Selective Alteration of Polymer Surfaces by Thermal Cleavage of Fluorinated Side Chains

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ABSTRACT: We have synthesized a series of fluorinated side chain block copolymers based on either a hydroborated polystyrene-*b*-polyisoprene or a poly(methyl methacrylate)-*b*-poly(2-hydroxyethyl methacrylate) backbone. Through polymer-analogous reactions, perfluorinated ester, fluorinated urethane, and fluorinated carbonate side chains were attached to the pendant hydroxyl groups. Their selective thermal degradation behavior was investigated using thermogravimetric analysis (TGA) and thermal desorption mass spectrometry (TDMS). In addition, we investigated the heat- and laser-induced selective alteration of polymer film surfaces by chemically highly selective cleavage of the fluorinated side chains using X-ray photoelectron spectroscopy (XPS), FT-infrared spectroscopy (FT-IR), and contact angle measurements. Finally, we demonstrate the potential to create a laterally patterned surface with different regions of chemically well-defined surface moieties from our fluorinated block copolymers by a "dry" laser process.

Introduction

The low surface energy of fluorinated polymers¹⁻⁴ allows for controlled alteration of surface properties of coatings or polymer blends. Upon blending a fluorinated polymer with another miscible component, the surface composition of the mixture is dominated by fluorinated groups due to their low surface energy leading to highly hydro- and oleophobic surfaces.⁵⁻⁷

Recently,8 we have developed polymers with fluorinated side chains, i.e., perfluorinated groups, in order to produce extremely low-energy surfaces. Furthermore, we have demonstrated that upon thermal treatment the fluorinated side chains can be cleaved selectively using a well-known ester pyrolysis reaction.⁹ The absence of fluorinated side chains at a polymer surface leads to a substantial increase of the surface energy, resulting in significantly different wetting properties compared to an untreated fluorine-rich surface. Since the thermal cleavage can be carried out locally, such fluorinated side chain polymers can be used to create chemically defined hydrophobic/hydrophilic patterns on surfaces. These properties may favorably support applications of surface patterning, e.g., printing or the preparation of microsample arrays. In addition, defined chemically structured surfaces can be formed which allow the study of wetting phenomena on chemically heterogeneous surfaces.^{10,11} Furthermore, well-defined laterally patterned surfaces are important for a variety of technological applications, e.g., as compatibilizers for polymer blends or as templates for growing biological cells with controlled shapes and sizes.12

The aim of our present study is to investigate the temperature dependence of the cleavage of different side chains in our polymers on their chemical nature. As

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shown previously, there is a significant difference in the selective side chain cleavage if one compares hydrocarbon ester side groups to perfluorocarbon ester side chains.⁸ Through incorporation of urethane and carbonate functionalities, which are supposed to decompose earlier than an ester linkage,^{13–15} we are searching for ways to lower the selective decomposition temperature.

Furthermore, we shall describe the possibility to create a laterally patterned surface with different chemically well-defined regions from our fluorinated block copolymers. These patterns can be produced from a "dry" laser treatment only, thus avoiding any wet or vapor chemical process to produce lateral patterns with well-defined surface moieties. However, a local posttreatment by a wet chemical surface reaction is greatly assisted by the fact that regions with different chemical moieties are also very different in hydrophobicity. Thus, our laser patterned surfaces can be used as templates to produce a variety of controlled chemically heterogeneous surfaces.

Experimental Section

The acronyms of the polymers are chosen according to a previous publication;⁸ i.e., SI-46/11 represents a block copolymer with a molecular weight of 46 kg/mol of the polystyrene (S) block and 11 kg/mol of the polyisoprene (I) block. Similarly, MH-26/5 denotes a poly(methyl methacrylate) block (M) of 26 kg/mol and a poly(2-hydroxyethyl methacrylate) (H) block of 5 kg/mol. Unless noted, all chemicals used in this work were purchased from Aldrich and used without further purification.

Synthesis of Hydroxylated Polystyrene-*b***-polyiso-prene Block Copolymers.** The polystyrene-*b*-polyisoprene block copolymers used in this study were synthesized as reported previously.⁸ Their composition is shown in Table 1. After hydroboration of the polyisoprene block the pendant hydroxyl groups were reacted with fluorinated isocyanates, a fluorinated chlorocarbonate, and perfluorinated carboxylic acid chlorides, yielding urethane, carbonate, and ester side groups, respectively.

Urethane Side Chains (URF1). The urethane side chains were introduced by reaction of the alcohol groups of the hydroxylated isoprene block with a fluorinated isocyanate as shown in Scheme 1. Care has to be taken in order to eliminate

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Table 1. Synthesized Polymers with Polystyrene-b-polyisoprene (SI) Backbone

polymen $(1.5.1.7)$ $(1.5.1.71)$ [kg/mol] muoninateu block $M_W(GLC)$ [kg/	morj poryuispersity
SI-26/7 250:100 25.9:6.9 21.2 35.2	1.02
SI-26/7-H1 ^c 25.9:11.1 30.0 39.4	1.03
SI-26/7-F3 25.9:28.2 52.1 41.7	1.03
SI-26/7-F7 25.9:48.2 65.0 micelle: 36 an	d 560 each monodisperse
SI-26/7-F8 25.9:53.2 67.3 micelle: 33 an	d 250 each monodisperse
SI-26/7-URF1 25.9:27.3 51.3 97.9 ^d	1.27 ^b
SI-46/11 440:160 45.6:10.8 19.2 63.6	1.03
SI-46/11-H1 ^c 45.6:20.2 30.7 65.3	1.03
SI-46/11-F3 45.6:44.8 49.6 63.7	1.05
SI-46/11-F7 45.6:76.8 62.7 a	
SI-46/11-F8 45.6:84.8 65.0 a	
SI-46/11-URF1 45.6:43.4 48.8 226.6 ^d	1.48^{b}
SI-46/11-OCOH1F2 45.6:44.6 49.4 67.8	1.05
SI-66/19 640:280 65.9:18.7 22.1 92.5	1.03
SI-66/19-H1 ^c 65.9:35.2 34.8 95.2	1.02
SI-66/19-URF1 65.9:75.8 53.5 503.7 ^d	1.65^{b}
SI-66/19-F3 65.9:78.3 54.3 a	
SI-66/19-F7 65.9:134.3 67.1 a	
SI-66/19-F8 65.9:148.3 69.2 a	

^{*a*} No signal could be detected by GPC. ^{*b*} Tailing due to extended interaction with column. ^{*c*} Acetylated after hydroboration to improve solubility. ^{*d*} PSS GR_AM columns, high molecular weight due to aggregation. Side chains: F3 = perfluorobutyryl, F7 = perfluoroctanoyl, F8 = perfluorononanoyl, H1 = acetyl, URF1 = α,α,α -trifluoro-*p*-toluyl, OCOH1F2 = fluorinated carbonate.





side reactions like allophanate formation by reaction of isocyanate with the urethane group. Therefore, only a slight (5%) excess of isocyanate is used for this reaction. In addition, considerable care has been taken to keep the reaction media moisture-free to avoid Hofmann degradation of the isocyanate to the corresponding amine, which would lead to urea formation and a reduced yield due to the higher nucleophilicity of the amine compared to that of the alcohol.

0.5 g (1.42 mmol of -OH) of SI-46/11-OH are dissolved in 15 mL of freshly distilled THF (refluxed over potassium for at least 3 days) in a nitrogen atmosphere and 0.22 mL of α, α, α trifluoro-*p*-toluyl isocyanate (ρ 1.31 g/mL, M_w 187.12 g/mol, 5% excess) were added at room temperature, and the reaction mixture was slowly heated to 40 °C and stirred overnight. Finally, the solution was heated to 85 °C to complete the reaction. After cooling to room temperature, the crude product was precipitated in water. The polymer was dissolved in 10 mL of THF and reprecipitated in *n*-hexane. This procedure was repeated twice before the product was dried under vacuum at room temperature.

Yield: 0.7 g (90%) of white and brittle powder (SI-46/11-URF1).

 1H NMR (CDCl₃, 250 MHz, TMS) δ [ppm]: 7.2–7.6 (–NH– $C_6H_4-CF_3$), 6.3–7.15 (aromatic polystyrene units), 3.6–4.5 (OOC–NH–)/(R– CH_2-O-), 0.5–2.3 (hydrocarbon backbone and aliphatic isoprene units).

IR (film on NaCl plate) $\tilde{\nu}$ [cm^{-1}]: 3323, 3025, 1709, 1602, 1546, 1328, 1164, 1119.

Fluorinated Carbonate Side Chains (SI-46/11-OCOH1F2). The carbonate side chains have been introduced via reaction of a fluorinated chlorocarbonate that has been synthesized previously using excess phosgene and the corresponding fluorinated alcohol as shown in Scheme 2. Care has to be taken to remove phosgene. As a consequence, cross-linking reactions via the phosgene could be eliminated, and the narrow molecular weight distribution of the starting block copolymer could be retained throughout the reaction.

3 mL (4 g, 0.04 mol) of phosgene was added at 0 °C to a 200 mL flask with 50 mL of freshly distilled THF. After that, a solution of 3.36 g (0.02 mol) of 1,1,1,3,3,3-hexafluoro-2-propanol and 2.02 mL (0.02 mol) of triethylamine in 10 mL of THF was added dropwise to the reaction mixture. A fine white precipitate appeared immediately. Then nitrogen is bubbled through the solution for 45 min at 10 °C in order to remove excess phosgene. After that, a solution of 1 g of SI-46/11-OH (2.8 mmol of -OH) and 2.02 mL (0.02 mol) of triethylamine in 70 mL of THF is added, and the reaction is allowed to proceed for 1 h at 10 °C before it is slowly heated to room temperature. Subsequently, distilled water is added to destroy excess 1,1,1,3,3,3-hexafluoro-2-propyl chlorocarbonate, until a clear solution appears. Finally, the crude product is precipitated in 600 mL of water, redissolved in methylene chloride, and washed with diluted hydrochloric acid and distilled water. The organic phase is concentrated to 20-30 mL, precipitated





in 300 mL of methanol, and filtrated. The polymer is redissolved in methylene chloride and reprecipitated in methanol two more times and finally dried under vacuum at room temperature.

Yield: 1 g (63%) of white powder (SI-46/11-OCOH1F2).

IR (film on NaCl plate) $\tilde{\nu}$ [cm⁻¹]: 3025, 2925, 1697, 1600, 1492, 1452, 1271, 1172, 757, 698.

Synthesis of Perfluorinated Side Chain Block Copolymers on the Basis of Poly(methyl methacrylate)-b-poly-(2-hydroxyethyl methacrylate) (PMMA-b-PHEMA). (a) Synthesis of 2-[(Trimethylsilyl)oxy]ethyl Methacrylate (TMS-HEMA). The trimethylsilyl protecting group was introduced as previously reported by Hirao et al.¹⁶ using hexamethyldisilazane and trimethyl chloride.

30 g (0.23 mol) of 2-hydroxyethyl methacrylate was added under a nitrogen atmosphere to a 50 mL round-bottom flask closed with a rubber septum. After that the mixture was cooled to 10 °C, and 37.5 g (0.23 mol) of hexamethyldisilazane was added dropwise via a syringe. Finally, a few drops of trimethylsilyl chloride were added as catalyst, and the reaction mixture was stirred overnight at room temperature. The next day ammonia was removed under reduced pressure, and the crude product was distilled from the reaction mixture and finally purified by fractionated distillation.

Yield: 30.4 g (65%) of colorless liquid. $K_{p(3)}$ 60–62 °C. Lit.:¹⁶

 $K_{p(2)}$ 71–72 °C. ¹H NMR (CDCl₃, 250 MHz, TMS) δ [ppm]: 6.20 (1H, m, H NMR (CDCl₃, 250 MHz, CCU) 4.40 (2H ± OCOC*H*a) HC=CCO), 5.60 (1H, m, HC=CCH₃), 4.40 (2H, t, OCOCH₂), 3.60 (2H, t, CH₂CH₂OSi), 2.20 (3H, s, CH₃), 0.18 (9H, s, $Si(CH_3)$

(b) Block Copolymerization of MMA and TMS-HEMA. The two methacrylate monomers were purified according to standard methods. The MMA was stirred with triethylaluminum for 2 h and finally condensed into a glass ampule with a rotaflo Teflon stopcock. The TMS-HEMA was twice stirred





over calcium hydride overnight and distilled under reduced pressure. After that it was treated with triethylaluminum and finally condensed into a glass ampule.

The polymerization is carried out in THF that is freshly distilled from potassium after refluxing for at least 3 days. On the day before the reaction, the solvent is titrated with a few drops of sec-BuLi (1.3 M solution in n-hexane) at -20 °C until a slightly yellowish color appears. The polymerization is initiated with sec-BuLi, capped with diphenylethylene (DPE), which gives diphenylhexyllithium as active initiator species as shown in Scheme 3. The reaction time of the polymerization of TMS-HEMA should not exceed 20-25 min in order to prevent proton abstraction by the living chain end from the protecting group.¹⁶ In this way, a very narrow molecular weight distribution can be achieved as shown in Table 2. GPC elugrams of both PMMA precursor and PMMA-b-PHEMA show single equally narrow peaks.

600 mL of distilled and titrated THF was cooled to -78 °C. 0.513 mL of sec-BuLi was added and capped with 0.26 mL of DPE, which results in a deep red color of the reaction mixture. After 5 min, the polymerization was started by adding 20 g of MMA, which causes an immediate disappearance of the red color and a temporary rise in temperature to -50 °C. After an additional 45 min, 7 g of TMS-HEMA was added quickly and polymerized for another 25 min. Finally, the reaction is stopped with 1 mL of degassed methanol. The polymer is precipitated in 3 L of methanol, which also leads to deprotection of the PHEMA block. Then the product is redissolved in THF and reprecipitated two more times in *n*-hexane and dried under vacuum at room temperature. The block ratio has been determined by ¹H NMR spectra using the integrated aromatic signals of the benzoylated block copolymers as well as the protons of the ethylene spacer as a reference.

Yield: 24 g (76%) of white powder (MH-26/5).

Table 2. Synthesized Polymers with Poly(methyl methacrylate)-b-poly(2-hydroxyethyl methacrylate) (MH) Backbone

polymer	deg of polymerization (PMMA:PHEMA)	block ratio (PMMA:F-PHEMA) [kg/mol]	vol fraction of fluorinated block	M _w (GPC) [kg/mol] ^a	polydispersity
MH-26/5 MH-26/5-Bz MH-26/5 F7	260:40	26:5 26:8.8 26:10 0	16.1 25.3	24.5 28.2 20.2	1.05 1.04
MH-26/5-F8 MH-26/5-F11		26:21.8 26:27.4	43.4 45.6 51.3	29.2 24.9 29.0	1.05 1.05 1.05

^{*a*} According to PS calibration, MMA precursor calculated using Mark–Houwink equation. Side chains: Bz = benzoyl, F7 = perfluorooctanoyl, F8 = perfluorononanoyl, F11 = perfluorododecyl.

¹H NMR (CDCl₃, 250 MHz, TMS) δ [ppm]: 8.05 and 7.5 aromatic hydrogen atoms, 4.4 (OCH₂CH₂OBz), 4.2 (OCH₂CH₂-OBz), 3.6 (OCH₃), 1.8 (CH₂), 0.8 (CH₃), benzoylated to improve solubility.

IR (film on NaCl plate) $\tilde{\nu}$ [cm⁻¹]: 3443, 2993, 2951, 1731, 1484, 1448, 1272, 1241, 1191, 1149, 1067, 987, 966, 749.

(c) Attachment of Perfluorinated Ester Side Chains. The introduction of the perfluorinated ester side chains is performed as published previously for hydroxylated PS-*b*-PI block copolymers.¹⁷ As shown in Table 1, the narrow molecular weight distribution of the starting block copolymer could be retained throughout the polymer-analogous reactions.

In a 10 mL round-bottom flask equipped with a rubber septum, 0.2 g of MH-26/5 (0.46 mmol of -OH) were dissolved in 5 mL of freshly distilled THF under a nitrogen atmosphere. Then 2 mL of absolute pyridine was added via a syringe, and finally 0.5 mL of perfluoroctanoic acid chloride (30% molar excess) was added dropwise to the reaction mixture. A fine white precipitate occurred immediately. The reaction was heated to 45 °C and allowed to proceed overnight, before it was stopped with 1.5 mL of methanol. Subsequently, the polymer was precipitated twice in a 50 mL methanol/water mixture (1:1, 2:1, v:v), redissolved in 5 mL of THF, and precipitated in 50 mL of *n*-hexane. Finally, it was dried under vacuum at room temperature.

Yield: 0.4 g (90%) of slightly yellowish powder (MH-26/ 5-F7).

IR (film on NaCl plate) $\tilde{\nu}$ [cm⁻¹]: 2951, 1788, 1731, 1484, 1448, 1241, 1206, 1149, 988, 748.

Experimental Setup

Sample Preparation. The polymer films were prepared from 5 wt % solutions of the fluorinated block copolymers in α, α, α -trifluorotoluene (SI blocks) and THF (MH blocks). Thin films (approximately 200 nm as obtained by scanning force microscopy (SFM) at an edge of a partially delaminated film) were prepared by spin-coating 0.1 mL of the solutions onto a 1×1 cm² piece of a polished silicon wafer (2000 min⁻¹, 20 s). Prior to use, all films were dried overnight under vacuum at room temperature and annealed at 140 °C for 3 h in a vacuum oven. The polymer films used for the laser writing experiments were prepared by casting from 5 wt % solutions in THF onto aluminum foil.

Gel Permeation Chromatography. GPC measurements were performed using a WATERS GPC equipped with dual detectors (RI and UV [$\lambda = 254$ nm]) and SDV-gel columns (PSS Mainz, Germany) of 5 μ m particle size having 10⁵, 10⁴, 10³, and 10² Å pore size. In addition, polyester-gel columns (GRAM, PSS Mainz, Germany) with 10 μ m particle size and 10⁴, 3 × 10³, and 10² Å pore size were used for polymers with urethane side chains. In each case, the elution solvent was THF at room temperature with an elution rate of 1 mL/min. Narrow polydispersity polystyrene samples were used as calibration standards.

Thermal Treatment. Thin polymer films spin-coated on silicon wafers were heated to 330 °C for 15 min in a vacuum heating chamber. Finally, the samples were cooled to room temperature, and the chamber was flushed with nitrogen.

LASER Treatment. The laser-induced decomposition studies were performed using a neodymium glass laser operated at 1064 nm and 295 mW. The velocity of the writing beam was set to 3.2 m/s.

Table 3. TGA Data of the SI Block Copolymers with				
Urethane and Carbonate Side Chains and MH Block				
Copolymers				

	calcd loss	exptl loss	1st	2nd
	of mass	of mass	degradation	degradation
polymer	[%]	[%]	step [°C]	step [°C]
SI-26/7-URF1	36	39	232	389
SI-46/11-URF1	36	35	326	397
SI-66/19-URF1	36	37	318	397
SI-46/11-	37	30	354	419
OCOH1F2				
MH-26/5	100	100	364	
MH-26/5-F7	33	а	316 ^b	354^b
MH-26/5-F8	37	а	339^{b}	370^{b}

^{*a*} No precise evaluation possible. ^{*b*} Evaluated by peak-fitting procedure. ^{*c*} Assuming first degradation step of thermal side chain cleavage.

FT-infrared spectrometry (FT-IR), ¹H NMR, X-ray photoelectron spectroscopy (XPS), contact angle measurements, thermogravimetric analysis (TGA), and thermodesorption mass spectrometry (TDMS) were performed as described in a previous paper.⁸

Results and Discussion

Degradation Study Using Thermogravimetric Analysis. In a previous paper,8 we presented polystyrene-*b*-polyisoprene block copolymers that allowed for selective thermal cleavage of fluorinated side chains attached by ester groups. In addition, we observed a distinct difference between perfluorocarbon and hydrocarbon ester side chains. Perfluorocarbon ester side chains showed distinctly lower decomposition temperatures than hydrocarbon ester side chains, which decomposed at temperatures similar to the degradation temperature of the polymer backbone itself. To increase the selectivity of the fluorinated side chain decomposition, our aim in the present study is to investigate the dependence of the cleavage temperature of different fluorinated side chains on their chemical structure. Urethane and carbonate functionalities are supposed to thermally decompose at lower temperatures compared to ester groups, thus allowing to thermally detach fluorinated side chains at lower temperatures and to facilitate processes to incorporate hydrophobic/hydrophilic patterns into polymer surfaces.

(a) Urethane Side Chains (–URF1). A series of polymers with the same urethane side chain (URF1) and different overall molecular weights of the SI blocks have been investigated by TGA; the results are shown in Table 3. As can bee seen, all urethane side chain polymers show a two-step degradation process. The second high-temperature process around 390–400 °C can be attributed to the decomposition of the polymer backbone as derived from earlier studies.⁸ N-Monosub-stituted urethanes are expected to decompose via a N–H hydrogen transfer initiated depolymerization mechanism which leads to the formation of isocyanate



Figure 1. TGA curve of SI-26/7-URF1 (allophanate structure).



Figure 2. FT-IR of SI-26/7-URF1 before (–) and after heating $(\cdot \cdot \cdot)$ at 340 °C for 1 h.

monomers at temperatures between 285 and 325 °C.14 We therefore assume that the first degradation step can be attributed to such thermal cleavage of the fluorinated urethane group in SI-46/11-URF1 and SI-66/19-URF1 at temperatures of 326 and 318 °C, respectively. SI-26/ 7-URF1 only shows a weak peak at this temperature (see Figure 1). However, a strong decomposition occurs at a much lower temperature of 232 °C. This decomposition step can be attributed to the cleavage of an allophanate structure, formed during synthesis of SI-26/7-URF1. According to literature, the allophanate structure is much more instable and decomposes at relatively low temperatures (200 °C¹⁸). Further evidence of an allophanate decomposition is found since the calculated loss of mass for this step matches well with the experimentally found loss. In addition, FT-IR specifically detects the disappearance of the allophanate vibration at 1654 cm⁻¹ after a thermal treatment (1 h at 340 °C) as shown in Figure 2, whereas all other signals attributed to α, α, α -trifluoro-*p*-toluyl side groups only decrease. All other degradation steps that appear at similar temperatures in every polymer investigated can be attributed to the side chain cleavage of the urethane and the degradation of the polymer backbone (as an example see Figure 3). The fine structure observed in the first derivative can be explained by an additional two-step process that involves partial cyclization of monomer generated during the depolymerization process and subsequent degradation.14,15,19

(b) Fluorinated Carbonate Side Chains (-OCO-H1F2). Only the SI-46/11-OH backbone was modified with a fluorinated chlorocarbonate. The resulting polymer shows two distinct degradation steps at 354 and



Figure 3. TGA curve of SI-46/11-URF1.



Figure 4. TGA curve of SI-46/11-OCOH1F2.

Table 4. TGA Data of the Perfluorinated Ester Side Chain Block Copolymers

polymer	calcd loss of mass [%]	exptl loss of mass [%]	1st degradation step [°C]	2nd degradation step [°C]
SI-46/11-F3	40	54	340	405
SI-46/11-F7	56	63	345	395
SI-46/11-F8	59	68	346	401
SI-66/19-F3	40	53	342	401
SI-66/19-F7	56	65	344	394
SI-66/19-F8	59	63	347	407

419 °C as shown in Table 3 and Figure 4, which are close to the cleavage temperature observed for perfluorinated ester side chains (see Table 4). We assume a decomposition of the carbonate side chain in the first degradation step as can be seen from the comparison of the calculated and experimentally found loss of mass, which agree quite well as shown in Table 3. Surprisingly, the block copolymer did not show any expected advantage with respect to a decrease of the decomposition temperature compared to the fluorinated ester side chains. However, the fluorinated carbonate side chain also allows for selective cleavage of fluorinated side chains without decomposition of the polymer backbone.

(c) Fluorinated Ester Side Chain Methacrylates. As it is impossible to perform any hydroboration reaction in the presence of a methacrylic acid ester, a monomer had to be found that already carries a hydroxyl function. Having in mind the previously discussed mechanism of thermal ester cleavage⁸ via a retro-en reaction in a six-membered-ring transition state, it is important to incorporate an ethylene spacer between the hydrocarbon backbone and the ester functionality. Therefore, the 2-hydroxyethyl methacrylate was used as monomer for the second block, as it fitted well into these presumptions and allowed well-known protection group chemistry as described earlier in this paper.

The fluorinated side chain block copolymers based on PMMA-*b*-PHEMA do not show any clearly separated degradation steps. Therefore, an evaluation of the experimentally found loss of mass was not possible, but the temperature, at which the second degradation step presumably occurs, could be estimated using a peakfitting procedure for the plot of the first derivative. If one compares the TGA curve of MH-26/5 and MH-26/ 5-F7 (not shown here), the main difference is a slight shoulder in the first derivative of the curve of MH 26/ 5-F7 with an assumed maximum at 316 °C (Table 3), which can be attributed to the decomposition of the fluorinated ester side chain. The same result is found for MH-26/5-F8, which is slightly shifted to higher temperatures. Obviously, the degradation temperature of the polymer backbone is much lower for the methacrylate (MH)-based copolymers compared to the polystyrene-*b*-polyisoprene (SI) copolymers, thus preventing selective cleavage of perfluorinated ester side chains for MH backbones. This behavior of the methacrylate-based fluorinated side chain block copolymers can be explained by the tendency of methacrylate polymers to depolymerize. Heating homopolymers of deliberately chosen molecular weight to 500 °C showed that depending on the nature of the neighboring group to the hydroxyl function the monomer yield was 20% (free -OH), 50% (acetyl group), or 70% (methyl group).²⁰ Fundamental studies^{21,22} on the degradation of PMMA have shown that the thermal degradation takes place by a depolymerization reaction with a maximum rate of decomposition at \sim 390 °C ($E_a = 130-230$ kJ/mol²²). Additionally, recent molecular orbital studies have underlined that in the case of poly(alkyl methacrylates) there is a significant influence of the side chain on the degradation process.²³ A long and bulky side group finally leads to a transition to a typical ester pyrolysis mechanism, e.g., poly(tert-butyl methacrylate), which decomposes by an ester decomposition mechanism yielding isobutene and poly(methacrylic acid) almost exclusively.²⁴ Furthermore, Lee et al.²⁵ demonstrated that free hydroxyl groups lead to a significant decrease in the decomposition temperature and energy as they attack the ester linkage and therefore facilitate the overall degradation.

The fact that our pure unmodified MH-26/5 degrades in a single step at 364 °C, which is nearly 30 °C lower than reported earlier²⁵ for pure PMMA, may be due to the strong influence of the hydroxyl groups. In the case of the fluorinated ester side chains already a few residual hydroxyl groups may be sufficient to induce an OH-assisted degradation.

(d) Fluorinated Ester Side Chain PS-*b*-PI Block Copolymers. To complete the experimental results concerning fluorinated side chain block copolymers based on a SI backbone, the block copolymers based on SI-46/11 and SI-66/19 backbones from previous studies⁸ were similarly investigated by TGA. These polymers exhibit the highest fluorine enrichment in the surface region as previously investigated by XPS. Therefore, they are most favorable as materials for thermally processed hydrophobic/hydrophilic patterned surfaces. The selectivity of thermal cleavage in thin polymer films



Figure 6. TDMS spectrum of SI-66/19-F8; heating rate 5 K/min.

will be investigated later in this work, after the bulk behavior has been determined by TGA measurements.

All perfluorinated ester side chain block copolymers in this study show a two-step degradation process that can be explained by selective cleavage of the perfluorinated ester side chain and the decomposition of the hydrocarbon backbone (see Table 4). The maxima of the first derivative reveal a temperature gap of approximately 60 °C, which is around 20 °C lower than the gap observed in the previous study due to a lower backbone decomposition temperature as shown in Table 4 and Figure 5. A clear explanation for this observation cannot be given at this point. Additionally, the calculated and experimentally obtained losses of mass do not fit as well as found for SI-26/7-F3 and -F7 in a previous study.8 Nevertheless, within the experimental error, these results again show the possibility to selectively cleave the fluorinated side chains by thermal treatment. The results will be further supported by TDMS measurements in the next section. The TDMS spectrum of SI-66/19-F8 is shown as an example in Figure 6. Here, the desorption maxima of the fluorocarbon and the hydrocarbon fragments can be found at 321 and 392 °C, respectively. Slight deviations in temperature between TGA and TDMS can be attributed to experimental errors for the different setups.

Degradation Study Using Thermodesorption Mass Spectrometry. Determination of Degradation Energies for Ester Bond Cleavage. Degradation energies for the ester bond cleavage of the SI-block copolymers were determined from heating rate variations in TDMS by several orders of magnitude. However, experiments were practically limited to heating rates



Figure 7. TDMS spectrum of SI-26/7-F7; heating rate 1 K/min.



Figure 8. TDMS spectrum of SI-26/7-F7; heating rate 100 K/min.

ranging from 1 to 100 K/min. Previous studies showed a very good agreement between the TDMS and TGA data using SI copolymers.⁸

As an example, SI-26/7-F7 was selected for the TDMS investigation and was heated starting from room temperature to 600 °C as shown in Figure 7 and Figure 8 for heating rates of 1 and 100 K/min, respectively. Here, fragments originating from the fluorocarbon side chain can be well distinguished from those of the hydrocarbon backbone. Fluorocarbon fragments are observed by a homologous series following the formula $C_nF_{2n+1}^+$ and $C_nF_{2n}^+$ (CF₃⁺/69 amu, $C_2F_5^+$ /119 amu, $C_3F_7^+$ /169 amu, $C_2F_5^+$ /119 amu, $C_5F_{11}^+$ /269 amu for the perfluoroctanoyl side chain). For the hydrocarbon backbone, the most intense fragments observed were the highly stable aromatic ions: $C_6H_5^+$ /77 amu, $C_6H_6^+$ /78 amu, $C_7H_7^+$ /91 amu, and $C_8H_8^+$ /104 amu. The relative yield of these ions was monitored during heating.

Degradation energies $E_{\rm D}$ were determined from a kinetic model similar to the Polanyi–Wigner model^{26,27} of thermal desorption. Here, the peak temperature of desorption (in our case decomposition) $T_{\rm p}$ at a heating rate β is determined, yielding^{28,29}

$$\ln(T_{\rm p}^{2}/\beta) = E_{\rm D}/RT_{\rm p} + \ln(E_{\rm D}/R\nu_{\rm m})$$
(1)

Plotting $\ln(T_p^2/\beta)$ vs $1/T_p$ yields a slope E_D/R as shown in Figure 9. The intersection with the ordinate gives the frequency factor ν_m that can be calculated by the term $\ln(E_D/R\nu_m)$. A first-order desorption process yields a constant desorption energy and a desorption temperature (i.e., temperature at peak maximum) that only depends on the heating rate. The same is assumed for



Figure 9. Evaluation of degradation energies for peak I (●) and peak II (■).

the decomposition process in our example. The temperatures at peak maximum and resulting decomposition energies are shown in Table 5.

The calculation of the frequency factor $v_{\rm m}$ which can be interpreted on a molecular level similarly as the Arrhenius frequency factor yields $1.1\times 10^{13}\,s^{-1}$ for peak I, which scales well compared to common Arrhenius factors for monomeric ester pyrolysis.⁹ The degradation energy of 167 kJ/mol for the first peak which is attributed to the cleavage of the fluorinated ester side chain is of the same order of magnitude as for example previously reported for the thermal decomposition of acetic acid esters that revealed activation energies for the pyrolysis of around 190 kJ/mol.⁹ The value calculated for our fluorinated ester is smaller than for the hydrocarbon ester cited in the literature. As previously reported,⁸ we assume that the strong electron withdrawing effect of the fluorocarbon chain leads to activation of the ester linkage resulting in the smaller decomposition energy.

XPS Investigations on Thermally Modified Polymer Films. Since the characteristics of the XPS spectra of fluorinated side chain block copolymers based on polystyrene-*b*-polyisoprene backbones were discussed in a previous paper,⁸ only the XPS spectra of the methacrylate-based block copolymers (poly(methyl methacrylate)-*b*-poly(2-hydroxyethyl-[*g*-perfluoroctanoyl] methacrylate) and their blends will be discussed in detail. A meaningful interpretation of the XPS data of the starting polymer films is necessary before dealing with thermally degraded polymer films.

The C 1s region of the high-resolution XPS spectrum of the pure block copolymer MH-26/5-F7 at a takeoff angle of 90° (Figure 10a) reveals complex signals extending over an energy interval of approximately 12 eV. Although there are six chemically differently bonded carbon atoms present in the polymer, only five could be resolved clearly and were used for curve-fitting procedures. According to published literature, ³⁰ the aliphatic carbon signals were calibrated to 284.6 eV. The resulting peak assignments are also given in Figure 10a and are based on the characteristic binding energies and agree well with previously established references.³⁰ The ratios of the different carbon moieties as obtained by curve fitting of the C 1s lines do not agree at all with the expected ratios of the fluorinated side chain of the fluorinated PHEMA block as expected for a pronounced surface segregation of the fluorinated PHEMA block. For the polymer MH-26/5-F7 one obtains the following ratios of CF₃:CF₂:O-C=O:CH₂-O groups for the per-

 Table 5. Degradation Temperatures and Energies for SI-26/7-F7

heating rate [K/min]	temp at peak max I [°C/K]	temp at peak max II [°C/K]	E _D for peak I [kJ/mol]	E _D for peak II [kJ/mol]	${ \nu_m \ {\rm for \ peak \ I} \over [10^{13} \ { m s}^{-1}] } }$	$ u_{ m m} $ for peak II [10 ¹³ s ⁻¹]
1	303/576	376/649	167 ^a	205 ^a	1.11	24.5
10	340/613	410/683				
100	385/658	460/733				

^{*a*} With an estimated error of $\pm 10\%$ derived from the error in temperature detection and the linear fit.



Figure 10. (a) C 1s regional scan of MH-26/5-F7. (b) C 1s regional scan of SI-46/11-F8 before (-) and after heating (\cdots) at 330 °C for 15 min. (c) 10% MH-26/5-F7 in APEC 35 before (-) and after (\cdots) laser-induced cleavage.

fluoroctanoyl side chain (F7, expected 1:6:1:1, observed 1:10:14:24). The high presence of CH_2-O groups suggests that a remarkable amount of PMMA block resides in the uppermost 50 Å of the polymer film as detected by XPS. This assumption is supported by a quantitative evaluation of the C 1s, O 1s, and F 1s peak integrals of the spectra measured at a takeoff angle perpendicular to the sample surface (90°). They show a fluorine amount in the uppermost 50 Å of the polymer film that is as low as calculated for the bulk composition (17 at. %).

Angle-dependent XPS measurements of films of the pure block copolymer reveal that the fluorine enrichment increases remarkably at smaller takeoff angles, reaching—within the experimental error—the value of the isolated fluorinated PHEMA block (45 at. %) at a relative depth of 0.2 (takeoff angle: 10°).

The result that the fluorine surface enrichment is detected in a much shallower surface layer than for the SI-block copolymers discussed in our previous study can be explained by the fact that the degree of polymerization (DP) of our fluorinated PHEMA blocks is much lower than the DP of the fluorinated isoprene blocks. Therefore, the domain spacing is smaller, which results in a much thinner fluorinated surface layer. In addition, a comparison between angle-dependent measurements of the pure block copolymer and its 10 wt % blend with polycarbonate APEC 35 (polycarbonate copolymer based on BPA and TMC bisphenols containing 35 wt % trimethylcyclohexylbisphenol (TMC) and 65 wt % bisphenol A (BPA, Bayer) is shown in Figure 11. A very similar fluorine enrichment in the upper surface area is observed, which implies that-similar to the fluorinated SI block copolymer blends⁸-only a small amount of fluorinated component is sufficient to change the surface characteristics remarkably. We used these blends for surface patterning experiments by laser-



Figure 11. Fluorine content in the upper surface region of MH-26/5-F7 (\blacksquare) and its 10 wt % blend (\blacktriangle) with APEC 35.

Table 6. XPS Results of Heated and Laser-Treated Films

	an	amount of fluorine [at. %]				
polymer	before heating	after heating	before laser	after laser		
SI-46/11-F3	32.5	<1				
SI-46/11-F8	45.8	<2				
10% MH-26/5-F7	18.7	<1	19.3	3.3		
in APEC 35						

induced thermal cleavage as presented in the next section.

(a) Thermal Cleavage of Fluorinated Side Chains. Film surfaces were investigated by XPS before and after heating. The results are summarized in Figure 10b and Table 6. For SI-46/11-F3 as an example, the fluorine content in the surface region of the film decreased from 32.5 at. % to less than 1 at. %. The fluorine content of SI-46/11-F8 decreases from nearly 46 at. % to lower than 2 at. % after the thermal treatment. The resulting XPS spectrum before and after thermal treatment is shown in Figure 10b. After thermal treatment the fluorinecontaining groups at binding energies from 289 to 295 eV are nearly absent. Also, a 10 wt % blend of MH-26/ 5-F7 in APEC 35 reveals a dramatic decrease in the fluorine signal from 19 at. % to lower than 1 at. %. After thermal treatment the corresponding XPS spectrum (not shown here) indicates only pure polycarbonate. These dramatic changes in the surface composition as summarized in Table 6 agree well with the TGA and TDMS studies which implied a complete removal of the fluorinated compounds from our block copolymer backbones.

To get more detailed information about the structure of the remaining block copolymer, 200 nm thick films were prepared by spin-coating onto double side polished silicon wafers. This sample support allows for FT-IR measurements at different times during the degradation process. As can be seen in Figure 12, the polymer SI-46/11-F8 shows a significant decrease in the CF_n (1140– 1260 cm⁻¹) and C=O (1786 cm⁻¹) vibrations without a significant change in the aromatic C=C (1600 cm⁻¹) or aromatic and aliphatic C–H (2800–3100 cm⁻¹) vibrations of the styrene block and backbone. Therefore, we can assume that the fluorinated side chain is cleaved



Figure 12. FT-IR of SI-46/11-F8 before (-) and after heating (···) at 330 °C for 15 min (thin film cast on double side polished silicon wafer).

off selectively, leaving the remaining polymer backbone completely intact. Additionally, we found that, as the fluorine content in the surface region decreases dramatically, the contact angles also reveal a significant change in hydrophilicity. For SI-46/11-F3, the static contact angle of water decreases from 100° to 51°, and for SI-46/11-F8 it drops from 113° to 86°, leading to a significantly increased hydrophilicity.

(b) Laser-Induced Cleavage of Fluorinated Side Chains. Thermal cleavage of fluorinated side chains can be similarly obtained by IR laser treatment of the polymer film surfaces. A film of a blend of 10 wt % MH-26/5-F7 in APEC 35 was irradiated at 1064 nm by a neodymium glass laser. As APEC 35 shows sufficient absorption, no additional laser dye had to be added. The laser-induced cleavage of the fluorinated side chains was investigated by XPS before and after laser treatment. To prevent surface contamination by fluorinated fragments, the samples were washed with methanol and ethanol after the laser treatment. These solvents do not alter the block copolymer film surfaces. Several reproducible XPS measurements revealed a significant decrease in the fluorine content on the surface of the polymer films (Figure 10c). The resulting XPS spectra of films that were heated by a furnace and laser-treated at 1064 nm give similar results that indicate only polycarbonate after the treatment. The amount of fluorine in the uppermost 50 Å decreases from nearly 20 at. % to values around 3 at. %, which is a change as remarkable as observed for the thermal heating process in a vacuum oven. In addition, wetting experiments reveal that the hydrophobicity of the surface (static contact angle: 103°) is altered to complete wetting. These first laser printing experiments indicate that the polymers may potentially be used for printing processes using water-based ink.

Conclusion

We have demonstrated that a variety of different fluorinated side groups (perfluorinated esters, fluorinated urethanes, and carbonates) incorporated into a hydroxy functional block copolymer can be cleaved selectively by means of thermal or laser-induced pyrolysis. Especially the latter technique has been proven to be able to selectively alter the surface composition in a chemically controlled way, i.e., to change the surface composition from one defined composition to another by cleavage of the respective fluorinated side chains.

Furthermore, we designed a block copolymer/homopolymer blend system (10 wt % MH-26/5-F7 in APEC 35) which allows to create hydrophobic surface patterns in thin polymer films.

Possible applications of these chemically structured surfaces range from printing plates using aqueous inks to fundamental studies related to wetting phenomena on defined chemically heterogeneous surfaces.

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