Switching surface polarity: synthesis and characterization of a fluorinated block copolymer with surface-active *tert*-butoxycarbonyl groups

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ABSTRACT: The surface behavior of a series of block copolymers constructed from poly(styrene-*b*-semifluorinated side-chain modified isoprene) copolymer was evaluated. The semifluorinated side groups were attached in a post-polymerization step. The presence of *tert*-butoxy carbonyl end groups permitted conversion of the polymer surface from a non-polar hydrocarbon to a polar hydroxylated structure. The microstructure of these block copolymers was investigated using both electron microscopy and small-angle x-ray diffraction. The surface properties of the as-prepared polymer films were dominated by the fluorinated block and were found to be independent of the underlying block copolymer microstructure. After removal of the *tert*-butoxy carbonyl end groups, a disordered, polar surface was produced. The surface properties of these films were studied using contact angle measurements and other surface analysis techniques. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: surface polarity; fluorinated block copolymer; *tert*-butoxycarbonyl

INTRODUCTION

Tailoring the surface energy and functionality of polymer films has become increasingly important in a variety of technical applications. Possible uses include, for example, new biological and electronics technologies such as combinatorial chemistry, microelectromechanical system (MEMS) and high-density semiconductor microchips. Many of these applications require very specific surface properties including tailored adhesion, lubrication, wetting and adsorption behavior. Of particular recent interest, the ability to pattern and switch the chemical nature of a surface controllably is increasingly desirable. Efforts to accomplish this have included microcontact printing of self-assembled monolayers, growth of polymers from lithographically defined initiation sites and patterning of photoresists. One of the special challenges is in translating these capabilities from thin monolayer films to the surfaces of polymers. The chemistry usually associated with photolithography results in a polar function, thus a logical starting strategy would involve use of a non-polar, low surface energy material.

It is well known that some of the important factors in the behavior of low-energy surfaces include both the precise nature of the atoms populating a surface and their physical arrangement. Fluorinated polymers have particularly low-energy surfaces and have been successfully used as surface modifiers of the corresponding polymer films.[1] As reported in recent studies of semifluorinated polymers, it is possible to create a low-energy surface that has the additional feature of surface stability. In such semifluorinated polymers, the surface exhibits a low critical surface energy (ca 8 mN m^{-1}) and a high water contact angle (ca 120°/advancing, 110°/receding). A remarkable resistance to surface reconstruction has also been observed for these polymers when exposed to a polar liquid such as water.[2] Such behavior may be important in applications involving non-biofouling or biocompatibility issues. The detailed synthesis and structure of low molar mass semifluorinated materials was first reported by Rabolt *et al.*[3] in 1984 where the mesogenic character of short CF$_2$ segments was recognized. There have been only a few studies of semifluorinated polymers with liquid crystal (LC) character. Beyou *et al.*[4] reported the synthesis and low surface energy character of semifluorinated LC polysiloxanes made via

hydrosilylation of poly(hydromethylsiloxane) and a semifluorinated LC vinyl compound. Semifluorinated methacrylate and acrylate polymers have been studied by Krupers and Möller.[5] All structures have in common low surface energies, as demonstrated by advancing water contact angles in the region of 120°.

On the other hand, polar polymer surfaces possessing polar functional groups such as the hydroxyl, carboxyl or amino groups are widely utilized for many applications including biocompatible materials for the introduction of biologically active surfaces, surfaces that resist protein absorption and sensor molecules for molecular recognition.[1] However, in general, it is difficult to create a polar surface which is composed of a large number of polar groups because any non-polar groups in the polymer must be masked at the air–solid (film) interface to produce a low energy thermodynamically stable surface. Therefore new materials must be developed to create a surface consisting of polar functional groups and simultaneously to control surface stability.

In this study, we examined a new approach for controlling both surface energy and functionality using a photoinduced surface polarity change. The basis of these new materials is the combination of the surface segregation behavior of a block copolymer with semi-fluorinated side-chains, and the use of chemically amplified chemistry for the deprotection of masked hydroxyl groups on the semifluorinated side-chains at a polymer surface. These semifluorinated block copolymers with removable protecting groups offer a number of possible advantages. The semifluorinated polymer blocks mask the underlying polymer structure while the non-polar *tert*-butoxycarbonyl (t-BOC) protecting groups hide the hydroxyl end groups of the semifluorinated side-chains. The surface polarity can be rapidly switched from a hydrophobic surface made up of the protected fluorinated component to a hydrophilic surface after removal of the protecting groups in the film during photoprocessing. A small amount of a fluorinated polymer can also be added to a corresponding homo-polymer and the resulting blend can have dramatically low surface energy properties. In studies of the molecular nature of such polymer blends using techniques such as near-edge x-ray absorption fine structure (NEXAFS), it has been shown that the surface is made up of the fluorinated component to the extent that the other component in these block copolymers is excluded from the surface region.

In this paper, we describe the synthesis and characterization of poly(styrene-*b*-semifluorinated iso-prene) block copolymers with t-BOC end groups and the deprotection of the t-BOC group in the solid state using photoassisted cleavage by means of a photoacid generator. The characterization of the polymer film was carried out with measurements of transmission electron microscopy (TEM) and small-angle x-ray scattering (SAXS). The surface polarity change was
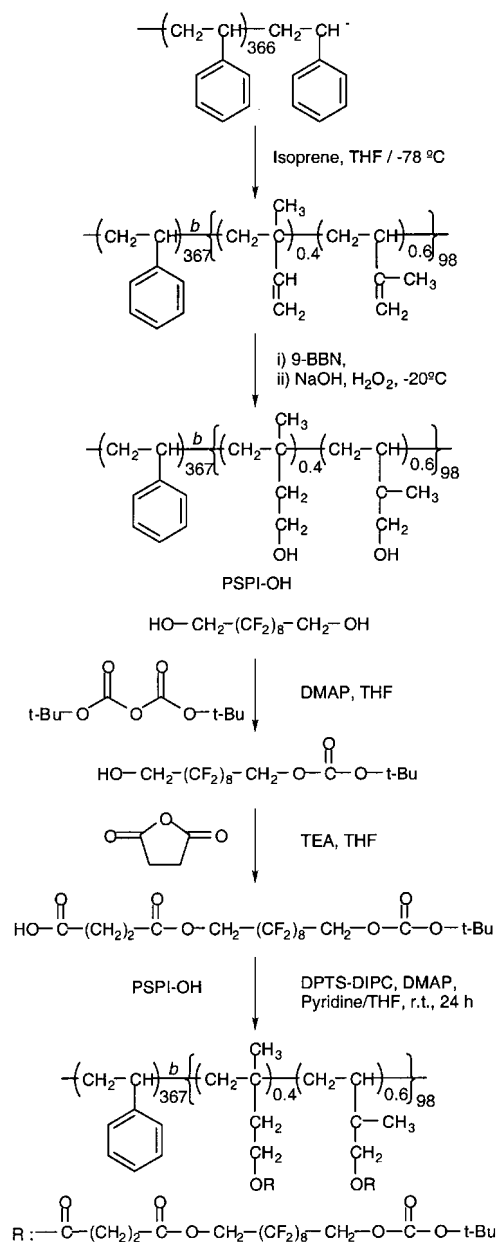

Scheme 1

investigated using both water contact angle and NEXAFS measurements.

RESULTS AND DISCUSSION

Block copolymers with fluorinated blocks have been used for a variety of applications largely focused on surface modification. In addition to these studies, such materials have been used recently as surfactants in supercritical CO_2[6] owing to their unusual character as a micelle-forming amphiphile in non-polar solvents.[7] Many approaches exist for the incorporation of fluorinated blocks, but they generally involve either the living
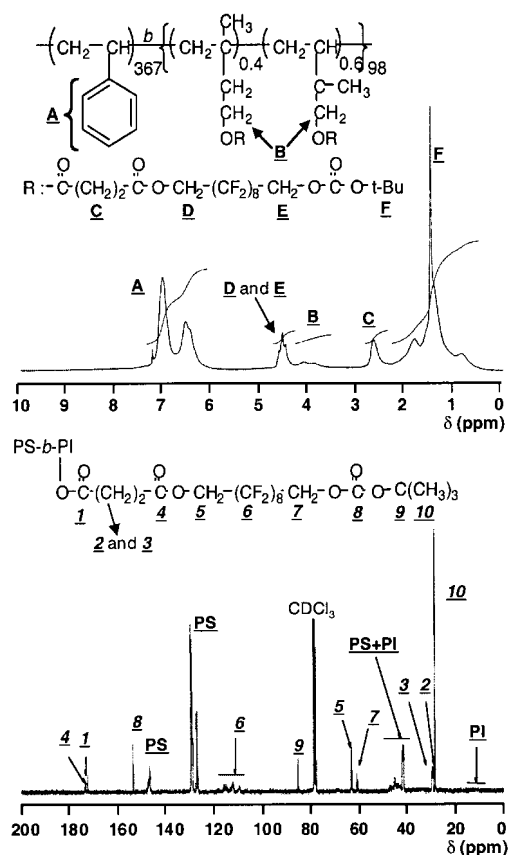
Figure 1. ^{1}H and ^{13}C NMR spectra of poly(styrene-*b*-semifluorinated side-chain modified isoprene) block copolymer in CDCl$_3$

polymerization of fluorinated monomers, largely acrylates,[7,8] or the modification of block copolymers prepared by anionic polymerization.[2,9,10] Recently, a new family of polymers was described using a mild direct fluorination reaction,[9] but most other examples involve the attachment of readily available fluorinated acids[2,11] as described in this paper.

Synthesis

The synthetic procedure for the preparation of poly(-styrene-*b*-semifluorinated side-chain) block copolymer with t-BOC terminal groups is illustrated in Scheme 1. The anionic polymerization of the poly(styrene-*b*-isoprene) block copolymer has been reported previously.[2] The semifluorinated (SF) acid side group with a t-BOC terminus was prepared by a straightforward synthesis. In the reaction, one of the hydroxy groups of an SF diol was protected with di-*tert*-butyl dicarbonate, and the other hydroxy group was then esterified with succinic anhydride. The hydrocarbon segment provided by the succinic anhydride served both as spacer and to improve the

solubility of the resulting SF acid that was obtained in good yield.

Esterification reactions using acid chlorides are known to be clean and efficient reactions. Such chemistry has been used previously for the effective attachment of fluorinated mesogenic groups to a polymer backbone.[2] However, when acid chlorides are prepared using a typical chlorinating agent such as thionyl chloride, hydrochloric acid is produced *in situ*. In our case, the acid chloride could not be synthesized from the t-BOC-protected SF acid because of its acid-labile nature. Condensing reagents such as carbodiimide are also useful for esterification reactions under mild conditions.[10,12–15] Therefore, we examined three different condensing reagents, 1,3-diisopropylcarbodiimide (DIPC), 1,3-dicyclohexylcarbodiimide (DCC) and 1,1′-carbonyldiimidazole (CDI), for the esterification reaction. In the case of DCC and CDI, the attachment yields were ∼65% as determined by ^{1}H NMR measurements. In contrast, when DIPC was used, the esterification reaction was much more efficient. It could be seen from IR spectroscopy that the hydroxy absorption peak of the hydroxylated poly(styrene-*b*-isoprene) was essentially eliminated in the modified polymer, thus indicating a high degree of SF group attachment. Three absorption peaks due to carbonyl groups appeared between 1740 and 1760 cm^{-1}. The peaks at 1740 and 1755 cm^{-1} are due to the ester group which links the SF segment to the polymer backbone and the ester group located in the middle of the SF segment, respectively. The absorption peak at 1760 cm^{-1} is instead due to the t-BOC carbonyl group.

The most conclusive spectroscopic evidence for successful preparation of the target block copolymer was provided by NMR spectroscopy; the ^{1}H and ^{13}C NMR spectra are shown in Fig. 1 together with assignments of the observed resonances. In the ^{1}H NMR spectrum, the proton signals of both methylene groups adjacent to the fluoromethylene groups appear at ∼4.55 ppm. The methylene proton signals resulting from the succinic anhydride group appeared at 2.66 ppm. In the ^{13}C NMR spectrum, three carbonyl signals were observed at 152.3, 171.0 and 171.9 ppm and are due to the t-BOC group and the two ester groups, respectively. The methylene groups that lie adjacent to the perfluoromethylene groups have signals that appear at 59.8 and 62.0 ppm as triplets due to coupling with fluorine. The extent of attachment of the SF acid to the hydroxylated poly(styrene-*b*-isoprene) was calculated to be 87% by using the integrated ratios of the methylene proton signals of the SF block and benzene ring proton signal of the polystyrene block. These observations support the formation of the expected block copolymer.

The thermal behavior of the block copolymer was examined by thermogravimetric analysis (TGA), the plot of which is shown in Fig. 2. The thermal stability of the polymers can be used to provide an assessment of the t-
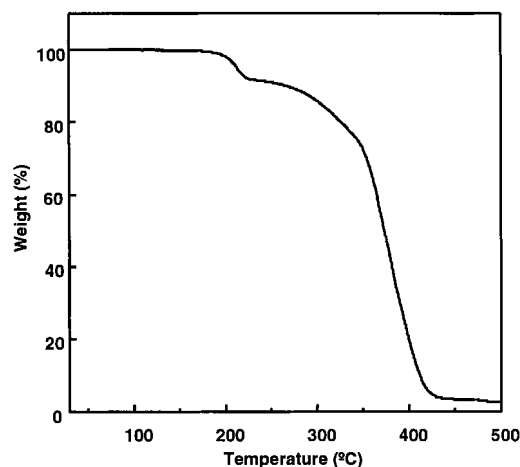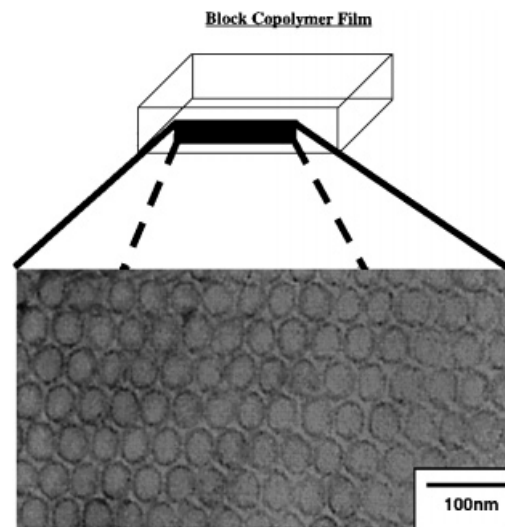
Figure 2. TGA of the thermal elimination of t-BOC protecting groups from the semifluorinated side group


Figure 3. TEM study of the cylinder microstructure of the block copolymer. The starting polymer had a lamellar microstructure, but after attachment of the large SF side groups, a cylinder microstructure was formed

BOC content of the modified polymer. The TGA curve shows that the block copolymer is thermally stable until $\sim175\,°C$. The weight loss due to the t-BOC groups begins at $175\,°C$ and continues until $\sim220\,°C$ in a nitrogen environment at a heating rate $10\,°C\ min^{-1}$. The weight loss above $220\,°C$ is 9.1%, which is in reasonable agreement with the expected value (8.4%) for t-BOC cleavage. After decomposition of the t-BOC group, further weight loss of the block copolymer gradually occurred at $\sim460\,°C$.

In order to eliminate the effect of thermal history on sample transitions, the sample was first heated to $160\,°C$, which is about $60\,°C$ above the glass transition of the polystyrene block, and held at this temperature for 1 min, before cooling to $-65\,°C$ at a rate of $10\,°C\ min^{-1}$. Two transitions were observed at 59.8 and $100.2\,°C$ in the block copolymer. The former transition is the glass transition of the SF modified block and the latter is due to the glass transition of the polystyrene block. A DSC cooling run also showed that these transitions were reversible. No evidence for LC behavior was observed in these block copolymers despite the similarity in structure to earlier SF polymers. Evidently the large t-BOC group prevented the formation of a mesophase.

The solid-state morphology of the block copolymer was studied by SAXS and TEM. Samples were prepared by solvent casting using a 5 wt% propylene glycol methyl ether acetate (PGMEA) solution. It should be noted that PGMEA was selected for the preparation of cast films because it was also used when spin-casting films for studies of t-BOC deprotection of films by chemically amplified chemistry. As shown in Fig. 3, the TEM image of the block copolymer with t-BOC end groups revealed a microphase-separated hexagonally packed cylinder morphology. The cylinder structure of the polystyrene domains appeared as a dark ring because of preferential staining by RuO_4 along the microdomain interface. This observation has been made before in materials where

diffusion of the stain occurs fastest along the micro-domain interface; thus we do not believe that it is due to aggregation of unreacted isoprene at the interface region. Thus, the remaining regions were identified as the semifluorinated side-chain modified isoprene domains. In the SAXS patterns of the modified block copolymer shown in Fig. 4, diffracted arcs in the small angle region were measured in the film edge direction and are consistent with a hexagonal cylinder structure. Scattering maxima were separately observed at 333, 372 and 440 Å from two sides of a cut sample perpendicular to the aligned cylinders [Fig. 4(a) and (c)] and these spacings are consistent with a hexagonal microstructure, in very good agreement with the TEM results.

Deprotection of the t-BOC groups

The photoacid-cleavable t-BOC group was chosen for protecting the terminal hydroxy function on the SF segment, because the chemistry of polarity change following t-BOC deprotection is the basis of many chemically amplified photoresists.[16] By using a t-BOC protecting group, the surface of the film is initially hydrophobic before exposure. After UV exposure in the presence of a photoacid generator, the surface becomes more hydrophilic owing to a change in the surface functionality to a hydroxy group. Combining these concepts, we sought to produce a new material which when processed into a low surface energy film, formed a material with a spontaneously organized surface having the mechanical robustness of a polymer film, and which could be lithographically patterned into a polar surface.
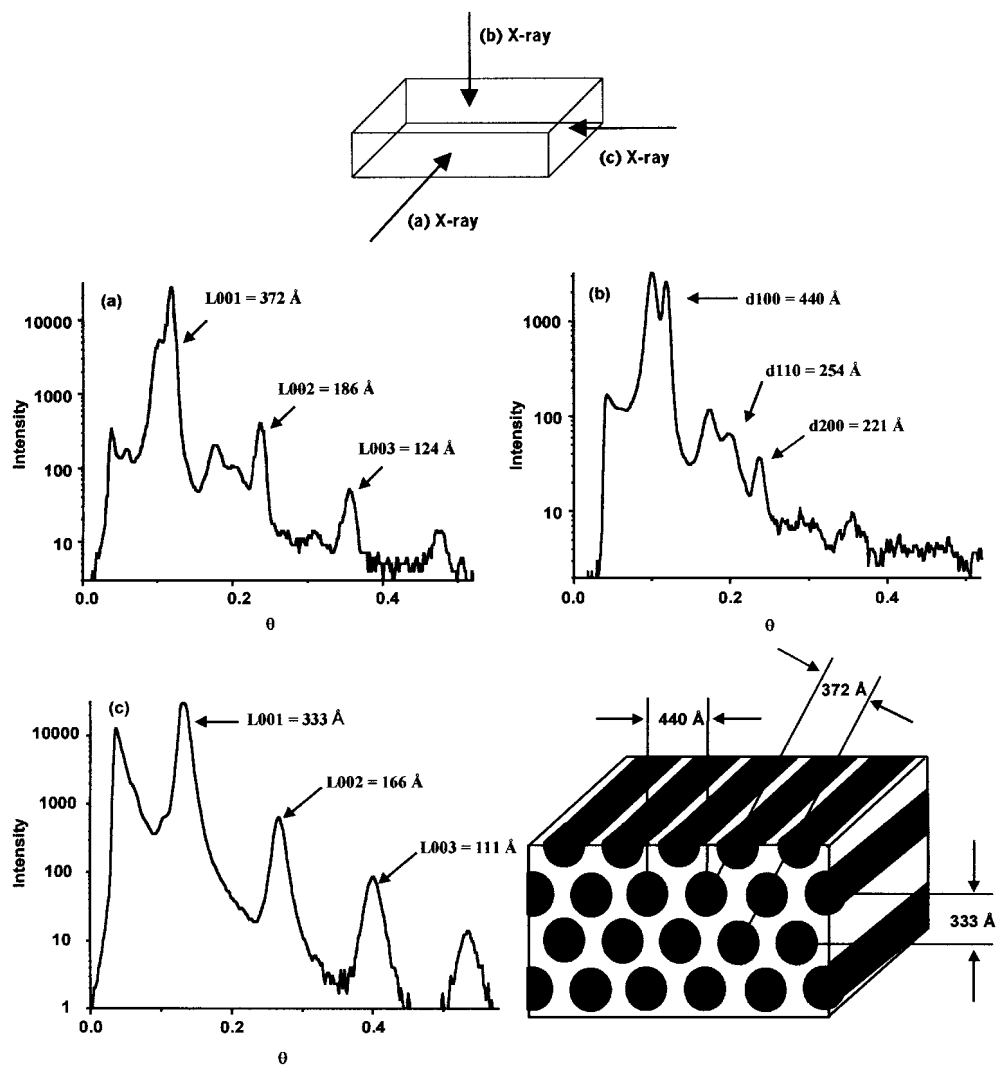
Figure 4. SAXS patterns of an aligned section of the semifluorinated block copolymer prior to removal of the t-BOC groups. (a, b) SAXS pattern from side of oriented section perpendicular to cylinders. (c) SAXS pattern with x-ray beam parallel to oriented cylinder direction

Both thermal and acid-catalyzed approaches can be used to remove the t-BOC masking groups on the hydroxylated semifluorinated segment. The deprotection of the t-BOC groups on the SF block copolymer film was examined using an acid-catalyzed cleavage reaction. Acid catalysis enables the use of a much lower heat treatment temperature and can be coupled to direct photopatterning provided that photoacid generators are the source of the acid. The expected t-BOC deprotection by a photochemically generated acid on the film surface is shown in Scheme 2. Cleavage of surface t-BOC groups provides a direct polarity switch by changing the surface groups from a methyl function of the t-BOC group to a hydroxy group after deprotection. Polymer films containing 8 wt% of bis(*tert*-butylphenyl)iodonium triflate (TBIT), a photoacid generator, were annealed at 120 °C for 60 s to remove the casting solvent, exposed to deep-UV light at 254 nm and subsequently annealed at 120 °C

for 60 s. In order to investigate the wetting behavior of the films, water contact angle measurements were used. The water contact angles of annealed and exposed films are listed in Table 1. Before exposure, films were prepared with 8 wt% TBIT and shown to have a contact angle of $\sim 100°$. This value is consistent with a very hydrophobic hydrocarbon surface populated with methyl groups, but would be inconsistent with either styrene or a fluorinated material. The advancing water contact angle of the polymer film exposed to a very low UV dose $(2.1 \, \text{mJ cm}^{-2})$ was still above 90° and again demonstrated a hydrophobic surface. However, on increasing the UV exposure dose, the advancing and receding water contact angles before and after UV exposure decreased by 14° and 15°, respectively. These lower contact angles indicate a more hydrophilic surface with increased polarity because of the change in surface chemistry from a methyl to a hydroxy group. In order to create a more

Table 1. Water contact angles of unexposed and exposed poly(styrene-*b*-semifluorinated modified isoprene) block copolymer films with t-BOC end groups

| Sample[a]	Water contact angle	Dose (mJ cm^{-2})			
		0.0	2.1	8.5	63.9
Annealed[b]	Advancing	101	83	79	75
	Receding	89	76	73	67

[a] All samples were prepared by spin coating with 5 wt% PGMEA solution on a silicon wafer.
[b] Annealing carried out at 120 °C for 3 days.

ordered surface of the type that has non-reconstructing character, the polymer films were annealed at 120 °C for 3 days and examined under the identical conditions. The advancing and receding water contact angles of the annealed film before UV exposure were only 3° and 1° higher, respectively, than for the unannealed film. However, the advancing and receding contact angles of the UV exposed (63.9 mJ cm^{-2}) and annealed films are 9° and 6°, respectively, less than the exposed unannealed films at the same dose. Comparing the contact angles of the unannealed films with annealed films after UV exposure, the annealed surfaces have a much more hydrophilic surface. This is expected since organization of the SF side-chains can occur during annealing and produce more highly ordered structures in the solid state.

Scheme 2
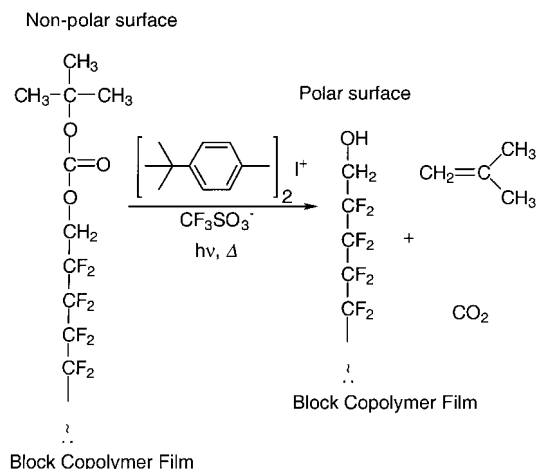
In order to examine the deprotection efficiency of the t-BOC groups, both the unexposed and UV exposed films of the polymer were investigated by Fourier transform (FT) IR spectroscopy [Fig. 5(a) and (b)]. The IR spectra before and after UV exposure are otherwise identical, except for regions associated with the carbonyl and hydroxy bands. The carbonyl bands of the polymer film had three distinct peaks, as discussed earlier. The observed peak absorbance before and after UV exposure
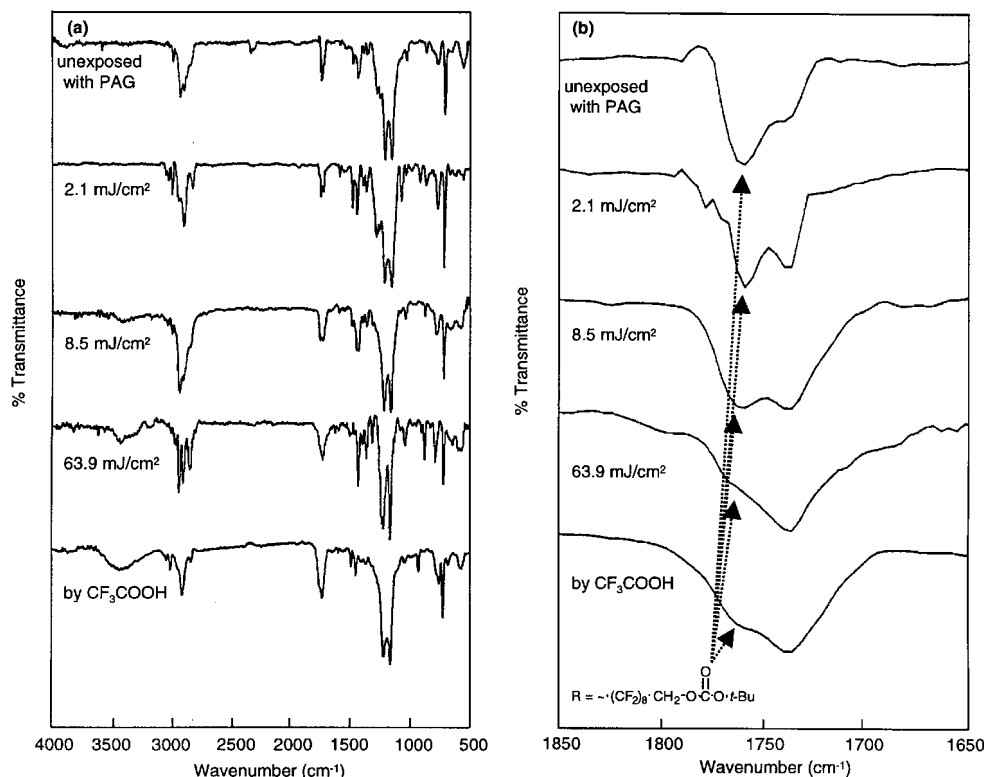
Figure 5. FTIR spectra as a function of exposure dose showing (a) entire spectral range and (b) region adjacent to carbonyl bands. For comparison, the spectrum of a sample deprotected using trifluoroacetic acid is also included

(dose = 63.9 mJ cm^{-2}) changed significantly in this region. The peak at 1760 cm^{-1} gradually decreased as the UV dose was increased [Fig. 5(b)], with no change in the other two ester carbonyl peaks. The absorbance at ~3400 cm^{-1} increased with increasing UV exposure dose. The t-BOC function of the SF side-chain was efficiently cleaved to form hydroxy groups by the deprotection reaction, as indicated by the strong absorbance at this wavenumber. Furthermore, the IR spectrum after UV exposure at 63.9 mJ cm^{-2} was in very good agreement with the IR spectrum of the fully t-BOC deprotected block copolymer which was obtained using deprotection by trifluoroacetic acid solution at room temperature for 1 h.

In addition to water contact angle measurements of the film surface, NEXAFS measurements were carried out for these polymers prior to and after UV exposure. This method can provide information about both surface composition and surface orientation.[17] This technique has been used previously to study non-reconstructing semifluorinated surfaces that gain their stability from the presence of LC forming structures on the polymer surface. NEXAFS has revealed previously that the SF groups were strongly oriented nearly normal to the surface in polymers with single and monodendron sidegroups.[18] The order on the surface was associated with enhanced surface stability in polar environments. One objective, therefore, of constructing the surface groups from semifluorinated segments was the goal of simultaneous high surface population and the introduction of the stability caused by the formation of an ordered phase. The presence of fluorine in the surface region was clearly demonstrated by the NEXAFS measurements. However, in neither case was there any evidence for surface order and orientation. This is consistent with thermal measurements that revealed no mesophase in either the protected or deprotected polymer with SF side groups. Thus the presence of both bulky, non-polar t-BOC groups prevented the formation of an ordered phase while their removal and the introduction of a polar hydroxy group to the SF function also inhibited formation of an LC phase. The consequence of this approach is that neither surface provides for temporal stability. The creation of new patternable structures that take these observations into consideration is now under way.

EXPERIMENTAL

Materials. 1H,1H,10H,10H-Perfluoro-1,10-decanediol (96%, Lancaster Synthesis), di-*tert*-butyl dicarbonate (99%, Aldrich), triethylamine (99%, Aldrich), pyridine (99.8%, Aldrich) and propylene glycol methyl ether acetate (PGMEA) (99%, Aldrich) were used as received. 1,3-Diisopropylcarbodiimide (99%, Aldrich) was used after purification by distillation under vacuum. Succinic anhydride (99 + %, Aldrich) was purified by recrystalli-

zation from chloroform. 4-(Dimethylamino)pyridine (99%, Aldrich) was recrystallized from benzene. 4-(Dimethylamino)pyridinium 4-toluenesulfonate was prepared by reaction of hydrated *p*-toluenesulfonic acid with 4-(dimethylamino)pyridine and used after purification by recrystallization from dichloromethane.[14] Tetrahydrofuran (THF)(Fisher) was distilled from sodium benzophenone ketyl under nitrogen. Hydroxylated poly(styrene-*b*-isoprene) block copolymer was synthesized by hydroboration of monodisperse poly(styrene-*b*-isoprene) block copolymer having a 1,2- and 3,4-polyisoprene content >97%.[2,19]

1H,1H,10H,10H-Perfluoro-1-tert-butoxycarbonyloxy-10-decanol. The t-BOC-protected SF monofunctional alcohol was synthesized by reaction of 1H,1H,10H,10H-perfluoro-1,10-decanediol with di-*tert*-butyl dicarbonate. To a single-necked round-bottomed 50 ml flask equipped with a nitrogen inlet and magnetic stirrer, the fluorinated diol (9.24 g, 20.0 mmol), the di-*tert*-butyl carbonate (1.74 g, 8.00 mmol) and dry THF (20 ml) were added under a nitrogen atmosphere. The mixture was stirred for 5 min while cooling at 0–5 °C and then a catalytic amount of 4-(dimethylamino)pyridine (61.0 mg, 0.500 mmol) was added to the mixture at this temperature. The reactor was then slowly warmed to room temperature and held at this temperature for 2 h. After the reaction, THF was evaporated. Column chromatography of the residue on silica gel with an eluent solvent mixture of *n*-hexane–dichloromethane (1:2) gave a colorless liquid (3.64 g, 6.47 mmol, 81%). IR (NaCl), ν (cm^{-1}) 3480 (O—H, st), 2990, 2920, 2880 (C—H, st), 1760 (C=O, st), 1210, 1150 (C—F, st). ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm) 1.49 (s, CH$_3$, 9H), 2.32 (t, J = 7.0 Hz, OH, 1H), 4.07 (tt, J = 7.0 Hz, J = 13.6 Hz, CH$_2$, 2H), 4.55 (t, J = 13.7 Hz, CH$_2$, 2H).

3-{(1H,1H,10H,10H-Perfluoro-1-tert-butoxycarbonyl-oxy-10-carbonyloxydecane)}propionic acid. To a one-necked round-bottomed 50 ml flask equipped with a nitrogen inlet and magnetic stirrer, 1H,1H,10H,10H-perfluoro-1-*tert*-butoxycarbonyloxy-10-decanol (3.37 g, 6.00 mmol), succinic anhydride (0.600 g, 6.00 mmol) and dry THF (5 ml) were added and dissolved at room temperature. One drop of triethylamine was added to the mixture with a syringe and the mixture was stirred for 2 h at this temperature. After the reaction, THF was evaporated. The residue was recrystallized from *n*-hexane to give a white solid. Yield 3.64 g (5.49 mmol, 92%). M.p. 54.5–55.5 °C. IR (KBr), ν (cm^{-1}) 3370–2600 (O—H, st), 2980, 2940 (C—H, st), 1760, 1755, 1700 (C=O, st), 1210, 1150 (C—F, st). ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm) 1.49 (s, CH$_3$, 9H), 2.73 (s, CH$_2$, 4H), 4.55 (t, J = 13.7 Hz, CH$_2$, 2H), 4.61 (t, J = 13.5 Hz, CH$_2$, 2H).

Synthesis of poly(styrene-b-semifluorinated side-chain modified isoprene) block copolymer with tert-butoxy-carbonyl end groups. To a one-necked round-bottomed 10 ml flask containing a stir bar, the SF acid (0.543 g, 0.821 mmol), pyridine (0.5 ml) and THF (2 ml) were added under a nitrogen atmosphere. After the acid had dissolved, 1,3-diisopropylcarbodiimide (0.103 g, 0.821 mmol), 4-(dimethylamino)pyridine (0.100 g, 0.821 mmol) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (0.241 g, 0.821 mmol) were added to the flask. After the mixture had been stirred for 1 h at room temperature, the solution turned purple. The hydroxylated block copolymer (300 mg, 0.632 mmol/OH) was dissolved in THF (3 ml), and the resulting solution was injected slowly into the reaction flask through a rubber septum. The reaction was maintained at room temperature for 24 h. Once the reaction was complete, the solution was poured into methanol–water (1:1). The resulting product was collected, washed with methanol–water and dissolved in THF, and then the solution poured into methanol–water (1:1) five times and into methanol twice to remove excess SF acid and urea side product. The modified polymer was collected, washed with methanol and dried *in vacuo* at 50 °C for 24 h. Yield 0.586 g (89%). IR (KBr), ν (cm^{-1}) 2980, 2940 (C— H, st), 1760, 1755, 1740 (C=O, st), 1600, 1500 (benzene, st), 1210, 1150 (C— F, st). ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm) 0.79-2.47 (br, CH$_3$, CH$_2$), 1.49 (s, CH$_3$, 9H), 2.66 (br, CH$_2$, 4H), 3.89–4.13 (br, CH$_2$, 4H), 4.55 (br, CH$_2$, 4H), 6.5–7.26 (br, benzene, 5H). ^{13}C NMR (100.12 MHz, CDCl$_3$), δ (ppm) 13.5, 27.6, 28.6, 28.8, 33.0, 40.7, 40.9, 42.9, 44.2, 46.0, 59.5, 59.8, 60.0, 61.7, 62.0, 62.2, 84.1, 108.5, 111.1, 112.0, 113.8, 114.3, 114.6, 114.8, 117.2, 125.7, 125.8, 127.5, 127.6, 127.9, 128.1, 128.4, 145.4, 145.9, 146.3, 152.3, 171.0, 171.9.

Removal of t-BOC groups by Acid hydrolysis. The block copolymer (20 mg, 0.0168 mmol/t-BOC) was dissolved at room temperature in THF (2 ml) in a single-necked round-bottomed 20 ml flask equipped with a nitrogen inlet and magnetic stirrer. Trifluoroacetic acid (1 ml) was injected into the flask and the reaction was maintained at room temperature for 1 h. After the reaction, the solution was poured into water (20 ml). The product was collected, washed with water and methanol and dried. Yield 17 mg (94%). IR (KBr), ν (cm^{-1}) 3400, (O— H, st), 2980, 2940 (C— H, st), 1755, 1740 (C=O, st), 1600, 1500 (benzene, st), 1210, 1150 (C— F, st). ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm) 0.79–2.47 (br, CH$_3$, CH$_2$), 2.66 (br, CH$_2$, 4H), 3.89–4.13 (br, CH$_2$, 4H), 4.05 (br, CH$_2$, 2H), 4.55 (br, CH$_2$, 2H), 6.5–7.26 (br, benzene, 5H).

Removal of t-BOC groups by chemically amplified chemistry. Solutions of the block copolymer were prepared by dissolving 5 wt% of the polymer in PGMEA. Approximately 8 wt% (with respect to the polymer) of TBIT, as photoacid generator (PAG), was added to the polymer solution. The solution was then filtered using a 0.2 μm pore size Teflon filter. Films of the polymer were made by manually dispensing the solution on to a silicon wafer, followed by spinning for 60 s at ca 2000 rpm. The samples were then baked at 120 °C for 60 s. Exposures were performed using an HTG contact aligner with a mercury arc lamp. Special mirror sets were used to obtain broadband illumination from 235 to 260 nm with an intensity of ∼3.5 mW cm^{-2} at 254 nm. The wafers were flood exposed for varying lengths of time (0.5, 2 and 15 s) to obtain different exposure doses. The exposed wafers were then baked at 120 °C for 60 s to effect the acid cleavage of the t-BOC groups by chemical amplification.

Physical characterization. Infrared spectra were measured using a Mattson 2020 Galaxy series Fourier transform infrared spectrometer with 4 cm^{-1} resolution using 64 scans. Samples were pressed in a KBr tablet or cast on an NaCl crystal plate.

^{1}H NMR spectra were obtained on a Varian 200 spectrometer at 200 MHz. The carbon spectrum was measured on a Varian FX-400 instrument at ^{13}C 100.12 MHz. Deuterated chloroform was used as the solvent.

Gel permeation chromatography (GPC) was carried out using four Waters Styragel HT columns operating at 31 °C. The effective molecular weight range of the columns is from 500 to 10^7. GPC data were collected by a Waters 490 programmable multi-wavelength detector. Molecular weights are quoted with respect to monodisperse polystyrene standards. THF was used as solvent and the GPC operated at 0.3 ml min^{-1}. Block copolymer was dissolved in THF at a concentration of 3.0 mg ml^{-1}. A polymer solution volume of 20 μl was used for GPC measurements.

Thermogravimetric analysis (TGA) measurement was performed on a Perkin-Elmer TGA-7 Series instrument. A sample of ca 5 mg was analyzed using a 10 °C min^{-1} heating and cooling rate. Nitrogen was used as purge gas at a flow-rate of 40 ml min^{-1}.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 Series instrument. Samples of ca 10 mg were analyzed using a 10 °C min^{-1} heating and cooling rate. Nitrogen was used as purge gas at a flow-rate of 40 ml min^{-1}.

Contact angles were determined using an NRL Contact Angle Goniometer Model 100-00 (Ramé-Hart) at 20 °C. Films were prepared by spin coating a 5 wt% block copolymer–PGMEA solution on a silicon wafer at room temperature. The contact angles were averaged over five measurements. The advancing contact angles were read by injecting 4 μl liquid drops. The receding contact angles were measured by removing 3 μl of liquid from the droplet while the static contact angles were obtained using a free drop of liquid (ca 4 μl) on the film surface.

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