.6−26.2
styrene	19.06	17.4−19.0
heptadecafluorodecyl acrylate	14.15	unknown
pentafluoropropyl acrylate	16.46	unknown
trifluoroethyl acrylate	17.46	unknown
pentafluorostyrene	unknown	16.77[b]

[a] All values obtained from published work by van Krevelen.[8]
[b] Value obtained from work by Su.[9]

is of the order of the interface broadening that occurs in diblock copolymers as a result of thermally stimulated fluctuations at the interface.[21]

In contrast, the same sample, once thermally treated to extend the chains, exhibited an rms surface roughness of 6.1 nm (Figure 6b). Though the roughness is random, it is much too large to be explained by the presence of thermally stimulated fluctuations. For all of the samples a larger surface roughness was observed after thermal treatment than was observed after solvent treatment. Figure 7 depicts AFM images for the (a) solvent extended and (b) thermal extended Si/SiO₂// PMA-*b*-PPFA brush, for which we observed a surface roughness increase from 1.9 to 4.2. nm. It should be kept in mind that while the conventional presentation used in Figures 6 and 7 leaves one with the impression that there are sharp "bumps" on the surface, the lateral and vertical scales are very different. In fact, the undulations in the surface are more nearly analogous to low rolling hills.

It is not yet clear exactly what features of the block copolymer brush structure result in these differences in roughness, but we may speculate on likely directions in which to look for an explanation. Once again we may consider the states through which the sample passes as the surface morphology captured by AFM is formed. When the Si/SiO₂//PS-*b*-PPFS block copolymer brush is thermally annealing, both blocks are apparently mobile. There is no solvent to mediate the block−block exchange interactions and the effective value of χ is much larger than in the case of the solvent-swollen brush. Thus, the internal structure of the brush will be strongly influenced by the tendency of the two blocks to segregate from one another on a nanoscale. This segregation phenomenon probably influences the surface morphology. In a thin film of exactly the correct amount of untethered ideal monodisperse block copolymer to form an integral number of lamellar domains, this segregation or ordering manifests itself purely in the vertical direction.[21] The surface is flat. However, in the presence of any lateral nonuniformities in chain length or graft-

ing density, this tendency to segregate could manifest itself in lateral variations in height in a film of tethered chains. When the Si/SiO₂//PS-*b*-PPFS sample is cooled only 10 or 20 °C from the annealing temperature, which is close to the bulk T_g's of the two blocks, it vitrifies without having to undergo a structural change as dramatic as the removal of the solvent from the swollen brush. We speculate, then, that the surface morphology of the thermally annealed brush may be quite close to that present at equilibrium at the annealing temperature. In fact, in the case of the Si/SiO₂//PMA-*b*-PPFA brush the top block is apparently still in a melt state at room temperature. In that case the inner block has vitrified presumably with the PMA/PPFA interface trapped with a shape very similar to that present at 60 °C, but the top surface is still mobile. It is known that sufficiently thin (e.g., 4.4 nm) small molecule liquid films can replicate the roughness of substrates upon which they form,[23] and it is possible that the shape of the glassy PMA-rich bottom layer influences somewhat the shape of the top surface. The influence of nonuniformities on brush surface morphology and the conformality of interfaces in diblock brushes are currently under investigation in our laboratories. If it is true that the comparatively large χ acting during thermal annealing plays a role in determining the rough surface structure, then we might anticipate different roughnesses for different pairs of blocks. It may be that the value of χ for the Si/SiO₂//PS-*b*-PPFS copolymer is larger than for the Si/SiO₂//PMA-*b*-PPFA copolymer, based on the estimates of solubility parameters summarized in Table 4. However, estimating the value of χ is nontrivial and refining this point will require further study.

Conclusions

The surfaces of semifluorinated diblock copolymer brushes were successfully rearranged using thermal treatment in air. These brushes were composed of a PS or a PMA hydrocarbon inner block and either a poly-(pentafluorostyrene) (PPFS) or a poly(fluoroalkyl acrylate) (PHFA, PPFA, or PTFA) outer block. The diblock copolymer brushes were first treated with a block-selective solvent for the hydrocarbon block. This treatment generated a sample with surface properties similar to those of the hydrocarbon polymer block, indicating a brush layer rearrangement. Thermal annealing allowed the fluoropolymer block to "bloom" to the polymer brush surface. The annealing temperature required to yield a surface rearrangement was related to the thermal transition of the block possessing the higher T_g. The rearrangement of the PS-based systems required a temperature of 100 °C and an annealing time that depended on the mobility, or T_g, of the fluoropolymer block. As the T_g of the fluoropolymer block decreased,

the time needed to obtain full brush extension decreased. When the hydrocarbon polymer layer was changed to PMA (which possesses a much lower T_g than PS), the time needed to obtain surface rearrangement dramatically decreased to 5 min or less, depending on the composition of the fluoropolymer brush. Also, the temperature needed to sufficiently anneal the polymer brush layer decreased to 60 °C when both blocks were acrylate. The fact that this temperature was still far above the bulk T_g of PMA suggests an interesting confinement effect occurs in the brushes with PMA inner blocks. Finally, using thermal annealing to drive the rearrangement of the diblock copolymer brushes yielded films with much larger nanoscale surface roughness than seen for brushes rearranged with solvent. It is speculated that the irregular nanomorphology observed by AFM results from the strong ordering possible when annealing in the (tethered) melt state and the possible influence of chain length polydispersity and lateral grafting density nonuniformity.

References and Notes

(1) Granville, A. M.; Boyes, S. G.; Akgun, B.; Foster, M. D.; Brittain, W. J. *Macromolecules* **2004**, *37*, 2790.
(2) McCloskey, C. B.; Yip, C. M.; Santerre, J. P. *Macromolecules* **2002**, *35*, 924.
(3) Huang, W.; Kim, J.-B.; Bruening, M. L.; Baker, G. L. *Macromolecules* **2002**, *35*, 1175.
(4) Brantley, E. L.; Jennings, G. K. *Macromolecules* **2004**, *37*, 1476.
(5) Li, K.; Wu, P.; Han, Z. *Polymer* **2002**, *43*, 4079.
(6) Kassis, C. M.; Steehler, J. K.; Betts, D. E.; Guan, Z.; Romack, T. J.; DeSimone, J. M.; Linton, R. W. *Macromolecules* **1996**, *29*, 3247.
(7) Krupers, M.; Möller, M. *Macromol. Chem. Phys.* **1997**, *198*, 2163.
(8) van Krevelen, D. W. *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*; Elsevier Science: Amsterdam, 1976; pp 136−143.
(9) Su, W. Ph.D. Dissertation, University of Akron, 1991.
(10) Pees, B.; Sindt, M.; Paul, J. M.; Mieloszynski, J. L. *Eur. Polym. J.* **2002**, *38*, 921.
(11) Forrest, J. A.; Dalnoki-Veress, K. *Adv. Colloid Interface Sci.* **2001**, *94*, 167.
(12) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Faraday Discuss.* **1994**, *98*, 219.
(13) Prucker, O.; Christian, S.; Bock, H.; Rühe, J.; Frank, C. W.; Knoll, W. *Macromol. Chem. Phys.* **1998**, *199*, 1435.
(14) Yamamoto, S.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2002**, *35*, 6077.
(15) (a) Porter, C. E.; Blum, F. D. *Macromolecules* **2000**, *33*, 7016. (b) Porter, C. E.; Blum, F. D. *Macromolecules* **2002**, *35*, 7448.
(16) (a) Lin, W.; Blum, F. D. *Macromolecules* **1997**, *30*, 5331. (b) Lin, W.; Blum, F. D. *Macromolecules* **1998**, *31*, 4135.
(17) Lemieux, M.; Minko, S.; Usov, D.; Stamm, M.; Tsukruk, V. V. *Langmuir* **2003**, *19*, 6126.
(18) Hartmann, L.; Kremer, F.; Pouret, P.; Leger, L. *J. Chem. Phys.* **2003**, *118*, 6052.
(19) Tate, R. S.; Fryer, D. S.; Pasqualini, S.; Montague, M. F.; de Pablo, J. J.; Nealey, P. F. *J. Chem. Phys.* **2001**, *115*, 9982.
(20) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(21) Matsen, M. W. *J. Phys.: Condens. Matter* **2002**, *14*, R21.
(22) Foster, M. D.; Sikka, M.; Singh, N.; Bates, F. S.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys.* **1992**, *96*, 8605.
(23) Tidswell, I. M.; Rabedeau, T. A.; Pershan, P. S.; Kosowsky, S. D. *Phys. Rev. Lett.* **1991**, *66*, 2108.