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Fluorinated Polymers: Liquid Crystalline Properties and Applications in Lithography

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ABSTRACT: Fluorinated polymers form an interesting class of materials with a wealth of unique properties including self-assembly, remarkably low surface energies, low absorbance to 157 nm UV light, and solubility in supercritical carbon dioxide. As a result many fluorinated polymers are of use in advanced technology applications. We review some of our work on the synthesis and characterization of block copolymers with fluorinated side chains, with special emphasis on surfaces formed using these polymers. The use of fluorinated polymers as photoresists for 157 nm lithography, with the possibility for processing in environmentally friendly supercritical carbon dioxide is also discussed. © 2004 The Japan Chemical Journal Forum and Wiley Periodicals, Inc. Chem Rec 4: 315–330; 2004: Published online in Wiley InterScience (www.interscience.wiley.com) DOI 10.1002/tcr.20022

Key words: fluorinated polymer; liquid crystalline block copolymers; self-assembly; low-energy surfaces; hydrophobic surfaces; 157 nm photoresist; supercritical carbon dioxide

Introduction

Fluorinated polymers have many unique characteristics, among which the oleophobic–hydrophobic nature of fluorinated polymer surfaces and their remarkable chemical resistance stand out. These properties arise due to the low intermolecular forces present in highly fluorinated organic compounds. Fluorine is the most electronegative element with a Pauling electronegativity value of 3.98, compared to 2.20 for hydrogen, and 2.55 for carbon.[1] Despite the polar nature of the C—F bond because of the high electronegativity of fluorine compared to carbon, perfluorinated linear alkanes and polymers such as poly(tetrafluoroethylene) (PTFE) ideally have no permanent dipole moment due to the symmetric distribution of charge in these molecules. The nonpolar nature of fluorinated polymers confers a range of properties, including water repellence, solubility in supercritical carbon dioxide, and low dielectric constant. Fluorinated polymers, by virtue of their low dielectric constant, good dimensional stability, good high-temperature stability, and low moisture absorption and low outgassing are being considered as interlayer dielectric materials to separate different circuit layers in microelectronic devices.[2] Recent reviews have also discussed the synthesis and properties of commercial semicrystalline fluorinated polymers[3] and the self-assembly of fluorinated block copolymers.[4]

This paper will review our research on fluorinated side-chain liquid crystalline polymers, the molecular structure of surfaces formed from these polymers, and applications of fluorinated polymers in marine antifouling coatings, photoresists

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for 157 nm lithography, and lithographic processing in supercritical carbon dioxide.

Fluorinated Polymers for Low-Energy Surfaces

In general, the wettability of an organic surface is determined by the nature and packing of the surface atoms or chemical groups.[5] The presence of nonpolar —CH_3 or —CF_3 groups at the surface lowers the surface energy, or water wettability of a surface. The surface energy decrease occurs in the order $\text{—CH}_2\text{—} > \text{—CH}_3 > \text{—CF}_2\text{—} > \text{—CF}_3$. This decrease is mainly due to an increase in chemical group size. Thus, the —CF_3 group with a hemispherical volume of $42.6\,\text{Å}^3$ covers the surface to a greater extent than the —CH_3 group with a hemispherical volume of $16.8\,\text{Å}^3$, and minimizes the interaction of water with any underlying polar groups.[3] Consequently, a surface that is densely packed with —CF_3 groups will show low surface energy, producing high water contact angle. However, self-assembled monolayers (SAMs) of $CH_3(CH_2)_nSH$ and $CF_3(CH_2)_nSH$ ($n = 9$ to 15) on gold have been reported to behave differently.[6] The advancing contact angle of water on SAMs with terminal —CF_3 groups was about 110°, lower than that of the SAMs with terminal —CH_3 groups ca. 115°. This was attributed to the dipole–oriented-dipole interactions between water molecules and the —CF_3 groups at the interface.

Liquid-Crystallinity in Perfluoroalkanes

Because of the larger van der Waals radius of the fluorine atom compared to the hydrogen atom, poly(tetrafluoroethylene) has a helical structure in the crystalline state, instead of the planar,

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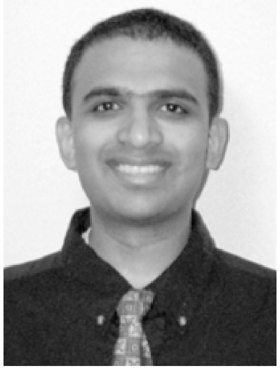

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fully extended, zig-zag conformation of polyethylene.[7] In the planar conformation, the distance between two fluorine atoms separated by two C—C bonds would be 2.54 Å, which is considerably lower than twice the van der Waals radius (1.4 Å) of the fluorine atom. On the contrary, in the helical conformation obtained by twisting each CF_2—CF_2 bond through an angle of about 17° from the planar *trans* position, this distance is 2.7 Å. Due to reduced van der Waals repulsion, the helical conformation is thermodynamically favored. The greater steric repulsions between non-bonded fluorine atoms also cause the potential barrier (4.0 kcal/mol) to rotation about the C—C bond in hexafluoroethane to be considerably larger than that for ethane (3.0 kcal/mol). It is to be expected, therefore, that perfluoroalkanes will have a rigid, rod-like conformation, which imparts liquid crystalline properties to these molecules. Rabolt et al. were among the first to report the detailed synthesis of low molar mass semifluorinated materials and recognized the mesogenic character of short CF_2 segments.[8] Semifluorinated alkanes, $F(CF_2)_m(CH_2)_nH$, and semifluorinated alkyl side groups in polymers show a strong tendency to form a smectic phase, and in this respect, are unique phenyl-free mesogens.[9,10]

Liquid-Crystalline Fluorinated Block Copolymers

Polymers with Linear Semifluorinated Side Chains

We have used the strategy of modifying anionically prepared polystyrene-*block*-polyisoprene with pendent double bonds and narrow molecular weight distributions to obtain block copolymers with semifluorinated (SF) side chains. Some of our early work has been described in a review by Reisinger and Hillmyer[11] which involved the addition of perfluoroalkylsilane groups to the double bonds of the isoprene block in the presence of platinum catalyst.[12] In the case of polyisoprene (PI), 95% of the pendent double bonds arising from 1,2-addition underwent the hydrosilylation reaction, while only 25% of the double bonds arising from 3,4-addition reacted. An improved procedure resulted in near quantitative conversion of the double bonds of poly(1,2-butadiene).[13] Hydroboration of the pendent vinyl groups using 9-borobicyclo[3.3.1]nonane (9-BBN) followed by oxidation with hydrogen peroxide is a facile way to quantitatively introduce hydroxyl group in the diene block.[14,15,16] Fluorinated block copolymers with a deuterated styrene block (*d*-PS) were prepared by reacting the hydroxyl groups of the isoprene block with heptafluorobutyryl chloride or 1H,1H,2H,2H-perflurooctyldimethylchlorosilane. Reaction of the former in the presence of pyridine was almost quantitative, while only ca. 60% of the hydroxyl groups coupled with the silane. The *d*-PS fluorinated block copolymer was blended with a higher molecular weight protonated PS homopolymer, and its kinetics of segregation to the polymer–air interface was determined by measuring the volume fraction of *d*-PS as a function of depth using forward recoil spectrometry.[17,18] In the case of the polymer with the heptafluorobutyryl side groups, it was found that the segregation was fairly rapid with an initial *d*-PS volume fraction of 5% (in bulk), with the equilibrium segregation achieved in about 50 h. However, at an initial *d*-PS volume fraction of 10%, the time required to attain the equilibrium distribution was found to be about 150 h. The slower equilibration was attributed to the formation of block copolymer micelles in the bulk. The advancing water contact angle increased with an increase in the equilibrium bulk volume fraction of *d*-PS, ϕ_∞, from about 90° and reached a plateau value of ca. 105° for $\phi_\infty \geq 0.02$. The receding contact angle was ca. 90°. The water contact angle on a surface, where the surface groups are predominantly —CF_3, is usually greater than 120°. For example, Graupe et al. found that the water contact angle on a highly

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ordered SAM of $F(CF_2)_m(CH_2)_nSH$ on gold was ca. 126° (for $m = 4$, $n = 12$, and $m = 10$, $n = 6$).[6] The lower contact angle of 105° is indicative of the fact that the block copolymers with heptafluorobutyryl side groups did not form a highly ordered surface covered by the terminal —CF_3 groups. The block copolymers prepared using the fluorinated silane, also did not give an advancing contact angle greater than 105°.

Wang et al. [10] prepared a series of semifluorinated alcohols, $F(CF_2)_m(CH_2)_nOH$, using the radical addition reaction[19] of perfluoroalkyl iodides to ω-alken-1-ols. The alcohols were then oxidized with nitrogen dioxide, and the resulting acids were converted to acid chlorides using thionyl chloride. The semifluorinated acid chlorides were then reacted with the hydroxylated PS/PI block copolymer to obtain quantitative attachment of the semifluorinated groups to the hydroxylated PI block. Differential scanning calorimetry of these block copolymers showed two distinct and reversible, first-order transitions at temperatures T_1 and T_2, with corresponding enthalpies ΔH_{m1} and ΔH_{m2}. Self-assembled films of these polymers were cast on silicon wafers from a 2% solution of the block copolymers in α,α,α-trifluorotoluene. Advancing and receding water contact angles were measured on these films, and the critical surface tension of the surfaces were determined from the Zisman plots using linear alkanes and low molecular weight methyl terminated poly(dimethylsiloxane)s. The results are shown in Table 1. The volume fraction of the fluorinated block was close to 0.55, and the block copolymers showed the expected lamellar morphology.[20] Furthermore, the lamellae of the fluorinated blocks had an internal structure. Powder X-ray diffraction measurements on the block copolymers showed that below the lower transition temperature, T_1, the rod-like helical semifluorinated side were arranged in a high order head-to-head bilayer smectic-B (S_B) phase. Upon heating, the hexagonal arrangement of the mesogens is disrupted and a low-order smectic-A (S_A) phase is formed. The temperature T_1 corresponds to the transition from S_B phase to S_A phase, while temperature T_2 corresponds to the transition to an isotropic phase. The increase in T_1 and T_2 for every additional —CF_2— group in the side chain was greater than the increase for every increment of —CH_2— group (20 ± 5°C versus 2.3 ± 1.8°C). The enthalpy of phase transition (per mole of mer in the fluorinated block) from S_B to S_A increased by ca. 1.1 kJ/mol per —CF_2— group and ca. 0.9 kJ/mol per —CH_2— group in the side chain. The transition enthalpy for S_A to isotropic phase did not vary with the number of —CF_2— or —CH_2— groups in the side chains. The S_A to isotropic phase transition temperature, T_2, is close to the melting temperature of the corresponding alcohols. For example, the melting temperatures of $F(CF_2)_8(CH_2)_{10}OH$ and $F(CF_2)_{10}(CH_2)_{10}OH$ are 78°C and 103°C, respectively, while the values of T_2 for block copolymers with side chains obtained from these precursors are 72°C and 114°C. However, the transition enthalpies, ΔH_{m2}, were rather low compared to the enthalpy of melting (29.4 kJ/mol and 21.3 kJ/mol, respectively) of the semifluorinated alcohols. This could be because of the restricted ability of the side groups to form a well-packed crystalline phase, since they are attached to the polymer backbone.

Surface Orientation

While the X-ray scattering data indicated that the lamellae were oriented parallel to the substrate surface, and the SF side groups preferred to pack so that they were parallel to the lamellae (Figure 1), the contact angle data shown in Table 1 suggested that the surface of the polymer was mainly occupied by —CF_3 groups. This would be possible only if the SF side groups were oriented more or less normal to the surface. If the side groups lay parallel to the surface, the surface would consist of —CH_2—, —CF_2— and even the polar carbonyl groups, besides the —CF_3 groups, which would result in advancing water contact angles below 120° and higher critical surface tension values. Clearly, the SF side groups did not have the same orientation at the surface as in the bulk. These fluorinated surfaces were highly resistant to surface reconstruction[21] in water, most probably due to the stabilizing influence of a S_B

Table 1. Effect of side chain on the properties of semifluorinated side chain block copolymers.

						Water contact angle			
m	n	T_1 (°C)	T_2 (°C)	ΔH_{m1} (kJ/mol)	ΔH_{m2} (kJ/mol)	Adv	Rec	Critical surface tension (mN/m)	$\langle \tau_{F\text{-helix}} \rangle$
6	10	19.9	31.3	4.13	0.56	111°	86°	10.8	46°
8	4	39.7	61.0	1.61	0.56	120°	109°	8.5	33°
8	6	47.8	66.7	3.13	0.72	120°	108°	8.5	35°
8	10	49.9	72.2	6.78	0.62	122°	110°	8.2	43°
10	10	97.1	114.4	8.72	0.59	123°	112°	8.0	38°

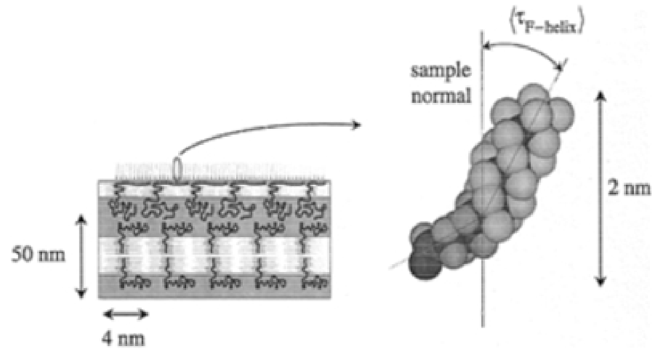


Fig. 1. Schematic illustrating the organization of the SF side groups [—CO—$(CH_2)_{n-1}$—$(CF_2)_mF$] in bulk and on the surface of the SF polymer film made of a symmetric PS/SF–PI diblock copolymer that exhibits lamellar morphology in the bulk. Reproduced with permission from Macromolecules 2000, 33, 1882. Copyright 2000 Am. Chem. Soc.

liquid crystalline ordered surface formed by the SF side groups. The near-surface orientation of the SF side groups were studied using Near-Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy, a technique that involves a polarized X-ray beam to probe the molecular composition and orientation of the top 5 nm of a surface.[20,22] The angle, θ, between the sample normal and the polarization vector of the X-ray beam was varied. From the variation of the intensity of the peak originating from the X-ray excitation of the carbon 1s electron to the σ^* orbital of the C—F bond with θ, the angle made by the fluorocarbon part of the SF side chain with the surface normal, called the average tilt angle of the fluorocarbon helix and denoted by $\langle\tau_{F\text{-helix}}\rangle$, was calculated (Figure 1). These values are also given in Table 1. An increase in the length of the fluorocarbon part of the SF side group leads to a smaller $\langle\tau_{F\text{-helix}}\rangle$. Similarly, decreasing the length of the hydrocarbon spacer leads to smaller $\langle\tau_{F\text{-helix}}\rangle$. Although the surfaces for the contact angle measurements were not annealed, while the surfaces for NEXAFS experiments were annealed in vacuum at 150°C, it can be concluded from Table 1 that a lower $\langle\tau_{F\text{-helix}}\rangle$ leads to higher water contact angles and lower critical surface energy. This is possibly due to the fact that the surface is packed to a greater extent with —CF_3 groups if the side chains are normal to the surface, that is, the tilt angle is low. X-ray Photoelectron Spectroscopy (XPS) results of intensity versus energy over a profiling depth of 4.5 nm (at a take-off angle of 35°) also confirmed that the surface region of the block copolymer ($m = 8$, $n = 6$) was almost exclusively the fluorinated block.[23]

Effect of Temperature on Surface Orientation

The temperature dependence of molecular orientation of the SF side chains was investigated using NEXAFS spectroscopy.[24] In the case of the block copolymer with —CO—$(CH_2)_3$—$(CF_2)_8F$ side groups ($m = 8$, $n = 4$ in Table 1), there were two temperature regions in which the surface orientation of the SF mesogens changed abruptly. The phase transitions at the surface occurred at higher temperatures than those in bulk. The first drop in surface orientation was attributed to the surface S_B to S_A transition. The second drop in the surface orientation occurred around the S_A to isotropic phase transition temperature in the bulk (ca. 61°C). However, even 30°C above this temperature, the surface orientation did not become completely isotropic. The surface orientation persisted well above the isotropic transition temperature in the bulk. The observed decrease in the orientation was attributed to the disordering produced in the surface layer when the subsurface mesogens became isotropic.

Effect of End Groups

The effect of changing the end group of the SF side chains from —CF_3 to —CF_2H was also investigated using NEXAFS and contact angle measurements.[25] The SF side groups were —CO—$(CH_2)_{10}$—$(CF_2)_m$—H or —CO—$(CH_2)_9$—$(CF_2)_m$—F, where $m = 8$ or 10. The water contact angles were significantly lower for the side chains with terminal —CF_2H groups. For example, the advancing and receding contact angles for the block copolymer with —CO—$(CH_2)_{10}$—$(CF_2)_{10}$—H side chains were 102° and 89°, respectively, instead of 123° and 112°, respectively, in the case of —CO—$(CH_2)_9$—$(CF_2)_{10}$–F side chains. The higher surface energy in the case of side chains with —CF_2H end groups was also reflected in the critical surface tension value being 16.5 mN/m compared to 8.0 mN/m with —CF_3 end group. This is possibly because of the more polar nature of the —CF_2H group than the —CF_3 group. The stability of the surface toward surface reconstruction was studied by immersion of the films in water for 4 weeks at room temperature. The water contact angles decreased to 70° and 60° after this period. X-ray and thermal measurements showed that block copolymers with —CF_3 end groups formed more stable and ordered mesophases than those with —CF_2H end groups, and were less prone to surface reconstruction.

Polymers with Semifluorinated Monodendron Side Groups

Semifluorinated monodendrons as side groups are expected to provide a greater coverage of the surface with —CF_3 groups by virtue of their size, than a simple semifluorinated side chain. Each monodendron can act as an "umbrella" and mask the underlying polar groups, producing a stable, hydrophobic surface. Figure 2 shows block copolymers with semifluorinated three armed and two armed monodendrons as side groups.

Xiang et al.[26] synthesized block copolymers with semifluorinated monodendron side groups using a convergent growth strategy. High attachment of the 2- or 3-armed monodendron acid chloride to hydroxylated poly(styrene-*b*-1,2/3,4-isoprene) was possible despite the steric hindrance of the bulky monodendron side groups. X-ray scattering data indicated that the polymers formed a smectic B mesophase at room temperature. Unlike the block copolymers with single SF side groups, DSC data indicated only a single first-order transition corresponding to the smectic B mesophase to the isotropic state. The transition temperature and enthalpy of the S_B to isotropic transition were affected by factors such as the length of the alkyl spacer, length of the mesogen, and the monodendron core. Table 2 compares the properties of the block copolymers with semifluorinated 2- and 3-armed monodendrons with those having simple (single-arm) SF side groups, —CO—(CH$_2$)$_{p\text{-}1}$—(CF$_2$)$_q$—F. When the number of fluorinated carbons was eight or more, it was found that all block copolymers with monodendron side groups had surface energies in the range 7–9 mN/m regardless of either the extent of attachment, or the monodendron structure. These values are close to the known critical surface tension of a uniform —CF$_3$ surface formed by monolayers of perfluorocarboxylic acids (e.g., 8.6 mN/m for perfluorohexanoic acid, and 7.9 mN/m for perfluorooctanoic acid).[27]

Sivaniah et al.[28] found that the block copolymers with semifluorinated three-arm monodendron side-groups ($p = 10$, $q = 8$) formed periodic surface structures that resembled domes with a radius of curvature of ca. 36 nm. The degree of organization and monodispersity of the sizes of these domes was related to the rate at which the samples were cooled from the isotropic to the smectic B phase. With slow cooling rates, it was possible to obtain ordering over a length-scale of a micron. The average center-to-center distance of these domes was remarkably constant (~18.5 ± 1 nm), irrespective of the relative lengths of the two blocks, or the degree of attachment of the monodendrons to the PI—OH block.

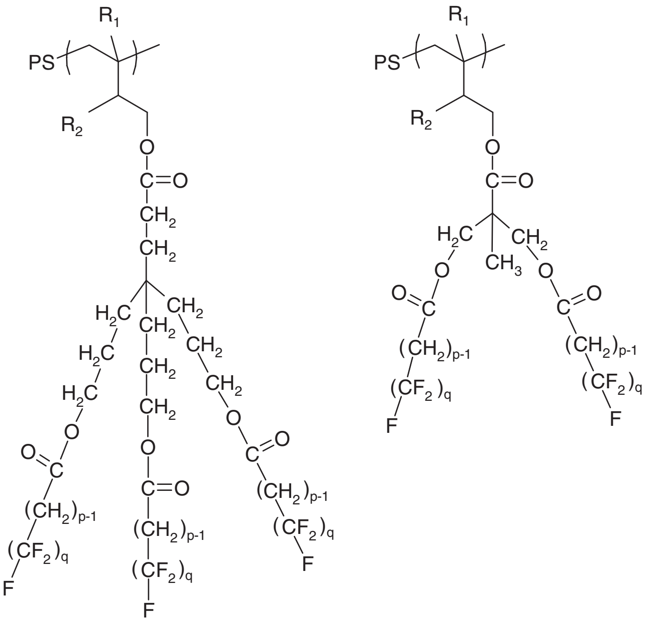


Fig. 2. Block copolymers with three-armed and two-armed monodendron semifluorinated side groups, where PS is the polystyrene block, R$_1$ = H (or CH$_3$), and R$_2$ = CH$_3$ (or H).

Polymers with Semifluorinated Aromatic Side Groups

Semifluorinated side groups containing a phenyl ring are expected to show enhanced self-assembly behavior compared to semifluorinated linear alkyl groups. Andruzzi et al. synthesized block copolymers with these mesogens by two different methods: attachment of semifluorinated acyl chlorides to hydroxylated poly(styrene-*b*-1,2/3,4-isoprene) and controlled free radical polymerization of 4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)oxymethylstyrene monomer (Figure 3),[29] and studied the bulk structure and surface orientation of these polymers.[30] Triblock copolymers with PS end blocks were also prepared by controlled radical polymerization. These polymers showed different morphologies such as highly ordered hexagonal cylinders, worm-like cylinders lacking in orientation, spheres of

Table 2. Properties of block copolymers with semifluorinated monodendron side chains.

p	q	No. of arms	Degree of attachment to PI-OH block (%)	T_1 (°C)	T_2 (°C)	Water contact angle Adv	Water contact angle Rec	Critical surface tension (mN/m)
10	8	1	~100	49.9	72.2	122°	110°	8.2
10	10	1	~100	97.1	114.4	123°	112°	8.0
10	8	2	66	47.8	—	121°	103°	9.2
10	10	2	38	67.7	—	122°	110°	8.2
10	8	3	53	62.4	—	120°	108°	8.5
10	10	3	58	95.4	—	124°	110°	7.7

polystyrene phase arranged within a liquid crystalline matrix in a body centered cubic arrangement, lamellar morphology, and ellipsoidal domains of the LC domains in a polystyrene matrix, depending on the number of fluorinated carbons in the side chains, the number of blocks, and molecular weights of the different blocks. NEXAFS spectroscopy showed that the surfaces had a remarkably high —CF_2— helix orientational order parameter, $S_{\text{F-helix.}}$[31] As an example, for an alkyl side chain with 8 fluorinated carbons, the presence of an aromatic ring increased the order parameter from 0.29 to 0.335. The SF aromatic side-chain block copolymers contained side chains with relatively short —CH_2— spacers, restricting the flexibility of the side chains to self-assemble. However, the presence of the phenyl group seems to increase the intermolecular interactions between the mesogenic side-group, resulting in higher order parameters. The higher isotropic transition temperatures (~210°C), rather high advancing water contact angles (~130°) and high resistance to surface reconstruction upon water-exposure, are all consistent with the improved packing of the side groups. The surface structures of similar polystyrene–*block*-poly(4-(perfluorooctylpropyloxy)styrene) block copolymers have been recently studied by Yokoyama et al. using XPS and dynamic secondary ion mass spectrometry.[32] They found that the surface orientation of the C_8F_{17} side groups depended on the weight fraction of the fluorinated block in the block copolymer.

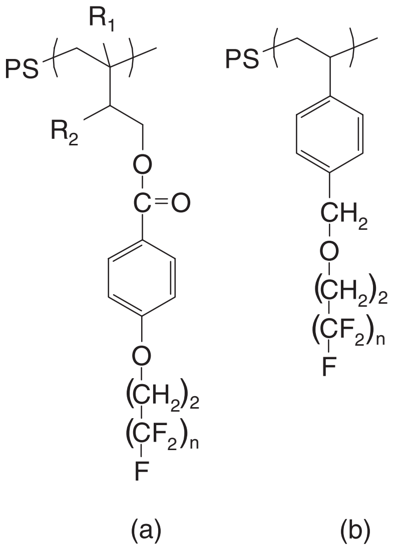


Fig. 3. Block copolymers with semifluorinated aromatic side groups. Polymers of type (a) were prepared by modification of anionically synthesized poly(styrene-*b*-1,2/3,4-isoprene), while those of type (b) were prepared by controlled radical polymerization; $R_1 = H$ (or CH_3) and $R_2 = CH_3$ (or H).

Gopalan et al.[33] prepared block copolymers with bulky fluorinated mesogenic groups attached to the polymer backbone without any spacers (Figure 4) by controlled free radical polymerization. The homopolymer of the liquid crystalline monomer had a glass transition temperature of 99°C, and an endothermic transition at 164°C ($\Delta H = 9.4$ kJ/mol) attributed to the smectic C (S_C) to nematic phase transition. X-ray diffraction results indicated a "herring bone" type packing arrangement in the smectic phase. In the block copolymer, the T_g of the fluorinated block was ca. 115°C, and the S_C to nematic transition temperature also increased to ca. 170°C. The wide-angle XRD results for the block copolymer were similar to those for the homopolymer. There was no significant change of the smectic layer spacing in the copolymer.

Pospiech et al. synthesized aromatic polyesters based on 5-hydroxy isophthalic acid with semifluorinated side chains and found that poly(*p*-phenylene isophthalate) with oxydecylperfluorodecyl side chains formed a self-organizing liquid crystalline structure that resulted in low values of surface free energy.[34,35]

Applications

Fluorinated Block-Copolymers as Surface Coatings for Marine Antifouling Applications

Youngblood et al. prepared glass microscope slides coated with block copolymers with SF side-chains.[36] These were bilayer

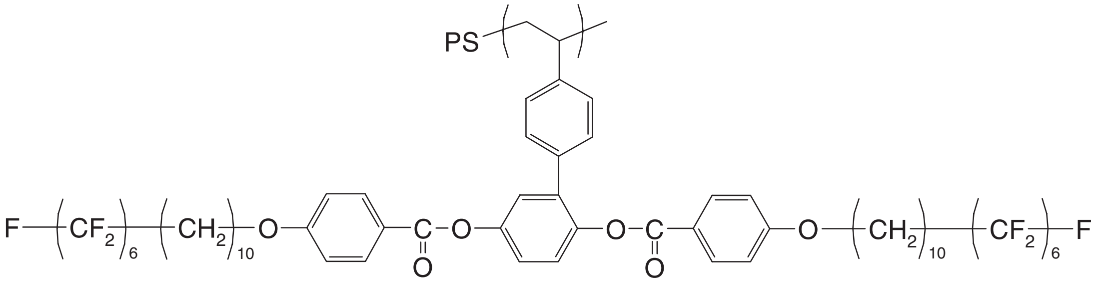


Fig. 4. Mesogen-jacketed[33] liquid crystalline polymer.

coatings with the lower layer consisting of a commercially available polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS) thermoplastic elastomer (Kraton 1652), and the upper layer was the fluorinated block copolymer. The role of the SEBS layer is to produce an elastomeric coating of sufficient thickness, while the top layer modified the surface energy. To avoid biofouling of a marine surface, the coating must have a low-modulus and low surface-energy, because the adhesion strength of a hard fouling organism, such as barnacle, is proportional to $(\gamma E)^{1/2}$ where γ is the surface energy and E is the modulus.[37] The SF groups were attached to the hydroxylated polyisoprene block via hydrolytically stable ether linkages. These surfaces were tested for settlement and removal of *Ulva* zoospores, a commonly encountered foulant. The slides were incubated in a suspension of the spores and were later exposed to a fully developed turbulent flow. The numbers of spores on the surfaces before and after the flow were determined. Approximately 70% of the spores were removed from this coating compared to ca. 20% from an uncoated glass substrate. Thus, the surfaces coated with the fluorinated block copolymers showed good fouling-release behavior. Hexemer et al. have characterized surfaces coated with block copolymers with semifluorinated 3-armed monodendron side groups.[38] The bilayer coatings, and the coatings obtained by spin-coating a blend of SEBS with the SF block copolymer, were characterized by contact angle measurements, atomic force microscopy, and NEXAFS spectroscopy. Uniform coverage of the surface by the SF block copolymer could be obtained by spin-casting a top layer as thin as 60 nm in the bilayer case, and using at least 10 wt % of the SF block copolymer in the blend. Smaller thicknesses of the top layer of the SF block copolymer, or lower contents in the blends resulted in islands of the fluorinated block, and incomplete surface coverage of the SEBS.

Patterning of Surface Functionality

Böker et al.[39] found that block copolymers with perfluorinated ester side chains underwent quantitative thermal ester cleavage at 340°C, with a loss of perfluorocarboxylic acid, leaving the backbone of the polymer completely intact. X-ray photoelectron spectroscopy (XPS) measurements of thin film samples of the fluorinated block copolymers after heating to 340°C for 15 min in a vacuum oven showed the absence of the fluorinated side chains on the surface of the visually unaltered polymer film. Thus, the advancing water contact angle dropped from 122° to 87° after thermal cleavage, in the case of a block copolymer with perfluorodecanoyl side chains. Since the thermal treatment can be carried out locally, surfaces with patterns of hydrophobic and hydrophilic areas can be produced. The thermal cleavage reaction results in vinyl groups that can be subjected to further chemical modification, giving chemically patterned surfaces.

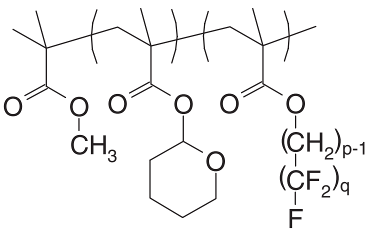
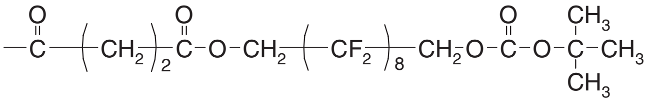


Fig. 5. Block copolymer of tetrahydropyranyl methacrylate and fluorinated methacrylates.



$$-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-CH_2-(CF_2)_8-CH_2O-\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

Fig. 6. *tert*-Butoxycarbonyl protected semifluorinated side chains.

Yang et al.[40] used group transfer polymerization to prepare block copolymers of tetrahydropyranyl (THP) methacrylate and several fluorinated methacrylates (Figure 5). Block copolymers with different volume ratios were prepared to give a range of microstructures and solubilities. These polymers could be used as high-resolution, chemically amplified photoresists capable of imaging with 193 nm radiation. Compared to the *tert*-butyl group that is widely used as a protecting group in photoresists, the acetal type THP-group is more labile and polar, and is readily cleaved after exposure to heat or acid. There is a significant change in the polymer solubility after deprotection. 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.

Switching Surface Polarity

Hayakawa et al.[41] synthesized block copolymers with removable protecting groups attached to the semifluorinated side chains. Figure 6 shows the side group attached to the polyisoprene block of a hydroxylated poly(styrene-*b*-isoprene) block copolymer. The non-polar *tert*-butoxycarbonyl protecting groups hide the hydroxyl end groups of the semifluorinated side chains. The surface became more hydrophilic after UV exposure in the presence of a photoacid generator, owing to a change in the surface functionality to a hydroxyl group. The advancing and receding water contact angles decreased from 101° and 89°, respectively, to 75° and 67°, respectively.

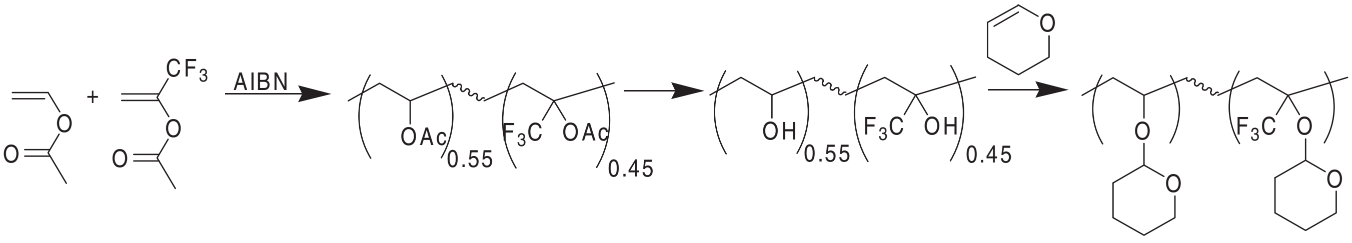


Fig.7. Synthesis of THP-protected fluorinated polyvinyl alcohol.

Fluorinated Polymer Resists for 157 nm Lithography

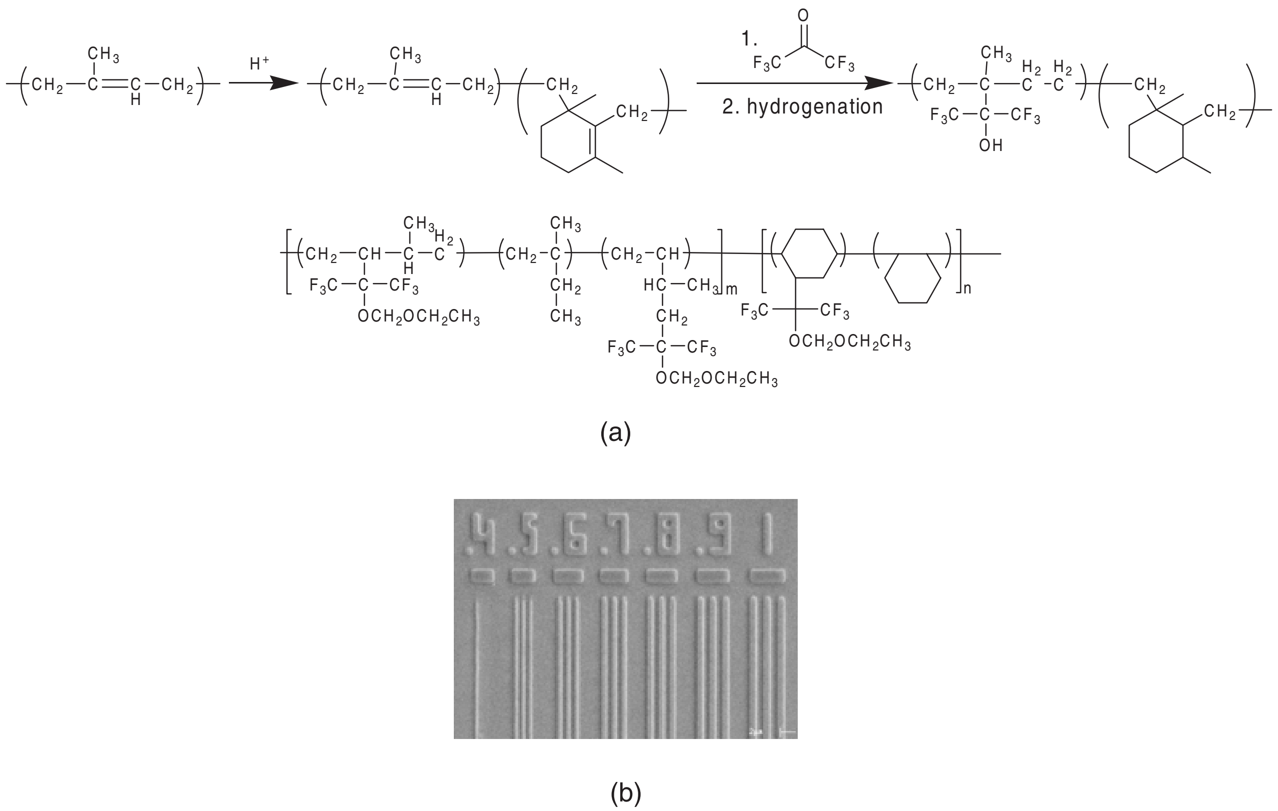
The idea of using fluorinated polymers as photoresists has flourished because of industrial interest in 157 nm lithography as the next-generation lithography wavelength to produce smaller feature sizes than currently possible with 193 nm or 248 nm lithography. Fluorine-containing polymers are highly transparent at 157 nm[42,43] and fluorocarbinols, with pK_a values comparable to those of phenols, can be used as acidic functional groups in the design of chemically amplified and aqueous-base developable resists.[44] Ito et al. developed poly(norbornene sulfone)-based polymers having protected hexafluoroisopropyl alcohol (HFIPA) as 193 nm resist.[45] Although the poor dry-etch resistance of poly(norbornene sulfone)-based resists limits their practical use for lithography, it is notable that when HFIPA-substituted norbornene undergoes alternating copolymerization with sulfur dioxide, the resulting copolymer exhibits high transparency at 157 nm with an absorption coefficient (A) of ~3 µm^{-1}.[46] Since this unusual transparency arises from the presence of fluorine atoms, fluorinated norbornene polymers, especially those prepared by metal catalyzed addition polymerization, have been actively investigated as transparent building blocks in the design of novel resists for 157 nm lithography.[47,48,49,50,51,52] In an effort to develop single-layer resists for 157 nm lithography, we have exploited a variety of fluorinated polymers. Our systems have been focused mainly on non-norbornene backbones. Norbornene polymers are very promising candidates as 157 nm photoresists, but there is a concern of possible metal contamination from residual catalyst. Instead, we have examined polymer systems that could be prepared using conventional free radical polymerization or anionic polymerization method.

Polyvinyl Alcohol

Among the polymers tested for absorbance at 157 nm by Kunz et al.,[42] poly(vinyl alcohol) (PVA) drew our initial attention because of its relatively low absorption coefficient ($A \sim 4\,\mu m^{-1}$) and ease of synthesis. However, since the absorbance and acidity of the polymer are not in acceptable range, we modified the structure by introducing trifluoromethyl group on the α-carbon. Poly(vinyl alcohol-*co*-trifluoromethyl vinyl alcohol) protected with an acid-cleavable tetrahydropyranyl (THP) group was prepared as a single-layer photoresist (Figure 7).[53,54,55] Compared to PVA, the new copolymer having CF_3 groups on the backbone showed improved transparency with an absorption coefficient of 3 µm^{-1}. Also, α-trifluoromethyl alcohol is acidic enough to render the polymer soluble in 0.26 *N* aqueous tetramethylammonium hydroxide (TMAH) solution. The THP-protected polymer was studied using 248 nm exposure and showed that it undergoes chemically amplified deprotection with high sensitivity. To improve transparency and etch resistance, and to modify the glass transition temperature, T_g, copolymerization of α-trifluromethylvinyl acetate with other comonomers,[56] including 2-[4-(2,2,2-trifluoro-1-ethoxymethoxy-1-trifluoromethylethyl)]styrene (StFA) and *p*-hydroxytetrafluorostyrene,[57] have been attempted.

Polydienes

Hydrocarbon polymers such as polydienes were studied as another platform for 157 nm resists because these do not contain any highly absorbing aromatic or carbonyl groups. Like PVA-based system, they need some modifications, which include introduction of fluorine-containing groups, removal of residual double bonds, and improvements in T_g and etch resistance. Polydienes can be easily prepared by anionic polymerization. The essential fluorocarbinol groups for lithographic applications could be introduced by the ene reaction of hexafluoroacetone (HFA) with the double bonds of the polydiene.[58,59] Finally, the unreacted double bonds could be removed by hydrogenation or epoxidization. Introduction of fluorocarbinol groups raises the glass transition temperature of the polydiene. For example, T_g of polyisoprene increased from –61°C to 53°C after the ene reaction.[60] To further increase T_g and etch resistance, two approaches were investigated. The first one was cyclization reaction of double bonds in polydienes using cationic initiator. The cyclized polyisoprenes exhibited higher T_g, ranging from 120°C to 170°C, after the ene reaction with HFIPA. The etch resistance of polydiene-based



(a)

(b)

Fig. 8. (a) Polydiene-based polymer resists, and (b) SEM image obtained from block copolymer of fluorinated diene: 248 nm exposure.

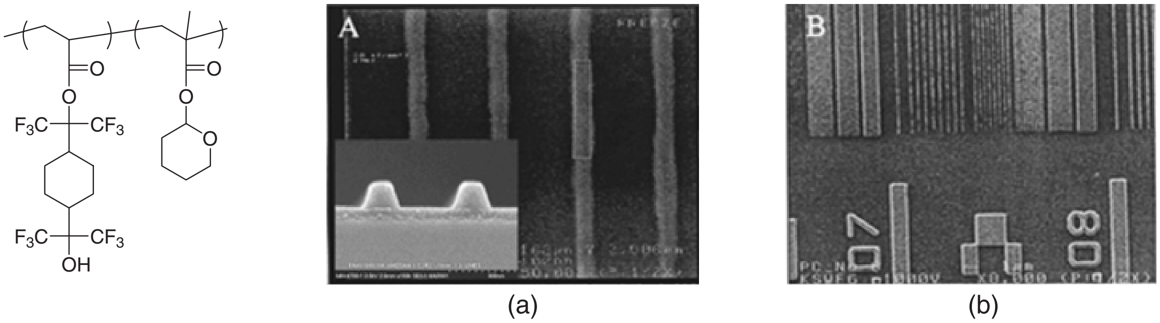
resists was increased by cyclization, and it was comparable to, or slightly higher than that of a Novolak-based resist under oxide and nitride etch conditions. The other approach was preparing block copolymers of isoprene with the cyclic monomer, cyclohexadiene. Since the cyclized portion was pre-established, it was easier as a result to control the properties. The copolymer had an absorption coefficient of ~3 μm^{-1} at 157 nm and showed promising image capability on the 248 nm exposure test (Figure 8).

Polyacrylates

In the course of studying conventional resist backbones for 157 nm applications, it was found that the transparency of conventional resist platforms could be significantly enhanced at 157 nm by judicious modification of highly absorbing groups,[61] and similar results were also confirmed by others.[62,63,64] For example, the homopolymer of 2-[4-(2-hydroxyhexafluoroisopropyl)cyclohexane]hexafluoroisopropyl-acrylate (1,4-AF) shows an absorption coefficient of 1.9 μm^{-1} despite having a highly absorbing carbonyl group. The unusual transparency of poly(1,4-AF) may be accounted for in terms of the electron-withdrawing effect of trifluoromethyl groups on the carboxyl group[65] as well as the volume effect of the trifluoromethyl group. Various copolymers have been prepared using 1,4-AF fluorinated acrylate monomer for use as 157 nm photoresists. The comonomers tested include methoxymethyl-protected 1,4-AF (MOMAF), StFA, *tert*-butyl methacrylate (*t*BuMA), tetrahydropyranyl methacryate (THPMA), 2-methyl adamentylacrylate (MAdMA), and *p*-*t*-butoxy-tetrafluorostyrene (SFOBu). The choice of comonomer was based on their ability to produce a solubility change by chemical amplification, better contrast, and etch resistance.

Copolymer systems using HFIPA as acidic group, poly(1,4-AF-*co*-MOMAF) and poly(1,4-AF-*co*-StFA), showed higher transparency at 157 nm ($A = 1.71$ and 2.38 μm^{-1}, respectively). However, despite the comparable acidity of HFIPA to phenol, the copolymers were not readily soluble in 0.26 *N* aqueous TMAH solution because of their poor wettability. Later study revealed that the wettability and solubility of poly(1,4-AF) could be improved by using proper surfactants.[66]

To achieve higher contrasts resulting from enhanced dissolution selectivity between exposed and unexposed areas, one of the methacrylates, such as *t*BuMA, THPMA, and MAdMA,



(a) (b)

Fig. 9. SEM images obtained with poly(1,4-AF-*co*-THPMA) on 157 nm exposure.

was used as a comonomer with 1,4-AF. In this hybrid system, imaging is achieved by the deprotection of (meth)acrylates, and HFIPA is used as a transparent acidic adjuvant. Surprisingly, only a modest deterioration in transparency was observed with the system containing 10~40 mol % methacrylate comonomer. With 30 mol % of THPMA, the hybrid system had an absorbance of 2.22 µm^{-1} at 157 nm. In contrast to the previous copolymer systems which contain only HFIPA as an acidic group, the hybrid system showed better lithographic characteristics. Poly(1,4-AF-*co*-THPMA)-based resists exhibited excellent adhesion, contrast, sensitivity, and solubility, not only at 248 nm, but also at 157 nm, and it was possible to achieve resolution down to 130 nm of 1 : 5 line and space patterns and 80 nm of isolated lines (Figure 9).

Methyl adamantyl methacrylate monomer which contains an alicyclic group was used as comonomer to render better etch resiatance.[67] In addition to improved etch resistance, poly(1,4-AF-*co*-MAdMA) showed a much higher dissolution contrast than poly (1,4-AF-*co*-THPMA) due to its hydrophobic protecting groups (Figure 10). The lithographic performances of this copolymer system at 248 nm exposure were significantly improved, showing better resolution without top-rounding. On evaluation at 157 nm exposure, the resist demonstrated 130 nm L/S (1/2) patterns, but some level of top-rounding was observed, most probably due to the high absorbance of the resist at 157 nm (3.4 µm^{-1}).

In pursuing a new comonomer that will provide all essential features including high transparency, improved etch resistance, and solubility in standard developer, we employed tetrafluorophenol as functional groups. The highly electron-withdrawing fluorine atom would be expected to reduce the absorbance of the aromatic group. Moreover, the acidity of the hydroxy groups increased to the level of carboxylic acids, improving the solubility of the polymer in a standard developer. Poly(1,4-AF-*co*-SFOBu) with 80 mol % of 1,4-AF was very transparent at 157 nm with an absorbance of 2.1 µm^{-1}. This is because of the better transparency of SFOBu compared to acrylate comonomers. Lithographic performance of these copolymers and poly(SFOBu) homopolymer was tested using a 248 nm stepper (Figure 11).

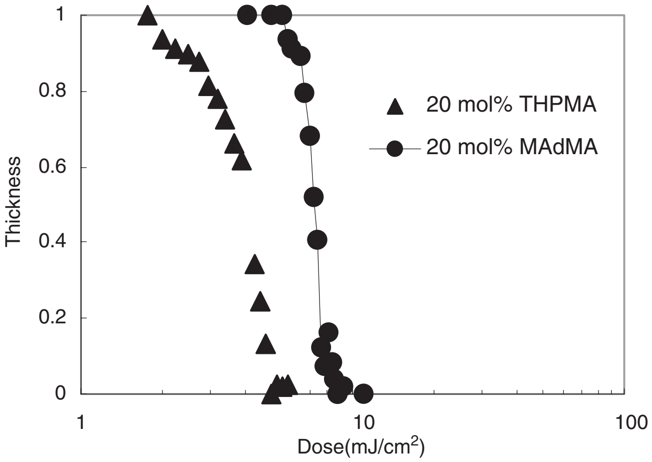


Fig. 10. Contrast curves obtained with poly(1,4-AF-*co*-MAdMA)-based resist and poly(1,4-AF-*co*-THPMA)-based resist.

Another variation on the acrylate copolymer system has been carried out by focusing on the fluorinated monomer. To increase transparency and etch resistance, a series of monomers having various amounts of fluorine atoms and ring structures were prepared. Multi-ring structures were used to improve etch resistance by increasing the C/H ratio. A homopolymer of acrylate containing decaline ring showed better etch resistance than poly(1,4-AF). However, there was some level of absorbance increase by decreasing the fluorine content (A = 2.6 µm^{-1}).[68]

Other types of monomers have also been synthesized to alleviate synthetic complexity. For example, during the synthesis of fluorocarbinol-substituted cyclohexane, the 1,3-isomer is the dominant product instead of the 1,4-isomer. Therefore, it is practically easier to prepare 1,3-AF than 1,4-AF. Moreover, homopolymer of 1,3-AF showed better transparency (A = 1.77 µm^{-1}) and a higher T_g of 95°C (77°C for poly(1,4-AF)). On testing lithographic performance using 248 nm stepper, the copolymer of this monomer, poly(1,3-AF_{60}-*co*-$MAdMA_{40}$), showed a resolution up to 250 nm.[68]

New fluorinated polymers from trifluoroacetone (TFA) have also been prepared since TFA is more environmentally friendly and more readily available than HFA. Acrylate monomers were synthesized from the fluorinated diol prepared by the trimerization of TFA via aldol condensation reactions (Figure 12).[69] The absorbance of the homopolymer at 157 nm was comparable to that of the HFA-based homopolymers (1.9~2.1 μm^{-1}); however, the etch resistance was lower due to the presence of oxygen in the ring structure.

Fluorinated Backbone Acrylates

The finding that α-trifluoromethyl acrylate polymers are unexpectedly transparent ($A \sim 3\,\mu m^{-1}$) prompted efforts to use them as 157 nm resist backbones. Since it is not easy to prepare homopolymers of α-trifluoromethacrylic monomers using free-radical initiators, two different approaches have been attempted. Anionic polymerization was used to prepare α-trifluoromethyl acrylate polymers.[70] An alternative method involved radical copolymerization with other monomers. α-trifluoromethacrylic monomers was copolymerized with other vinyl monomers such as methacrylates and styrenes (StFA), although their incorporation in the copolymer was below 50% in many cases.[71] Alternating copolymerization of α-trifluoromethyl acrylate with electron-rich norbornenes has also been studied.[72,73] In this case, the copolymer composition was less affected by the initial feed ratio and had some fixed values at around 2/1 (α-trifluoromethyl acrylate/norbornene derivative) depending on the comonomer structure.

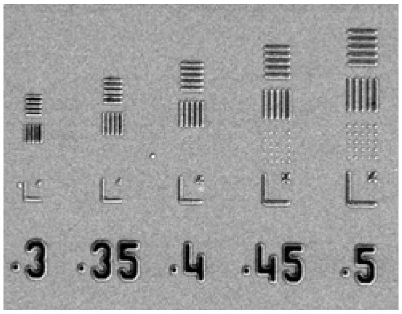


Fig. 11. SEM micrograph obtained from poly(1,4-AF-*co*-SFOBu) on 248 nm exposure. Reproduced with permission from Chem Mater 2002, 14, 1306–1313. Copyright 2002 Am. Chem. Soc.

We have also prepared α-trifluoromethyl acrylate based copolymer systems. 2-[4-(2-hydroxyhexafluoroisopropyl) cyclohexane]hexafluoroisopropyl (α-trifluoromethyl)acrylate (FAF) and α-trifluoromethyl-substituted methyl adamantyl methacrylate were synthesized and polymerized using potassium acetate and 18-crown-6.[67] A VUV–VASE absorption spectrum of the copolymer showed that it was unexpectedly transparent at 157 nm ($A = 1.6\,\mu m^{-1}$) despite the fact that both monomers contained a carbonyl group (Figure 13).

However, as observed in the literature, it was not convenient to polymerize α-trifluoromethyl acrylate, both for reasons of polymerization and because the resulting polymer films were hydrophobic. Instead, we devised α-monofluoroacrylate systems. The energy gap between the SOMO and HOMO levels of these monomers is reduced and it becomes possible to polymerize them using a free radical initiator.[74,75,76] The homopolymer of 2-[4-(2-hydroxyhexafluoro-isopropyl)cyclohexane] hexafluoroisopropyl-α-monofluoroacrylate (FA) was prepared by AIBN-initiated polymerization and showed a lower absorption coefficient of 1.7 μm^{-1} at 157 nm, than poly(1,4-AF).[68]

Alternating Copolymers

As in the 193 nm photoresist systems, alternating copolymer systems of electron-rich olefins with electron-poor monomers using free radical initiators have also been used as 157 nm photoresists. Cyclopolymerization of monomers containing both electron-rich and electron-deficient double bonds in a single molecule was utilized.[68,77] Copolymers of norbornenes with tetrafluoroethlyene have also been prepared. To incorporate polar functional groups for proper adhesion and solubility, copolymers of polar norbornenes[70] and/or terpolymer systems with α-monofluoroacrylates[78,79,80] have been

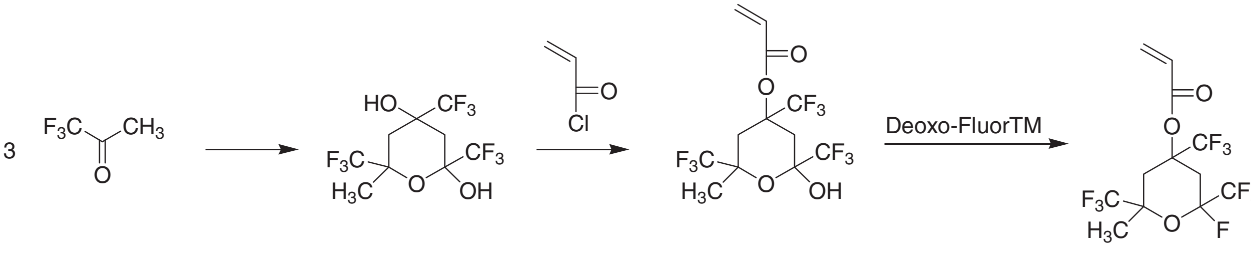


Fig. 12. Syntheses of fluorinated monomers based on trifluoromethyl acetone.

attempted. Our approach was made using trifluoroacrylate and/or 2,2,3,4,4-pentafluorobut-3-enoic acid ester instead of tetrafluoroethylene. An alternating copolymer with a norbornene derivative was found to have high T_g (155°C) and gave clear images on exposure tests using a 248 nm stepper. [57]

Fluorinated Polymers in Supercritical Carbon Dioxide Technology

Supercritical fluid (SCF) technology has been gaining considerable attention over the last two decades in the area of polymer synthesis and processing. Interest in this solvent is due to its unique combination of gas and liquid-like properties, including adjustable solvent strength to tailor selectivity and yields, higher diffusion coefficient and lower viscosity than common solvents, and rapid diffusion of CO_2 through condensed phases such as polymers. Though supercritical (SC) CO_2 has been found to be a very good solvent for small molecules, it acts as an extremely poor solvent for many polymers. While conventional hydrophilic or lipophilic polymers are relatively insoluble in SC CO_2, fluorinated polymers and silicon-containing polymers fall into the CO_2-philic category. SC CO_2 has been used as a solvent for free radical polymerization of fluorinated monomers.[81,82]

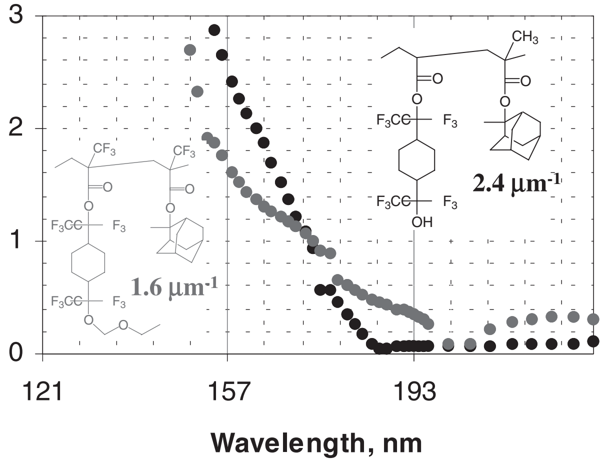


Fig. 13. VUV–VASE spectra of acrylate and α-trifluoromethyl acrylate copolymers.

Use of SC CO_2 in photoresist processing has drawn marked interest due to its environmentally benign nature. As a solvent, carbon dioxide is environmentally acceptable as it is nontoxic, nonflammable, inexpensive, and usable at mild temperatures.[83] Additionally, solvent recovery is fast and complete while collapse of sub-micron patterned structures due to capillary forces is prevented during solvent removal. There have been several efforts in preparing fluorinated polymer photoresists that can be developed using SC carbon dioxide.[84,85] We have prepared block and random copolymers of perfluoroalkyl methacrylates (FMA) with *t*BuMA[86] or THPMA,[87,88,89] and demonstrated negative-tone images with resolution as low as 100-nm using 193 nm and e-beam exposure. Figure 14 shows the imaging mechanism used in this study. The very nonpolar fluoromethacrylates, which are soluble in SC CO_2, were chosen for copolymerization with the acid-cleavable THPMA so that the classical chemically amplified polarity change in the presence of a proton could be utilized. After exposure to radiation, the THPMA block is converted to a more polar methacrylic acid (MAA), which is insoluble in SC CO_2, giving rise to a solubility change.

Positive tone photoresists have also been developed using *in-situ* silylation of poly(MAA-*b*-FMA). As in the negative tone system, a block copolymer of THPMA and FMA was exposed at 248 nm to deprotect the THP groups by generated acids, resulting in MAA with significantly decreased solubility in SC CO_2. The patterned region was treated with either hexamethyldisilazane (HMDS) or trimethyldisilazane (TMDS) vapor to reprotect carboxylic acid with trimethylsilyl groups. As a result the patterned regions regained solubility in SC CO_2. A

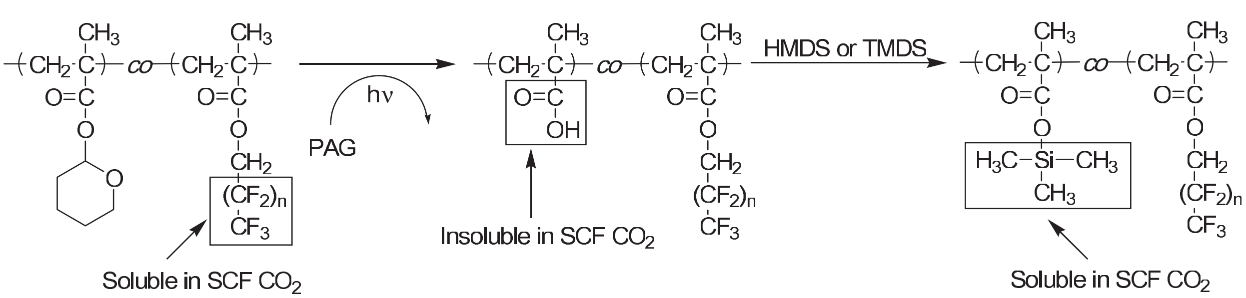


Fig. 14. Imaging mechanism of fluorinated polymers using SC CO_2 as developer.

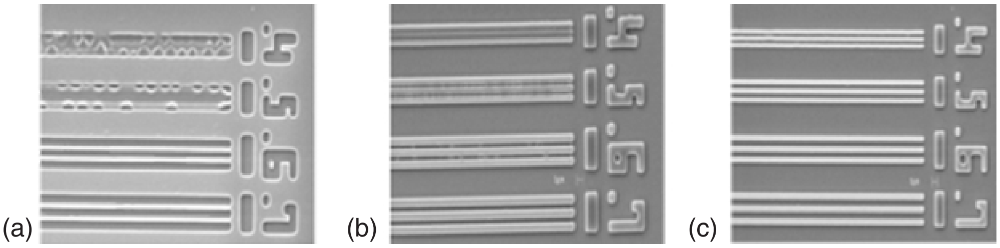


Fig. 15. THPMA–FMA random copolymer resist patterned by 248-nm exposure: (a) SC CO_2 processed negative-tone images, (b) positive-tone images processed after silylation with HMDS, and (c) positive-tone images processed after silylation with TMDS. Reproduced with permission from Chem Mater 2003, 15, 4893–4895. Copyright 2003 Am. Chem. Soc.

subsequent UV flood exposure step activated unreacted photoacid generators throughout the sample. Cleavage of nonpolar THP protecting groups then occurs everywhere except in the originally patterned regions. Development in SC CO_2 thus removes the patterned regions, making this a positive-tone resist. Exposure tests using a 248 nm stepper demonstrated images with a resolution of 400 nm (Figure 15). When TMDS was used as silylating agent, it was possible to produce images with reduced swelling.

Summary

Polymer analogous reactions on block copolymers prepared by anionic polymerization is an efficient method for the synthesis of well-defined fluorinated block copolymers. We have also used controlled free radical polymerization for direct preparation of fluorinated block copolymers. Such polymers, with semifluorinated side groups, show an ordered arrangement at the air–polymer interface, resulting in low-energy surfaces. We have discussed some examples from our laboratory on the synthesis of novel fluorinated monomers and polymers for use as 157 nm photoresists. With a potential to replace toxic antifouling coatings in marine applications and with possibilities for biomedical coatings, or enabling the replacement of hazardous solvents in microlithography with supercritical carbon dioxide, fluorinated polymers are expected to play an increasingly important role in many technologies in the near future.

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