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Low-Surface-Energy Fluoromethacrylate Block Copolymers with Patternable Elements

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A series of block polymers were synthesized from tetrahydropyranyl methacrylate (THPMA) and several fluorinated methacrylates. By changing both the length of the fluorinated side chain and the nature of its end group, the surface properties of these polymers were greatly influenced. The polymers with perfluoroheptyl groups showed the lowest surface tension, ~7 mN/m, whereas those with perfluoropropyl groups showed surface tension around 12 mN/m. The surface tension changed dramatically when the perfluorinated side chain with a CF_2H end group was capped, increasing to 18 mN/m for three $-CF_2-$ units. The relative volume ratios of different block copolymers did not affect the resulting surface energy. After thermal decomposition of labile THP− groups in these polymers, acid and acid anhydride groups were produced. Thermal cross-linking of these groups increased mechanical robustness and led to better surface stability and adhesion of the polymer to the substrate. Because these polymers were designed for their lithographic abilities, some aspects of their photoimaging properties are discussed.

Introduction

Precise control of the surface properties of polymeric materials by means of self-organization is a major objective of current science and technology. Such self-organization can be driven by several mechanisms including phase separation of block copolymers, liquid crystallinity, hydrogen bonding, and surface segregation.[1] Under some circumstances, these mechanisms may be used together to form an ordered surface structure. As an example, block copolymers microphase-separate to preferred microstructures, but when low-surface-energy blocks are incorporated, surface and interface segregation will also take place to create further organization in the region of the low-energy surface. The objective of this investigation was to examine the effect of block copolymer architecture on the surface properties of a family of fluoropolymers that contain lithographically patternable, photoacid cleavable tetrahydropyranyl (THP−) groups. In the process of lithographic patterning, very hydrophobic acid groups are formed in the nonfluorinated block. From the point of view of the imaging process, understanding these chemical changes and its effect on surface behavior is of great importance.

Fluorinated materials are well-known as low-surface-energy materials with potential uses in surface coatings, surfactants, or emulsifiers,[2] some of which are soluble in supercritical carbon dioxide.[3,4] A monolayer of these materials, properly organized, will make a very low-energy surface. For example, the Langmuir−Blodgett (LB) technique has been applied to fluoroalkanes to produce surfaces with perhaps the lowest surface energy known, as a result of its uniformly organized trifluoromethyl (CF_3) array at the air−film interface.[5] An alternative way to produce low-energy surfaces and to avoid the complicated LB technique is to introduce self-organizing fluorinated groups onto a polymer side chain.[6−12] As shown in our previous work,[8] liquid crystalline, semifluorinated groups may be readily introduced into a polymer by chemical modification of the backbone. After self-organization of the liquid crystalline mesogen, a stable, nonreconstructing, low-

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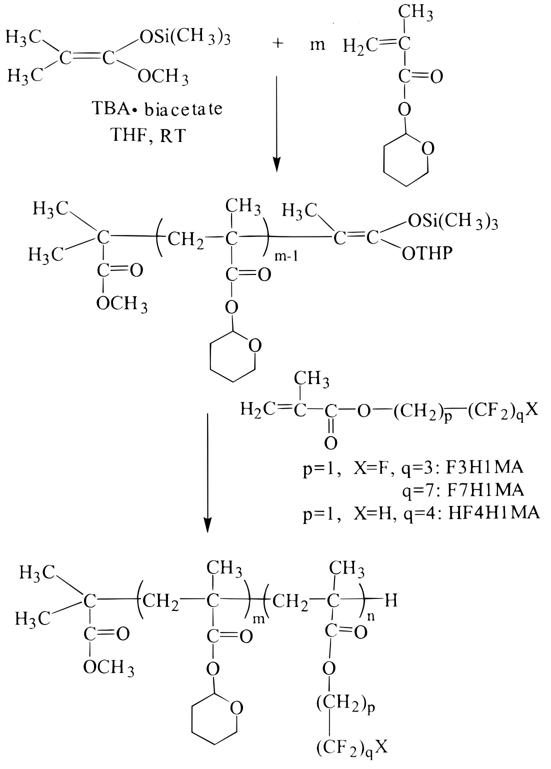
Scheme 1: Group Transfer Polymerization of Block Copolymers



energy surface may be produced that rivals those produced by the LB technique.

Although the focus of this paper is on the surface properties of these new block copolymers, an equally important motivation for this work is in the area of submicrometer lithography. These polymers have been designed to be high-resolution, chemically amplified photoresists capable of imaging with 193 nm radiation.[13] In prior work, we have demonstrated that siloxane- and fluorine-containing block copolymers are superior to the comparable random copolymers as negative-tone, supercritical CO_2 developed photoresists.[14,15] The presence of the fluorinated groups gives them solubility in supercritical CO_2 that others and we are examining as superior-performance, environmentally friendly developer solvents. The work on the successful production of lithographic features $< 0.25\ \mu$m will be reported separately.[13]

In this paper, a series of block polymers with separate acid- and heat-cleavable tetrahydropyranyl methacrylate (THPMA) and fluorinated methacrylate blocks (see Scheme 1) were synthesized by group transfer polymerization. Block copolymers with different volume ratios were prepared to give a range of microstructures and solubilities. Several structural aspects contribute to surface behavior, including the average surface composition, molecular orientation, surface packing, and specific surface groups.[16,17] A uniform CF_3 group coverage on the polymer surface would afford the lowest surface energy structure,[18] and due to the self-assembly behavior of these block copolymers, this fluorinated end group does tend to populate the surface region. Coverage by the end group may be greatly affected by casting solvent, annealing temperature, and the fluorinated side chain length.[8,19] In addition, the surface energy can be significantly affected depending on the types of closely packed end groups on the surface.[20] To study this effect, polymers with CF_2H end groups on the fluorinated segment were compared to those with CF_3 groups.

As determined by contact angle measurements, the block copolymers with six $-CF_2-$ units and a CF_3 end group showed the lowest surface energy, ~7 mN/m, whereas those with two $-CF_2-$ units and a CF_3 end group showed surface energies of ~12 mN/m. By simply replacing the perfluorinated side chain by a side group with a CF_2H end group and three $-CF_2-$ units, the surface energy increased to ~18 mN/m. Although the volume ratio of the block copolymer segments did affect its microstructure (and its solubility in supercritical CO_2), it had no significant effect on the critical surface tension.

Although many fluorinated polymers possess low surface energies, surface reconstruction has greatly limited the practical application of these materials. An example of polymers with stable surfaces is a series of semifluorinated block copolymers that form a highly ordered smectic B phase that resists reconstruction of the surface region.[8] Other materials that depend on formation of a cross-linked sublayer have also been reported.[21] As low-surface-energy materials with labile groups, the surface stability of these polymers was investigated as well. It was found that after removing the labile THP$-$ groups to form acid groups, stable surfaces were produced. In this paper, the synthesis and surface characterization of these new materials is described. An explanation is given for the ability of these polymers to form a stable, nonreconstructing surface.

Experimental Section

Solvent. Tetrahydrofuran (THF) (Aldrich) was freshly distilled from sodium/benzophenone under nitrogen before polymerization.

Initiator. Methyl trimethylsilyl dimethylketene acetal {[(1-methoxy-2-methyl-1-propenyl)oxy]trimethylsilane, MTDA} (Aldrich) was distilled and stored under nitrogen.

Monomers. 2-Tetrahydropyranyl methacrylate (THPMA) was synthesized as described in the literature.[22] Commercially available monomers, 1*H*,1*H*-heptafluoro-*n*-butyl methacrylate (F3H1MA, Lancaster), 1*H*,1*H*-perfluorooctyl methacrylate, or

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1*H*,1*H*-pentadecafluorooctyl methacrylate (F7H1MA, Lancaster), and 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (HF4H1MA, Lancaster) were first purified by stirring with CaH$_2$ for 24−48 h, followed by vacuum-distillation into a cold trap. The monomer was transferred to a monomer reservoir under nitrogen and stored at −20 °C.

Catalyst. Tetrabutylammonium biacetate was prepared using literature methods[23] and was dissolved in freshly distilled THF to give a 0.04 M solution. A small amount of water (6 mol equiv) was added to facilitate dissolution.

Polymerization. The block polymers with UV-imageable tetrahydropyranyl methacrylates (THPMA) and fluorinated methacrylates were synthesized by group transfer polymerization (GTP). The synthetic procedure is illustrated in Scheme 1. As an example, to a 100 mL three-necked round-bottom flask fitted with a thermometer, a stopcock with septum, and a stir bar, 8 mL of freshly distilled tetrahydrofuran (THF) was introduced under N$_2$. The initiator, methyl trimethylsilyl dimethylketene acetal (MTDA) (67 μL, 0.33 mmol), and the catalyst, 0.04 M tetra(*n*-butyl) ammonium biacetate (8.3 μL, 0.34×10^{-3} mmol), were injected and stirred for a short time to eliminate impurities. Then, 1.35 mL of THPMA was added slowly over 3 min. The temperature increased immediately from room temperature, 22 °C, to 38 °C and decreased slowly. After the temperature dropped to room temperature, the solution was further stirred for another half an hour. Fluorinated methacrylate was added all at once with an immediate temperature increase to 41 °C, and the color of the solution turned light yellow. The reaction was quenched with methanol and precipitated in a 10-fold excess of methanol or methanol/water, followed by being dried in vacuo. The block copolymer was obtained, 2.7 g, with a yield of 82%.

Polymer Characterization. The molecular weight of the polymers was determined by gel permeation chromatography (GPC) using four Waters Styragel HT columns at 30 °C, with poly(methyl methacrylate) (PMMA) as standard in THF. The copolymer compositions were calculated from ^{1}H NMR (CDCl$_3$ or THF-d_8) spectra obtained on a Varian 200 spectrometer. The glass-transition temperatures were studied by differential scanning calorimetry (DSC) measurements on a Perkin-Elmer DSC-7 Series instrument at a 10 °C/min heating rate under nitrogen. The thermal decomposition temperature was determined using a TA Instruments thermogravimetric analyzer (TGA) 951 under nitrogen at a heating rate of 10 °C/min.

FT-IR. Infrared measurements were made using a Mattson 2020 Galaxy Series FT-IR spectrometer with a resolution of 4 cm^{-1}. For time-resolved FT-IR, a polymer solution was cast between two sodium chloride windows or cast on a double-polished silicon wafer. The wafer was put on the Mettler hot stage (FP82HT) and then mounted into the spectrometer.

Contact Angle Measurements. Contact angles were determined with a NRL contact angle goniometer model 100-00 (Ramé−Hart Inc.) at room temperature by averaging four fresh points. The samples were prepared by spin casting 2 wt % polymer solution in either THF or α,α,α-trifluorotoluene (TFT) at a speed of 3000 rpm for 60 s on a silicon wafer at room temperature. Critical surface tensions were measured using nine linear alkanes and two low-molecular-weight trimethylsiloxy-terminated poly(dimethylsiloxanes) (Gelest, Inc.).

X-ray Photoelectron Spectroscopy (XPS). The measurements were performed using a SSL-100-3 photoelectron spectrometer with monochromated Al Kα X-ray ($h\upsilon = 1486.6$ eV) irradiation. The spot size of the X-ray beam was a 600 μm^2 square. The XPS data were acquired at takeoff angle of 55°, corresponding to a depth of 6.6 nm, based on an estimated inelastic mean free path for a C$_{1s}$ photoelectron of 27 Å originating from organic materials.[24] The samples were prepared in the same way as that for contact angle measurements.

Small-Angle X-ray Scattering (SAXS). The *d* spacings of the block copolymers were measured using real-time SAXS at the Cornell High Energy Synchrotron Source (CHESS). The wavelength of monochromated X-ray radiation used was 1.55 Å. The X-ray intensity was record on a CCD camera with resolution of 50 μm per pixel.

Results and Discussion

Synthesis. With the rapid development of the semiconductor industry, photolithography has been driven to shorter wavelengths to achieve smaller critical dimensions in microelectronic circuits. Methacrylate polymers are possible alternatives to novalac or poly(hydroxystyrene) for 193 nm radiation lithography because of their low absorption in this wavelength region. In the early 1980s, the concept of chemical amplification was introduced to photoresist systems.[25] A photoacid generator (PAG) is incorporated to form acid when exposed to radiation of the appropriate wavelength. Acid will react with an acid labile group such as the tetrahydropyranyl (THP) or *tert*-butyl groups to generate an unprotected group. One PAG molecule may catalyze 500−1000 deprotection steps,[26] but the deprotection rate is greatly affected by factors such as the polarity of the PAG and acid labile groups, the distribution of PAG in polymer domains, and the diffusion of photoacid. By careful choice of polar PAG−polymer combinations, the PAG may selectively partition to the photoacid cleavable block, and deprotection becomes much more efficient.

In this report, several lithographically processable block copolymers based on tetrahydropyranyl methacrylate (THPMA) and fluoromethacrylate monomers were synthesized by group transfer polymerization, using THF as a solvent. Compared to conventional random copolymers, block copolymers have several advantages as negative-tone resists in terms of sensitivity and contrast, resulting in part from micelle formation during development. The THPMA and fluoromethacrylate monomers (F7H1MA, F3H1MA, or HF4H1MA) were added sequentially to maintain solubility during polymerization. The acetal type THP-group is intrinsically more labile and polar than the *tert*-butyl group. It is readily cleaved after exposure to heat or acid, and the polymer solubility is greatly changed. Although the *tert*-butyl group is widely used as a protecting group, it is very hydrophobic and shows measurable deprotection only at high-exposure dose.[27] By changing the molar ratio of each monomer to balance the polarity of each block, an optimal solubility change before and after exposure can be achieved.

As a polar monomer, THPMA was introduced first in the polymerization reaction. Trimethylsilyl dimethylketene acetal (MTDA) and tetra(*n*-butyl) ammonium biacetate (TBAB) were chosen as initiator and catalyst, respectively, instead of the more reactive bifluoride catalyst to avoid side reactions. The temperature increased immediately after the THPMA monomer was injected into the reaction vessel. After 40 to 60 min, fluoromethacrylate was injected, and the temperature increased immediately from room temperature to 40 °C,

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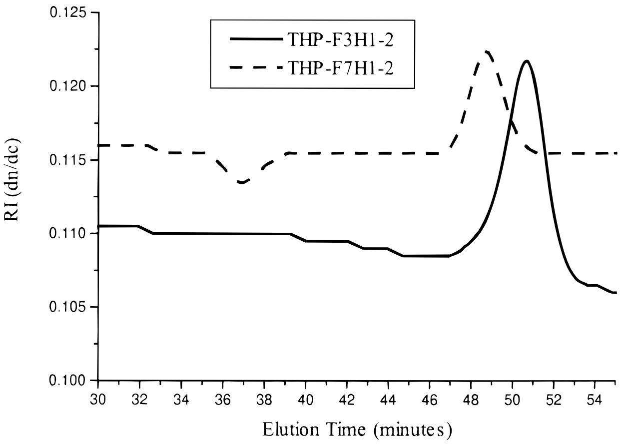

Figure 1. GPC traces of block copolymers with different fluorinated side chain lengths.

Table 1: Properties of Block Copolymers

sample	feed ratio (v/v%)	comp. (v/v%)	$M_n \times 10^{-3a}$	d	T_g (°C)
THP−F3H1-1	50:50	62:38^b	6.1	1.13	53.9
THP−F3H1-5	50:50	47:53^b	6.55	1.11	52.2
THP−F3H1-6	33:66	38:62^b	5.9	1.17	57.8
THP−F3H1-7	20:80	29:71^b	5.43	1.12	59.6
THP−F H1-2	50:50	46:54^c	10.1, 466	1.1,1.06	55.5
THP−F7H1-3	40:60	37:63^c	8.2, 424	1.07,1.24	51.9
THP−F7H1-4	27:73	23:77^c	7.7, 611	1.08, 1.12	50.2
THP−F7H1-7	75:25	78:23^c	8.47	1.11	52.0
THP−HF4-2	50:50	48:52^b	6.0	1.27	38.7
THP−HF4-3	33:67	37:63^b	7.2	1.23	37.9

[a] Measured with GPC using refractive index detector and PMMA as calibration standards. [b] Measured from ^{1}H NMR at room temperature (23 °C), in either THF-d_8 or CDCl3. [c] Measured from ^{1}H NMR at 40 °C, in THF-d_8/CFCl3 solvent mixture.

indicating a fast polymerization. If the addition sequence was reversed, only homopolymers of poly(F3H1MA) were obtained with low yield. Although the monomer F7H1MA could easily dissolve in THF, the polymer could not. Once the monomer was added, the solution became cloudy, which indicated some propagation, but it subsequently precipitated out. For better control of solubility and resist performance in lithographic applications, the molecular weight was designed to be modest (<10K).

GPC traces were measured in THF using PMMA as standard. It was found that the peak height did not increase very much when increasing polymer concentration. They all had a narrow monodisperse positive peak, except for THP−F7H1MAs that had another relatively broad negative peak at shorter elution time (see Figure 1). The negative peak position changed for different concentration solutions, whereas the positive peak did not. When the temperature was increased to 40 °C, the negative peak disappeared. The absence of a THPMA homopolymer peak indicated the living character of the polymerization and excellent coupling.

The negative GPC peak can be explained by the formation of micelles. With a longer fluorinated side chain, the immiscibility of this block in solvent increased. It is reasonable that the polymer can strongly microphase-separate and associate to form a dense fluoropolymer core micelle in THF. The dense core will have a smaller refractive index compared to that of the outer shell, which is formed by the THPMA block and THF solvent ($n_{\mathrm{THF}} = 1.407$, $n_{\mathrm{PF3H1MA}} = 1.37$, $n_{\mathrm{PHF4H1MA}} = 1.36$, and $n_{\mathrm{PF7H1MA}} \approx 1.35$). The differential refractive index will thus produce a negative peak. The average observed molecular weight is more than 50 times (a typical association number for micelle) higher than that of the single chain. We may conclude that the association equilibrium process is very fast compared to the GPC separation process (30−40 min). Such micelle formation has also been found by Möller and co-workers in their methacrylate block copolymers with semifluorinated side chains.[12] A negative peak was found at shorter elution time in GPC, and the micelle structure was resolved by both transmission electron microscopy (TEM) and scanning force microscopy (SFM). We will discuss this in more detail in the ^{1}H NMR measurements. The observed molecular weight of the block copolymers was usually smaller than that designed while the yield remained high (>80%). The hydrodynamic volume of fluorinated block copolymers is very different from that of PMMA, which was used as calibration standard. The properties of the block copolymers are summarized in Table 1.

The compositions of the block copolymers (THP−F3H1MA and THP−F7H1MA) were calculated from ^{1}H NMR by comparing the integrated area of the methine proton in THPMA (OCO−C**H**−O) to the methylene protons in FqHpMA (OCO−C**H₂**−CF₂) (see Figure 2). The composition of THP−HF4H1MA was calculated by comparing the integrals of the methylene protons in the THPMA ring (O−C**H₂**−CH₂) and those in HF4H1MA (OCO−C**H₂**−CF₂) because the methine proton in THPMA (OCO−C**H**−O) overlapped with the end group proton in HF4H1MA (−CF₂**H**). At room temperature, in either THF-d_8 or $CDCl_3$, the calculated volume ratio of THP−F3H1MA and THP−HF4H1MA matched our design very well, whereas the ratio of THP−F7H1MA was much less than expected, even after using a longer delay time. If $CFCl_3$ was added as cosolvent, the peak intensity of methylene protons in the fluorinated blocks increased but was still lower than expected. After increasing the temperature to 40 °C, the calculated molar ratio was close to that designed (see Figure 2 and Table 2). This phenomenon typically indicates micelle formation and is consistent with our GPC results. It is well-known that fluorinated polymers have poor solubility in common organic solvents, such as THF, and tend to associate into micelles in solution.[12] By adding selective solvent $CFCl_3$ and increasing temperature, the solubility of block copolymers was increased, and the equilibrium shifted from micelle to single chain. The integral of CH_2 in the F7H1MA block increased and could be easily resolved. When supercritical CO_2 is the solvent of choice, reverse micelles may form. DeSimone and co-workers have used SAXS, SANS, and light scattering (LS),[4,28,29,30] whereas Chu's group has used laser light scattering (LLS)[31,32] to intensively study the

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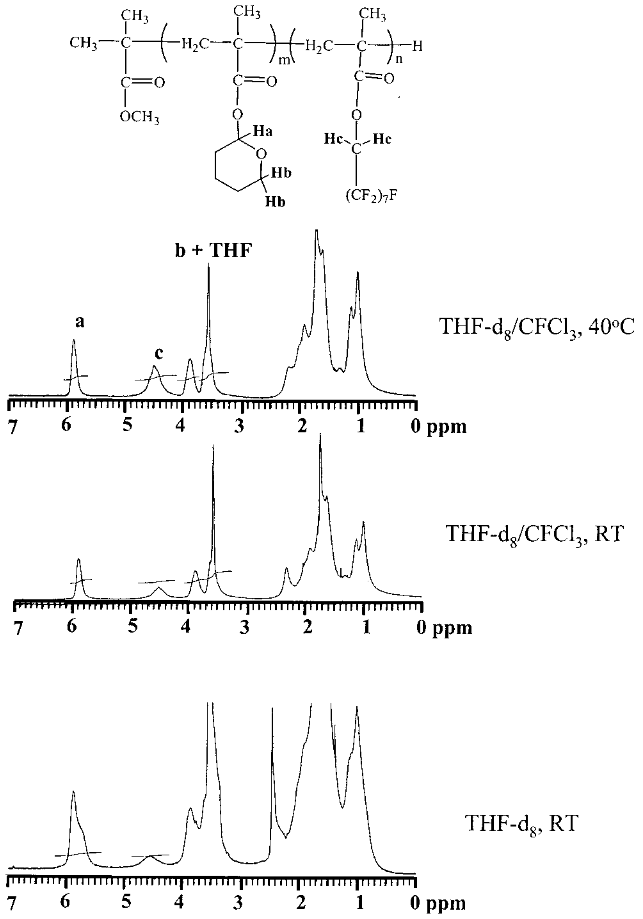

Figure 2. ^{1}H NMR spectra of THPMA−F7H1MA-2 in different solvents and at different temperatures.

Table 2: Volume Ratios of THP−F7H1MA at Different Temperatures

sample	feed ratio (v/v%)	comp. (v/v%, 23 °C)	comp. (v/v%, 40 °C)
THP−F7H1-1	75:25	89:11	78:23
THP−F7H1-2	50:50	61:39	46:54
THP−F7H1-3	40:60	58:42	37:63
THP−F7H1-4	27:73	37:61	23:77
THP−F7H1-5	33:66	45:55	32:68
THP−F7H1-6	33:66	63:37	45:55
THP−F7H1-7	75:25	92:8	78:23

mechanism of micelle formation and micelle structures of fluorinated block copolymers in supercritical CO_2. It was found that micelle formation permitted better polymer solubility than was possible for single polymer chains in supercritical CO_2. If they were used as photoresists for development in supercritical CO_2,[13] we believe more photocleavable units of THPMA can be incorporated per chain without compromising supercritical CO_2 solubility at the development stage due to the micelle formation, and light sensitivity will be improved. Further confirmation of the micelle structure in our materials is underway.

Thermal Transitions. Polymer glass-transition temperatures were measured by DSC, and the results are listed in Table 1. All data were collected during a second heating run to eliminate thermal history at a rate of 10 °C/min. From TGA measurements, the THPMA block was found to undergo elimination at ~140 °C. To avoid thermal decomposition in these measurements, the sample was heated to only 130 °C, and only the T_g of fluorinated methacrylate block was observed. As seen from Table 1, the T_g of the F3H1MA block is between 52 and 60 °C, that of the F7H1MA block is ~48−55 °C, and that of HF4H1MA is around 39 °C. The T_g data agree with the reported values for the corresponding homopolymers very well.[33] The F7H1MA block was found to be amorphous, and T_g was decreased due to the increased bulkiness of the longer $-CF_2$ side chain.[34] The observed values of T_g were independent of copolymer composition and confirmed the block copolymer character of these polymers.

Table 3: Dynamic Water Contact Angles and Critical Surface Tension of Block Copolymers

	from TFT[a]		from THF[b]		from TFT[b]		
polymers	adv.	rec.	adv.	rec.	adv.	rec.	γ_c[c]
THP−F3H1-1	108	91	108	90	109	93	12.0
THP−F3H1-5	106	93	108	92	110	93	12.2
THP−F3H1-6	109	93			109	93	12.5
THP−F3H1-7	117	96			111	93	12.0
THP−F7H1-7	110	91			117	107	7.4
THP−F7H1-2	117	95	108	90	119	107	7.5
THP−F7H1-3	118	99	108	92	119	112	6.5
THP−F7H1-4	117	97			120	110	6.7
THP−HF4H1-2	90	81	95	88	96	88	18.6
THP−HF4H1-3	91	82	96	88	96	88	18.0

[a] Measured at room temperature. [b] Measured at 70 °C for 12 h. [c]Measured in milliNewtons/meter from the samples cast from TFT and annealed at 70 °C for 12 h.

Surface Properties. Dynamic contact angles were measured by the vertical rod method[35] and are listed in Table 3. The difference between advancing contact angle (θ_a) and receding contact angle (θ_r) is related to contact angle hysteresis. Previously, it was reported by Johnson and Dettre[19] that fluorinated methacrylate homopolymers (FnH2MA) formed a layered structure when $n \geq 6$ to create more closely packed side chains and lower energy surfaces. However, this side chain effect was not observed in our polymer films cast from THF and annealed at 70 °C. There was no difference in water contact angles between those of the THP−F3H1MA and those of the THP−F7H1MA (see Table 3). When the polymers were instead cast from TFT and annealed at 70 °C, for THP−F3H1MA samples, the advancing water contact angles were ~110° and the receding values were 16−18° lower; for THP−F7H1MA polymers with seven $-CF_2-$ units, both the advancing and receding water contact angles were higher, ~120° and 110°, respectively. The advancing and receding water contact angles of THP−F7H1MA were ~10° and 20° higher, respectively, than those cast from THF, thus suggesting the expected surface layer.

Besides casting solvent, annealing temperature may also play very important roles in surface formation. The samples of THP−F3H1MA cast from TFT showed similar results before and after annealing, and the receding water contact angles of THP−F7H1MA were more than 10° higher after annealing. Compared to

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(33) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley-Interscience: New York, 1989. T_g of poly(1*H*,1*H*-heptafluorobutyl methacrylate) is 58 °C; T_g of poly(1*H*,1*H*,5*H*-octafluoropentyl methacrylate) is 36 °C.

(34) Ramharack, R.; Nguyen, T. H. *J. Polym. Sci. Part C: Polym. Lett.* **1987**, *25*, 93.

(35) Johnson, R. E.; Dettre, R. H. In *Surface and Colloid Science*; Matijeviæ, E., Ed.; Wiley-Interscience: New York, 1969; Vol. 2, pp 85−153.

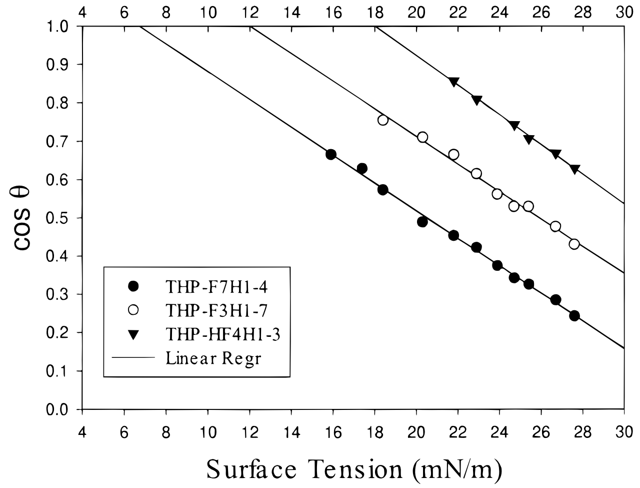

Figure 3. Zisman plots of THPMA−FqHpMA versus selected hydrocarbon and silicone liquids.

Table 4: X-ray Photoelectron Spectroscopy Results of Block Copolymers

sample	bulk[a] C%	bulk[a] F%	bulk[a] O%	surface α = 55° C%	surface α = 55° F%	surface α = 55° O%	surface α = 55° CF_3 + CF_2/C_{total}%
THP−F3H1-7	54.1	30.8	15.1	47.7	39.4	12.9	32.0
THP−HF4H1-2	60.0	23.0	17.0	45.8	40.9	13.3	30.7
THP−HF4H1-3	57.0	27.4	15.6	43.5	45.2	11.3	37.0
THP−F7H1-7	65.9	14.0	20.1	33.4	56.9	7.7	47.1
THP−F7H1-2	55.0	30.8	14.2	40.3	51.6	8.0	46.1
THP−F7H1-3	52.1	35.2	12.7	35.1	58.3	6.6	53.0
THP−F7H1-4	47.8	42.8	10.4	33.5	60.4	6.1	49.9
THP−F3H1-7[b]				40.6	48.0	11.4	29.9
THP−HF4H1-2[b]				43.8	44.9	11.3	33.4
THP−HF4H1-3[b]				42.1	47.3	10.6	37.5
THP−F7H1-7[b]				36.9	53.4	9.7	42.5
THP−F7H1-2[b]				35.0	58.5	6.5	50.0
THP−F7H1-3[b]				33.5	59.7	6.7	48.9
THP−F7H1-4[b]				34.0	59.7	6.3	47.3

[a] Compositions were calculated from ^1H NMR data. [b] Block copolymers were annealed at 140 °C for 48 h.

TFT, the polar solvent THF is not a selective solvent for the fluoromethacrylate block, thus limiting complete microphase separation. Different surface groups, CF_3, CF_2, and CH_3, may populate the surface, which shows no preferential ordering with changing side chain length. On the other hand, TFT is a good solvent for the fluorinated block. In this solvent, phase separation is more complete and the fluorinated methacrylate block dominates the surface. With annealing above the T_g's of fluoromethacrylate blocks, the fluorinated side chains better self-organize on the surface and decrease contact angle hysteresis, which is sensitive to chemical heterogeneity and surface roughness. The consistently high receding contact angles of THP−F7H1MA indicate that the extent of CF_3 group coverage is better with the longer, more rigid perfluorinated side chain. The critical surface tensions were extrapolated from Zisman plots (see Figure 3and Table 3). Consistent with the water contact angle results, THP−F7H1MA had a very low critical surface tension, ~7.0 ± 0.4 mN/m, much lower than that of F7H1MA homopolymer, ca. 11dyn/cm.[34]

The importance of surface chemistry on these materials becomes quite evident when slightly changing the fluorinated CF_3 end group to a CF_2H function.[18,20,36] With three $-CF_2-$ units and a CF_2H segment cap, sample THP−HF4H1MA had advancing and receding water contact angles of ~96° and 88°, respectively. Annealing had some affect on THP−HF4H1MA cast from TFT, but the use of a different solvent, either THF or TFT, showed no big difference. With either a shorter perfluorinated side chain or a CF_2H end group, the THP−F3H1MA and THP−HF4H1MA block copolymers had higher extrapolated critical surface tensions of 12.2 ± 0.2 and 18.3 ± 0.3 mN/m, respectively.

Huang and co-workers have measured the surface tension of a series of fluorinated liquid-crystal films with different fluorinated end groups and a hydroalkyl group, $C_{11}H_{23}$, on the other end of the molecules.[20] They found that for compounds with $CH_2C_3F_7$, $CH_2C_4F_9$, and $CH_2(CF_2)_3CF_2H$ end groups, the values of surface tension were 14.6 ± 0.2, 14.0 ± 0.2, and 18.3 ± 0.3 mN/m, respectively. With only simple atom replacement to transform the CF_3 to the CF_2H end group, the surface tension is increased by more than 20%. The surface tension for Huang's compounds with $CH_2(CF_2)_3CF_2H$ end groups is similar to our data from annealed THP−HF4H1MA. In the case of the $CH_2C_3F_7$ side chain, although our polymers have no liquid-crystal properties to direct the orientation of CF_3 groups, domination of the surface by CF_3 groups may still be inferred. In contrast, Huang et al. measured the surface tension of a free-standing liquid-crystal film, in which there was no preferential ordering of molecular "heads" (CF_3) or "tails" (CH_3), resulting in a surface tension relatively higher than that of the phase-separated THP−F3H1MA. When replacing the end group from CF_3 to CF_2H, the hydrophobicity of the fluorinated side chain is dramatically decreased and the phase separation of THP−HF4H1MA is not complete. THP−HF4H1MA behaves like Huang's compounds, with different end groups competing for surface coverage, and the surface tension is higher than that of a uniformly packed CF_2H surface, 15 dyn/cm.[19,36,18]

Block copolymers with various volume ratios were synthesized to optimize their solubility in supercritical CO_2. It was found that the microstructure did not have an important effect on the water contact angles and the surface tension, even when the fluorinated block was a minority phase. According to Langmuir's *principle of independent surface action*,[16] the surface wettability is determined by the nature and arrangement of surface atoms and groups. We may infer that the surface compositions of block copolymers with the same monomer in the fluorinated block are nearly identical to each other despite the different bulk compositions.

To further understand the nature of the solid-state surfaces, some preliminary work on X-ray photoelectron spectroscopy (XPS) has been carried out (see Table 4). At a takeoff angle of 55°, corresponding to a depth of 6.6 nm, for THP−F7H1MA, we found a remarkable enrichment of fluorine at the surface. Although the fluorine composition in the bulk block copolymers ranged from 14% to 43%, the surface fluorine fractional content for the many fluorinated block copolymers was very close, changing from 52% to 60% and the CF_3 peak intensity was much larger than that of the hydrocarbon peak. This measurement confirms our conclusion de-

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rived from water contact angle measurements that the surface is dominated by trifluoromethyl groups when the polymer has a longer fluorinated side chain of about seven $-CF_2-$ units or more. Ideally, the more CF_3 groups on the surface, the lower the surface energy, the higher the contact angle, and the smaller the hysteresis.[18] For THP−F3H1MA, the fluorine content on the surface (39%) is just slightly higher than that of the bulk (31%) whereas the $CF_3 + CF_2$ total carbon content is lower than that of THP−F7H1MA. For THP−HF4H1MA, the surface fluorine content (41−45%) is higher than that of the bulk (23−27%) but lower than the surface fluorine content of THP−F7H1MA. Although its surface fluorine content is close to that of THP−F3H1MA, the surface energy of THP−HF4H1MA is much higher. This again indicates that differences of surface tension are mostly due to the specific end groups on the THP−HF4H1MA surface.

Surface Stability and Thermal Cross-Linking. As a result of the great interest in low-surface-energy materials, many fluorinated polymers have been studied, but most of them have a common problem: surface reconstruction. As low-surface-energy materials, the surface stability of our fluorinated block copolymers is a very important issue. First, the film cast on silicon wafer was immersed into water but was found to form a very unstable surface. The film came off the silicon wafer after 1 day due to the poor adhesion between the polymer and Si wafer in water.

Several strategies exist for forming stable, low-energy surfaces. It has been previously reported by our group that smectic B packing of a semifluorinated liquid-crystal polymer can stabilize surface properties.[8] Water castable, fluorinated coatings have also been described that derive their surface stability from cross-linking carboxylic acid groups with oxazoline rings to form amide−ester bonds.[21] The perfluoroalkyl groups are thus immobilized on the surface so that water wettability and hysteresis decreases with increased cross-linking density and film toughness is improved. Thermal treatment of the block copolymers of this study has also been found to form stable surfaces evidently by cross-linking the underlying domains of the nonfluorinated block.

The homopolymer of THPMA is known to be sensitive to heat and acid. From TGA study, the block copolymers were found to start decomposition around 140 °C at a heating rate of 10 °C/min. It has been reported that after heating at 140 °C for 48 h, tetrahydropyranyl group may be completely removed from polymers.[37] The block copolymers were heated at 140 °C for either 3 or 48 h, and water contact angles were measured (see Table 5). They showed no difference compared to those before deprotection. Then, they were immersed into water for 2 weeks to study their surface stability (see Figure 4). It was found that after this treatment the films did not come off the Si wafer and the water contact angles did not drop dramatically after the film was immersed in water. For films heated at 140 °C for 3 h, advancing water contact angles of deprotected THP−F7H1MA decreased ~20° over 11 days, whereas those of the deprotected THP−F3H1MA decreased ~30 degrees. The receding contact angles of both of them decreased more than 30°, depending on composition.

Table 5: Water Contact Angles of Block Copolymers Heated at 140 °C for Different Time Periods

	3 h		48 h	
original polymer	adv.	rec.	adv.	rec.
THP-*b*-F3H1-1	110	88	110	93
THP-*b*-F3H1-5	110	93	110	93
THP-*b*-F3H1-6	110	95	109	93
THP-*b*-F3H1-7	111	95	109	96
THP-*b*-F7H1-7	118	107	119	109
THP-*b*-F7H1-2	118	108	119	113
THP-*b*-F7H1-3	118	107	119	111
THP-*b*-F7H1-4	119	108	121	114
THP-*b*-HF4H1-2			96	87
THP-*b*-HF4H1-3			96	88

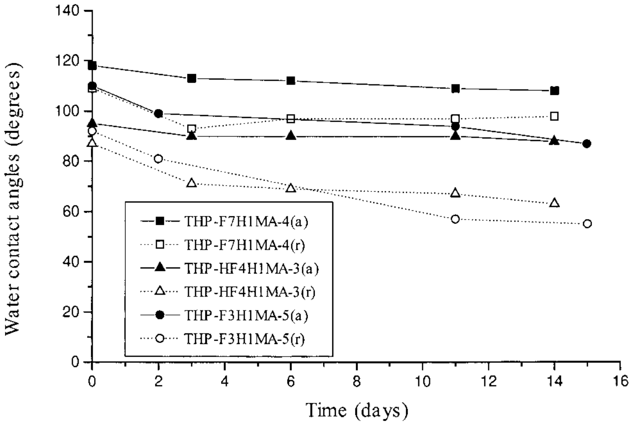

Figure 4. Time-dependent advancing (a) and receding (r) water contact angles of deprotected block copolymers (140 °C, 48 h). Before thermal treating, the film fell off the silicon substrate after being immersed in water for 1 day.

It was expected there would be a significant change of advancing contact angles because acid would form after removal of the tetrahydropyranyl group. The films annealed for 48 h were even more stable. After 15 days, the advancing water contact angles of deprotected THP−F7H1MA, THP−HF4H1MA, and THP−F3H1MA dropped only about 15, 10, and 20°, respectively; the receding angles dropped 15−30, 20, and 30−40°, respectively. It was also found that before deprotection the polymer films were soluble in THF or TFT, whereas after deprotection, the films were insoluble in common organic solvents or water but could be dissolved in an aqueous base, tetramethylammonium hydroxide. The deprotected homopolymer of THPMA was used for comparison. Before decomposition, the poly(THPMA) very easily dissolved in water. The advancing and receding water contact angles were 91° and 57° respectively. After deprotection at 140 °C for 48 h, the film no longer dissolved in water and had advancing and receding water contact angles of 97° and 42°, respectively.

XPS data were compared before and after deprotection (see Table 4). It was found that, except for the deprotected THP−F3H1MA film, the surface fluorine content (*F*%) measured at a takeoff angle of 55° showed almost no change after the deprotection annealing, which meant that the surface composition was unaffected by the change of bulk composition. Although the XPS measurements in our report were done at one takeoff angle, it was expected that the fluorine content

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(37) Patrickios, C. S.; Hertler, W. R.; Abbott, N. L.; Hatton, T. A. *Macromolecules* **1994**, *27*, 930.

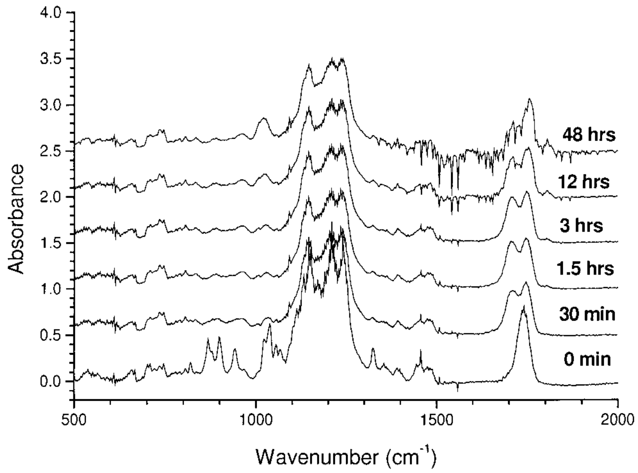

Figure 5. Time-dependent FT-IR spectra of thermal deprotection of THP−F7H1-2 at 140 °C for 48 h. The film was coated on a double-polished Si wafer.

would increase with smaller takeoff angles (decreasing probing depth), and a similar trend would be observed on the surface. By taking advantage of the powerful technique of near-edge X-ray absorption fine-structure (NEXAFS), it is possible to study the end group orientation within the top 2 nm surface.[38,39] From our recent NEXAFS results, it may be clearly shown that for THP−F7H1MA the surface CF_2 segment was oriented toward the surface tilted only slightly from the sample normal for both samples before and after thermal deprotection. This molecular ordering was not observed in the systems of THP−F3H1MA and THP−HF4H1MA. More detailed results will be presented in the future.

On the basis of our knowledge of the thermal cross-linking of acid and the FT-IR data, we believe that acid anhydride was formed during heating of polymer films. According to the literature,[40] after poly(methacrylic acid) is heated in a vacuum at 200 °C, it loses water and dehydrates to form a nonvolatile product. This residue is insoluble in common solvents, such as water and methanol, but it can dissolve in concentrated base. From FT-IR data, Grant and Grassie suggested that anhydride was formed and that the six-membered glutaric anhydride was more predominant than the isobutyric type. Taylor and co-workers[22] also confirmed the formation of both intra- and intermolecular anhydrides by heating a copolymer of benzyl methacrylate−methacrylic acid (after removal of the tetrahydropyranyl group) at 190 °C. To avoid the possible decomposition of the fluorinated side chain at such a high temperature, we monitored THP−F7H1MA-2 at 140 °C by time-resolved FT-IR for 48 h. The polymer film was coated on a double-polished Si wafer (see Figure 5). It was found that after 30 min acid was generated. With decreased peak intensity at 1740 cm^{-1} (ester $v_{c=o}$), a peak at 1712 cm^{-1} (dimerized acid $v_{c=o}$) appeared. After 1.5 h, a very small peak appeared at 1806 cm^{-1} (anhydride $v_{c=o}$) and increased during next 40 h; the stretching of C=O band shifted to 1755 cm^{-1}; the peak at 1037 cm^{-1} (ν_{O-C-C}) decreased during isothermal heating and a broad new peak around 1025 cm^{-1} (ν_{C-O-C}) appeared and increased. All of these indicated the acid anhydrides were formed.

There are different mechanisms and structures for acid anhydride formation, including formation of intramolecular six- or five-membered anhydride rings and production of intermolecular anhydrides. As a result of less ring strain, the six-membered rings usually show absorption at frequencies lower than those of five-membered rings and have the least separation of carbonyl frequencies. The small separation (51 cm^{-1}) and higher intensity at lower frequency (1755 cm^{-1}) suggests that the glutaric type anhydride is the predominant structure in our annealed polymers. Their insolubility in THF and water indicates the existence of cross-linking by the acid anhydride. Longer annealing times at 140 °C lead to more complete anhydride formation and higher cross-linking density. Both cross-links and the stiffness of the anhydride structure prevent diffusion of water into the polymer films, whereas polar groups are anchored in the underlayer created by the microphase. The polar groups are unable to rise to the surface to interact with polar liquids such as water so that the surface remains populated by nonpolar CF_3, CF_2, or CF_2H end groups, thus creating a more stable low-energy surface. The greater the cross-link density, the lower the surface reconstruction. The better adhesion between cross-linked polymer films and the Si wafer may be explained by interaction between −OH groups on the hydrophilic Si surface and some free acid, formed in the early stages of heating. Combining these observations with data from XPS studies, they suggest that the surface properties are stabilized after thermal deprotection and cross-linking, and the surface stability is improved by altering the structure of the supporting underlayer in the bulk.

Conclusions

A series of low-surface-energy, fluoromethacrylate block copolymers were synthesized. By varying the length of the fluorinated side chain, the surface properties may be changed. These polymers also tend to form micelles in common organic solvents. The polymers with six $-CF_2-$ units and a CF_3 end group showed the lowest critical surface tension, ~7 mN/m. Simply replacing the CF_3 end group with CF_2H groups greatly changes the surface properties. The relative volume ratios of different block copolymers do not appear to affect the critical surface tension. After removal of the thermally labile groups (THP−) in these polymers, acid and acid anhydride groups are produced. Thermal cross-linking of these groups leads to both better adhesion and surface stability in these polymers.

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