

# Novel hydrofluorocarbon polymers for use as pellicles in 157 nm semiconductor photolithography: fundamentals of transparency

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## Abstract

With the advent of 157 nm as the next photolithographic wavelength, there has been a need to find transparent and radiation durable polymers for use as soft pellicles. Pellicles are ~1 μm thick polymer membranes used in the photolithographic reproduction of semiconductor integrated circuits to prevent dust particles on the surface of the photomask from imaging into the photoresist coated wafer. Practical pellicle films must transmit at least 98% of incident light and have sufficient radiation durability to withstand kilojoules of optical irradiation at the lithographic wavelength. As exposure wavelengths have become shorter the electronics industry has been able to achieve adequate transparency only by moving from nitrocellulose polymers to perfluorinated polymers as, for example, Teflon<sup>®</sup> AF 1600 and Cytop<sup>™</sup> for use in 193 nm photolithography. Unfortunately, the transparency advantages of perfluorinated polymers fail spectacularly at 157 nm; 1 μm thick films of Teflon<sup>®</sup> AF 1600 and Cytop<sup>™</sup> have 157 nm transparency of no more than 38 and 2%, respectively, with 157 nm pellicle lifetimes measured in millijoules.

Polymers such as  $-(\text{CH}_2\text{CHF})_x\text{C}(\text{CF}_3)_2\text{CH}_2)_y-$ , or  $-(\text{CH}_2\text{CF}_2)_x[2,2\text{-bis}(\text{trifluoromethyl})\text{-4,5-difluoro-1,3-dioxole}]_y-$  with chains that alternate fluorocarbon segments with either oxygen or hydrocarbon segments frequently show >98% transparency at 157 nm, if amorphous. These polymers are made from monomers, such as vinylidene fluoride (VF<sub>2</sub>) and hexafluoroisobutylene, which themselves exhibit good alternation of CH<sub>2</sub> and CF<sub>2</sub> in their structures. In addition, we find that ether linkages also can serve to force alternation. In addition, we find that fluorocarbon segments shorter than six carbons, and hydrocarbon segments less than two carbons or less than three carbons if partially fluorinated also promote 157 nm transparency. We also find that even with these design principles, it is advantageous to avoid small rings, as arise in the cyclobutanes. These results suggest a steric component to transparency in addition to the importance of alternation.

Upon irradiation these polymers undergo photochemical darkening and therefore none has demonstrated the kilojoule radiation durability lifetimes required to be commercially attractive. This is likely because these exposure lifetimes require every bond to absorb ~10 photons, each photon having an energy roughly twice common bond energies. We have studied intrinsic (composition, molecular weight) and extrinsic (trace metals, impurities, environmental contaminants, oxygen, water) contributions to optical absorption and photochemical darkening in these polymers. Studies of photochemical darkening in model molecules illustrate the dynamics of photochemical darkening and that appreciable lifetimes can be achieved in fluorocarbons. To a first approximation the polymers that have lower 157 nm optical absorbance also tend to show the longest lifetimes. These results imply that quantum yield, or the extent to which the polymer structure can harmlessly dissipate the energy, can be important as well.

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## 1. Introduction

The electronics industry continues to make tremendous gains in miniaturization and circuit complexity. For decades now, the industry has been able to follow Moore's Law whereby the number of transistors on a silicon chip has

doubled about every 18 months. The main driver behind this continued miniaturization of chip circuitry is the continuing advances in photolithography to reduce integrated circuit feature sizes. The photolithographic process starts with a circuit pattern etched in chrome metal on glass [1]. Illumination of the patterned photomask in the optical stepper projects an image of the circuit pattern that is captured as a latent image by a photosensitive polymer layer, known as a photoresist, on the silicon wafer. The shorter the wavelength

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of light used, the smaller the circuit features that can be copied. Much commercial production is presently being done with light having a wavelength of 248 nm using either a lamp or a KrF excimer laser light source. The use of 193 nm ArF excimer laser light is just entering commercial practice while photolithography based on 157 nm F<sub>2</sub> excimer lasers is now in the development stage.

Organic polymers play several critical roles in the photolithographic process. We have already mentioned photoresists, submicrometer thick films of photosensitive polymer that capture projected circuit patterns. One of the major issues for resists is that 157 nm light is absorbed so strongly that the top of a film can be overexposed at the same time the bottom of the film is underexposed leading to undesirable photoresist line profiles after development [2]. This is true even when resist films are only several tenths of a micrometer thick [1]. For purposes of sharp pattern development, experience suggests that at least 40% of incident light should make it to the bottom of the resist layer. The first polymer to demonstrate that such transparencies are possible [3] was Teflon<sup>®</sup> AF, the copolymer of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD) with tetrafluoroethylene (TFE). Teflon<sup>®</sup> AF of course cannot function as a resist itself because it lacks the chemical groups needed for photosensitivity and aqueous base development. This has led to development of new fluoropolymers for use as photoresists at 157 nm [4].

Another critical role for polymers in photolithography is that of the pellicle, a transparent dust cover for the photomask [5]. The chrome photomask, which serves as the master image of the circuit layout, has circuit features down to tenths of a micrometer. Dust particles that lodge on the photomask will print as a defect each time the master is copied to a chip, thereby dropping the yield of functional chips immediately to 0%. To prevent this, an ~0.8 μm thick film called a pellicle is held several millimeters above the photomask on a frame. Now when a dust particle deposits, it attaches to the pellicle film where the particle is held up and out of the focal plane so that it no longer copies. The two most chemically challenging specifications the electronics industry has placed on pellicle films are that they transmit most of the incident light and that they can be used repeatedly without showing significant changes in their optical characteristics [6,7]. This is the challenge we have undertaken in the present work, to produce a polymeric pellicle membrane with sufficient transparency and radiation durability for use with 157 nm F<sub>2</sub> excimer laser irradiation.

### 1.1. Optical requirements of pellicles

The electronics industry has specified that a pellicle film should pass at least 98% of incident 157 nm light. For measurements on pellicle films this can be expressed as an optical absorbance *A*,

$$A = \log_{10} \left( \frac{T_0}{T} \right) \quad (1)$$

where *T*<sub>0</sub> is the intensity of the incident light and *T* the intensity of the transmitted light. An obvious way to increase the intensity of the transmitted light is to decrease film thickness. This is an acceptable strategy down to thicknesses of about 0.8 μm beyond which polymer films become too fragile to stretch tautly and defect-free across a 5 in. × 5 in. pellicle frame. This thickness dependence is accounted for by reporting a film's absorbance per micrometer (*A*/μm),

$$A/\mu\text{m} = \log_{10} \left( \frac{T_0/T}{t} \right) \quad (2)$$

where *t* is the thickness of the film measured in micrometers.

*A*/μm measurements are convenient for ranking transparency differences between films, keeping in mind that such comparisons include not only the effects of polymer structure but also of polymer purity and processing. A 98% transparent film 0.8 μm thick would have an *A*/μm of 0.011. Were the same material as thick as a piece of paper (~76 μm), it would transmit only 20% of incident light. So, even though a pellicle candidate may set records with respect to the transmission of 157 nm light, all such polymers presently absorb significant quantities of light. The radiation durability problems discussed later should thus come as no surprise.

When working with 0.8 μm thick films, the best pellicles all too soon become so transparent that they can no longer be meaningfully distinguished with conventional transmission based absorbance measurements of thin films with micrometer scale thickness. This occurs for *A*/μm values <0.01. Much of the uncertainty comes from the anti-reflective effect of thin polymer when coated on CaF<sub>2</sub>. That is, the small amount of light absorbed by a highly transparent film is lost in comparison to the transmission increase resulting from decreased reflectivity from the anti-reflective effect. In the worst of such cases, *T*<sub>sample</sub> is greater than *T*<sub>substrate</sub> and the calculated absorbance goes negative. These aspects of the characterization of thin polymer films are discussed in greater detail in reference [5].

### 1.2. Additional property requirements for soft pellicles

The pellicle consists of a precisely designed membrane, which acts as a tuned etalon [8], on a pellicle frame that is adhesively mounted to the reticle or photomask. Beyond the optics of the pellicle, pellicles also have a large number of ancillary properties that are essential. The multiple property requirements embodied in pellicles require a materials design approach. Currently, no materials are known to meet the optical transparency performance requirements at the 157 nm lithography wavelength. The use of new materials requires that careful attention be given to design of the tuned etalon to control the pellicle reflectance and transmission. To achieve the desired pellicle lifetimes, new radiation tolerant materials will need to be developed that meet stringent radiation durability requirements. To produce unsupported pellicle membranes, the polymer must also be designed to

achieve the required spinning, film formation, and mechanical properties, and have minimal outgassing in use.

### 1.3. Novel polymers for 157 nm soft pellicles

Previously, it has been believed that perfluorinated polymers have the shortest wavelength cutoffs, highest transparencies and lowest absorbances [2,3]. What we report here is that higher transparencies and lower absorbances can be achieved at 157 nm using hydrofluorocarbon polymers which minimize hydrocarbon and fluorocarbon run lengths and force a regular alternation of fluorocarbon and hydrocarbon segments down the polymer chain.

## 2. Experimental

### 2.1. Optical spectroscopy and characterization

#### 2.1.1. Optical absorbance determined using vacuum ultraviolet spectroscopy

VUV spectroscopy including both transmission and reflectance measurements has become an established technique for electronic structure studies of large band-gap, insulating materials such as polysilanes [9] and fluoropolymers. The details of the VUV-laser plasma light source (LPLS) spectrophotometer have been discussed previously [10]. The spectrophotometer utilizes a LPLS [11], and a 1 m monochromator with Al/MgF<sub>2</sub> and iridium coated optics. The energy range of this windowless instrument is 1.7–44 eV (700–28 nm), which extends beyond the air-cutoff of 6 eV and the window-cutoff of 10 eV. The resolution of the instrument is 0.2–0.6 nm, which corresponds to 16 meV resolution at 10 eV and 200 meV resolution at 35 eV.

A Perkin-Elmer Lambda 9 spectrophotometer, with transmission and reflectance attachments and using xenon and deuterium lamps, was used to cover the UV-Vis/NIR spectral regions. The wavelength (energy) resolution is 2 nm (40 meV) at 5.0 eV. Transmission was measured over the complete energy range of the instrument to check the accuracy of the VUV transmission spectra. The results agreed well with the data from the VUV spectrophotometers. Data were spliced together in the overlapping wavelength region using a multiplicative scaling factor on the VUV transmission to bring it into agreement with the UV-Vis results.

In addition, the use of VUV spectroscopic ellipsometry is useful as an independent technique for characterization of materials in this spectral range [5]. The VUV spectroscopic ellipsometer uses a deuterium and a xenon lamp, and can also be used to measure the transmission spectrum of polymer films on a substrate, or a pellicle membrane directly.

Once the transmission spectra of the substrate and the film coated on that substrate are determined, the film transmission and optical density can be determined using Eqs. (3)

and (4), respectively. The  $A/\mu\text{m}$  is then determined by dividing the optical density by the film thickness, as shown in Eq. (5). The optical  $A/\mu\text{m}$  reported here are base 10:

$$T_{\text{film}} = 100 \times \frac{T_{\text{sample}}}{T_{\text{substrate}}} \quad (3)$$

$$\text{OD}_{\text{film}} = \log_{10} \left( \frac{100}{T_{\text{film}}} \right) \quad (4)$$

$$A_{\text{film}} (\mu\text{m}^{-1}) = A_{\text{film}}/\mu\text{m} = \frac{\log_{10}(T_{\text{substrate}}/T_{\text{sample}})}{t_{\text{film}}} \quad (5)$$

The transmission measurement of liquid samples was made in a Harrick Scientific Corp. Demountable Liquid Cell model DLC-M13. Teflon<sup>®</sup> AF spacers of 6 or 25  $\mu\text{m}$  thickness were used in order to establish the desired path lengths and sandwiched between two 2 mm thick 0.5 in. diameter CaF<sub>2</sub> windows. Care was taken to avoid bubbles in the 8 mm diameter window aperture.

#### 2.1.2. Measurement of photochemical darkening

The 157 nm exposure was performed in a nitrogen purged environment. The energy in the incident and transmitted beams were monitored using pyroelectric detectors and a Ratiometer was used to measure the in situ variation of the relative sample transmission with increasing laser radiation dose. The details of these methods and measurements have been discussed previously [7].

#### 2.1.3. Accuracy of transmission based optical measurements

As in all experimental measurements, the accuracy of the measured values is a function of the sample and measurement apparatus. The inherent sensitivity of spectral transmission and absorbance measurements is affected by the optical path length of the sample, and the transmission drop that occurs as light transmits through the sample in the measurement. As the transmission drop decreases, the accuracy of the absorbance measurement decreases. A transmission difference of  $\sim 0.1\%$  is near the limit of the measurement method. In such a case, a thicker sample, with a longer path length, is required to keep the measured transmission drop larger than the instrument's sensitivity.

### 2.2. Synthesis

The polymers synthesized, and their compositional analysis, are summarized in Table 1. Differential scanning calorimetry (DSC) measurements were performed under nitrogen, heating twice at 10 °C/min using a TA Instruments Model 2910. Unless mentioned otherwise, glass transition ( $T_g$ ) and melting point ( $T_m$ ) temperatures are taken from the second heats. Inherent viscosities (IV) were determined on 0.5 wt.% solutions at 25 °C by automated glass capillary viscometry using a Cannon Autovisc<sup>®</sup>. Polymer compositions were determined either by elemental analysis or by NMR spectra run on polymer solutions. Unless specified otherwise,

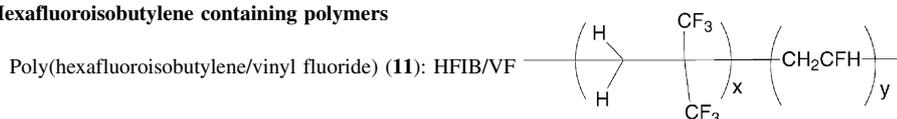
Table 1

Fluoropolymers: synthesis and compositional analysis

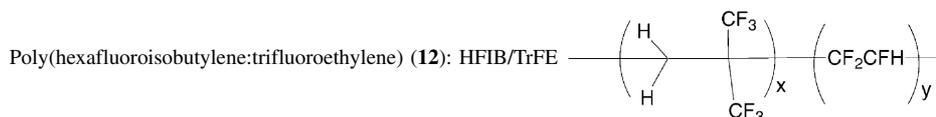
## Vinylidene fluoride copolymers

Poly(vinylidene fluoride/hexafluoropropylene) (1): VF <sub>2</sub> /HFP		21:79 VF <sub>2</sub> :HFP, NMR, acetone-d <sub>6</sub> , <i>T<sub>g</sub></i> = −22.5 °C, IV = 0.753 dl/g, acetone
Poly(vinylidene fluoride/chlorotrifluoroethylene) (5): VF <sub>2</sub> /CTFE		Calc. (C <sub>2</sub> F <sub>2</sub> H <sub>2</sub> ) <sub>5</sub> (C <sub>2</sub> F <sub>3</sub> Cl) <sub>4</sub> : 27.50% C, 1.28% H, 18.04% Cl. Found: 27.26% C, 1.41% H, 17.91% Cl. <i>T<sub>g</sub></i> = 99 °C, IV = 0.546 dl/g, acetone
Poly(vinylidene fluoride/perfluoromethylvinylether) (4): VF <sub>2</sub> /PMVE		Calc. (C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> ) <sub>13</sub> (C <sub>3</sub> F <sub>6</sub> O) <sub>10</sub> : 26.98% C, 1.05% H. Found: 27.21% C, 0.88% H. <i>T<sub>g</sub></i> = −29 °C, IV = 0.166 dl/g, 2-heptanone
Poly(vinylidene fluoride/perfluoropropylvinyl ether) (6): VF <sub>2</sub> /PPVE		Calc. (C <sub>2</sub> F <sub>2</sub> H <sub>2</sub> ) <sub>7</sub> (C <sub>5</sub> F <sub>10</sub> O) <sub>5</sub> : 26.34% C, 0.79% H. Found: 26.17% C, 0.88% H. <i>T<sub>g</sub></i> = −32 °C, IV = 0.169 dl/g, hexafluorobenzene
Poly(vinylidene fluoride/perfluorodimethyldioxole) (2): VF <sub>2</sub> /PDD		Calc. (C <sub>5</sub> F <sub>8</sub> O <sub>2</sub> ) <sub>1</sub> (C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> ) <sub>1</sub> : 29.05% C, 1.08% H. Found: 28.99% C, 1.11% H. <i>T<sub>g</sub></i> = 56 °C (first heat), <i>T<sub>g</sub></i> not detected on second heat
Poly(vinylidene fluoride/2-(difluoromethylene)-4,4,5-trifluoro-5-(trifluoromethyl)-1,3-dioxolane (10):		Calc. (C <sub>5</sub> F <sub>8</sub> O <sub>2</sub> ) <sub>1</sub> (C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> ) <sub>2</sub> : 29.05% C, 1.08% H. Found: 28.71% C, 1.38% H. <i>T<sub>g</sub></i> = 100 °C (first heat), <i>T<sub>m</sub></i> = 165 °C (second heat), IV = 0.287 dl/g, hexafluorobenzene
Poly(CH <sub>2</sub> =CF <sub>2</sub> /CF <sub>2</sub> =CHOFCF <sub>2</sub> CF <sub>3</sub> ) (7): VF <sub>2</sub> /PEDVE, VF <sub>2</sub> analogue		Calc. (C <sub>4</sub> F <sub>7</sub> OH) <sub>10</sub> (C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> ) <sub>11</sub> : 27.74% C, 1.20% H. Found: 27.89% C, 0.91% H. <i>T<sub>g</sub></i> = −5 °C
Poly(CH <sub>2</sub> =CF <sub>2</sub> /CF <sub>2</sub> =CHOFCF <sub>2</sub> CF <sub>2</sub> H) (3): VF <sub>2</sub> /TEDVE, VF <sub>2</sub> analogue		Calc. (C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> ) <sub>3</sub> (C <sub>4</sub> H <sub>2</sub> F <sub>6</sub> O) <sub>2</sub> : 30.45% C, 1.83% H. Found: 30.65% C, 1.41% H. <i>T<sub>g</sub></i> = −11 °C, IV = 0.122 dl/g, acetone
Poly[CH <sub>2</sub> =CF <sub>2</sub> /(CH <sub>2</sub> =C(CF <sub>3</sub> )CF <sub>2</sub> OCF(CF <sub>3</sub> ) <sub>2</sub> )] (8): VF <sub>2</sub> /DHB,		49:51 VF <sub>2</sub> :DHB, NMR, hexafluorobenzene. Neither <i>T<sub>g</sub></i> nor <i>T<sub>m</sub></i> detected, IV = 0.083 dl/g, hexafluorobenzene
Poly[CH <sub>2</sub> =CF <sub>2</sub> /(CH <sub>2</sub> =C(CF <sub>3</sub> )CF <sub>2</sub> OCH(CF <sub>3</sub> ) <sub>2</sub> )] (9): VF <sub>2</sub> /THB,		47:53 VF <sub>2</sub> :THB, NMR, hexafluorobenzene, <i>T<sub>g</sub></i> = 47 °C, IV = 0.116 dl/g, hexafluorobenzene

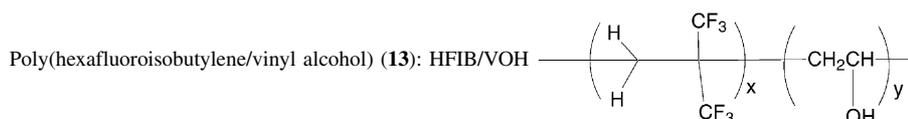
Table 1 (Continued)

**Hexafluoroisobutylene containing polymers**

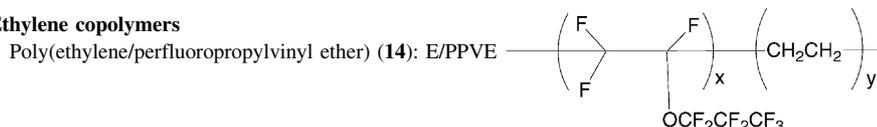
Calc.  $(\text{C}_4\text{F}_6\text{H}_2)_{47}(\text{C}_2\text{H}_3\text{F})_{53}$ :  
34.79% C, 2.51% H. Found:  
34.80% C, 2.57% H.  $T_g = 70^\circ\text{C}$ ,  
IV = 0.379, tetrahydrofuran



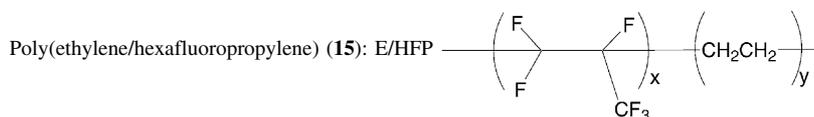
54:46 HFIB:TrFE, NMR,  
acetone- $d_6$ ,  $T_g = 70^\circ\text{C}$ ,  
IV = 0.055 dl/g, acetone



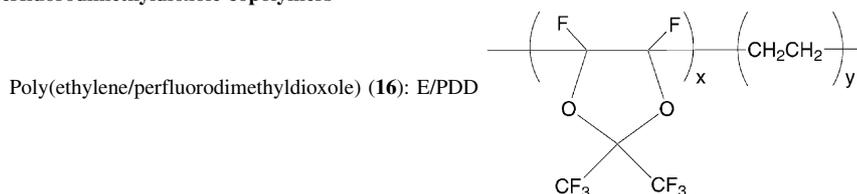
Calc.  $(\text{C}_4\text{H}_2\text{F}_6)_1(\text{C}_2\text{H}_4\text{O})_1$ :  
34.63% C, 2.91% H. Found:  
34.34% C, 2.73% H.  $T_g = 90^\circ\text{C}$

**Ethylene copolymers**

47:53 PPVE:E,  $^1\text{H}$  NMR and  
 $^{19}\text{F}$  NMR, hexafluorobenzene,  
 $T_g = -15.5^\circ\text{C}$ , IV = 0.341 dl/g,  
hexafluorobenzene

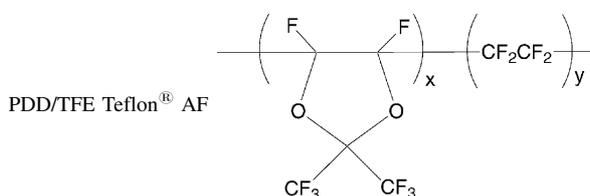
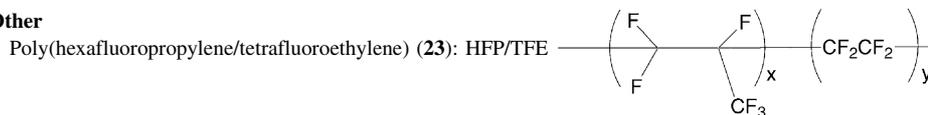


Calc.  $(\text{C}_2\text{H}_4)_{57}(\text{C}_3\text{F}_6)_{43}$ : 36.26% C,  
2.85% H. Found: 36.22% C,  
2.82% H.  $T_g = -15^\circ\text{C}$

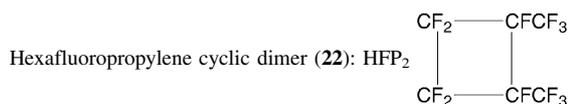
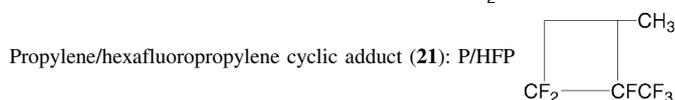
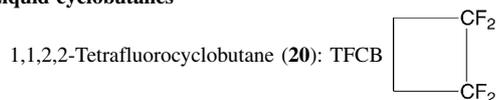
**Perfluorodimethyldioxole copolymers**

51:49 PDD:E,  $^1\text{H}$  NMR and  
 $^{19}\text{F}$  NMR, hexafluorobenzene,  
 $T_g = 71^\circ\text{C}$ , IV = 0.318 dl/g,  
hexafluorobenzene

Poly(perfluorodimethyldioxole/tetrafluoroethylene) (17, 18 and 19):

**Other**

Ratio HFP/TFE = 50:50 HFP:TFE,  
NMR, hexafluorobenzene,  
IV = 0.407 dl/g, Fluoroinert<sup>®</sup>  
FC-75

**Liquid cyclobutanes**

fluorine NMR was used. NMR compositions are reported in mole percents. Most of polymerizations were initiated with hexafluoropropylene oxide dimmer peroxide “DP”,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)(\text{C}=\text{O})\text{OO}(\text{C}=\text{O})\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CF}_3$  [23].

### 2.2.1. Vinylidene fluoride copolymers

**2.2.1.1. Poly(vinylidene fluoride/hexafluoropropylene) (1): VF<sub>2</sub>/HFP.** A poly(vinylidene fluoride/hexafluoropropylene) (VF<sub>2</sub>:HFP) sample made by the method of [12] was characterized.

Solutions of VF<sub>2</sub>:HFP were spin coated at spin speeds of 3000 and 6000 rpm onto CaF<sub>2</sub> substrates to produce polymer films of 69,800 and 1641 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

The 157 nm absorbance per micrometer determined from the thicker polymer film is 0.015 per micrometer. The 193 nm absorbance per micrometer determined is 0.005 per micrometer. The 248 nm absorbance per micrometer determined is 0.003 per micrometer.

**2.2.1.2. Poly(vinylidene fluoride/perfluorodimethyldioxole) (2): VF<sub>2</sub>/PDD.** A 75 ml autoclave was loaded with 25 ml of CF<sub>2</sub>CICCl<sub>2</sub>F, pre-chilled to less than –20 °C, loaded further with 0.3 g of Perkadox™ 16 N [bis(4-*t*-butylcyclohexyl)-peroxydicarbonate] and 20 g of perfluorodimethyldioxole (PDD), evacuated, and 10.4 g of VF<sub>2</sub> added. Heating 18 h at 70 °C gave a thick oil. Evaporation in air, drying 22 h under pump vacuum, and drying 24 h in a 75 °C oven gave 17 g of hard white foam.

A viscous solution was prepared by rolling 4 g of poly(PDD/VF<sub>2</sub>) with 16 g of hexafluorobenzene and filtering through a 0.45 μm glass fiber syringe filter [Whatman, Autovial™]. The filtrate was used to spin coat thick films on optical substrate for absorption measurements. Solutions of VF<sub>2</sub>:PDD were spin coated at spin speeds of 6000 rpm onto CaF<sub>2</sub> substrates to produce polymer films of 2097 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

The 157 nm absorbance per micrometer determined from the thicker polymer film is –0.04 per micrometer. For this very transparent material, this demonstrates an antireflective coating effect thereby producing a negative value of the 157 nm absorbance per micrometer. The 193 nm absorbance per micrometer determined is 0.02 per micrometer. The 248 nm absorbance per micrometer determined is 0.08 per micrometer.

**2.2.1.3. Poly(CH<sub>2</sub>=CF<sub>2</sub>/CF<sub>2</sub>=CHO CF<sub>2</sub>CF<sub>2</sub>H) (3): VF<sub>2</sub>/TEDVE, VF<sub>2</sub> analogue**

*1,1,2,2-Tetrafluoroethyl-2,2-difluorovinyl ether, CF<sub>2</sub>=CHO CF<sub>2</sub>CF<sub>2</sub>H.* Monomer was prepared using modified literature procedure [13].

- Preparation of 1,1,2,2-tetrafluoroethyl-2-chloro-2,2-difluoroethyl ether. A mixture of 2-chloro-2,2-difluoroethanol (22.0 g), *t*-butanol (45 ml), KOH (10.0 g) and TFE (25 g) was shaken at room temperature for 8 h in a autoclave. The bottom layer of the reaction mixture was isolated and washed with water (40 ml) to give a crude product, 1,1,2,2-tetrafluoroethyl-2-chloro-2,2-difluoroethyl ether, 29.5 g, yield 72% [13]. This product was used for next step without further purification.
- Preparation of 1,1,2,2-tetrafluoroethyl-2,2-difluorovinyl ether. A mixture of 1,1,2,2-tetrafluoroethyl-2-chloro-2,2-difluoroethyl ether (29.0 g), KOH (10.0 g), and DMSO (5 ml) was heated to reflux on a spinning band distillation apparatus. The product was distilled out to give 9.6 g of 1,1,2,2-tetrafluoroethyl-2,2-difluorovinyl ether, bp 38 °C (39.7 °C [13]), yield 40%.

<sup>19</sup>F NMR (CDCl<sub>3</sub>) –92.3 (s, 2F), –92.7 (ddt, *J* = 57, 14, 3 Hz, 1F), –110.5 (dd, *J* = 54, 3 Hz, 1F), –137.4 (dt, *J* = 52, 5 Hz, 2F) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 5.84 (tt, *J* = 52, 3 Hz, 1H), 6.10 (dd, *J* = 13, 4 Hz, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) 98.9 (dd, *J* = 61, 16 Hz), 107.2 (tt, *J* = 252, 40 Hz), 116.3 (tt, *J* = 273, 40 Hz), 157.0 (dd, *J* = 293, 281 Hz) ppm.

*CF<sub>2</sub>=CHO CF<sub>2</sub>CF<sub>2</sub>H copolymerization with CH<sub>2</sub>=CF<sub>2</sub>.* A 75 ml stainless steel autoclave chilled to less than –20 °C was loaded with 9.4 g of CF<sub>2</sub>=CHO CF<sub>2</sub>CF<sub>2</sub>H monomer, 10 ml of CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub> solvent, and 5 ml of ~0.17 M DP in CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub>. The autoclave was chilled, evacuated and further loaded with ~4 g of VF<sub>2</sub>. The autoclave was shaken overnight at room temperature. The resulting hazy fluid was dried under nitrogen, then under pump vacuum, and finally for 23 h in a 77 °C vacuum oven, giving 4.6 g of tacky gum.

*Solution preparation and spinning.* A clear, colorless solution was made by rolling 2.5 g of polymer with 10 g of 2-heptanone solvent and passing through a 0.45 μm glass fiber microfiber syringe filter (Whatman Autovial™). Solutions of polymer 3 were spin coated in a conventional atmosphere spinner at spin speeds of 1000 rpm for 60 s onto CaF<sub>2</sub> substrates with a subsequent post apply bake at 120 °C for 2 min to produce polymer films of 9400 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

*Absorption results.* The 157 nm absorbance per micrometer determined is –0.002 per micrometer. The 193 nm absorbance per micrometer determined is –0.001 per micrometer. The 248 nm absorbance per micrometer determined is 0.003 per micrometer.

**2.2.1.4. Poly(vinylidene fluoride/perfluoromethylvinylether) (4): VF<sub>2</sub>/PMVE.** A 210 ml autoclave was loaded with 50 ml of CF<sub>2</sub>CICCl<sub>2</sub>F, chilled to less than –20 °C, and 10 ml of ~0.2 M DP in CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub> added. The autoclave

was evacuated and loaded with 33 g perfluoro(methylvinyl ether) (PMVE) and 13 g VF<sub>2</sub>. Shaking the autoclave overnight at room temperature gave solution that was evaporated down to soft polymer and then further dried for 29 h under pump vacuum and for 20 h in a 75 °C vacuum oven. This gave 31 g of soft polymer suitable for use as a glue.

A solution was made by rolling 4 g of this polymer with 16 g of hexafluorobenzene. This solution was passed through a 0.45 µm glass microfiber syringe filter (Whatman, Autovial™) and the filtrate used to spin coat thick films on optical substrate for absorption measurements. Solutions of 13:10 VF<sub>2</sub>:PMVE were spin coated onto CaF<sub>2</sub> substrates to produce polymer films of 25,970 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

The 157 nm absorbance per micrometer determined is 0.034 per micrometer. The 193 nm absorbance per micrometer determined is 0.015 per micrometer. The 248 nm absorbance per micrometer determined is 0.018 per micrometer.

**2.2.1.5. Poly(vinylidene fluoride/chlorotrifluoroethylene) (5): VF<sub>2</sub>/CTFE.** A 75 ml autoclave chilled to less than –20 °C was loaded with 25 ml of CF<sub>2</sub>CICCl<sub>2</sub>F and 5 ml of ~0.1 M DP in CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub>. The autoclave was evacuated and loaded with 9.6 g of VF<sub>2</sub> and 17 g of chlorotrifluoroethylene (CTFE). Shaking the autoclave overnight at room temperature gave viscous white fluid that was evaporated down to stretchy solid and then dried for 1 h under pump vacuum and for 30 h in a 75 °C vacuum oven. This gave 19 g of product.

Rolling 3 g poly(VF<sub>2</sub>/CTFE) with 20 g of 2-heptanone gave solution that was filtered through an 0.45 µm glass fiber syringe filter (Whatman, Autovial™). The filtrate was used to spin coat thick films on optical substrate for absorption measurements. Solutions of 5:4 VF<sub>2</sub>:CTFE were spin coated onto CaF<sub>2</sub> substrates to produce polymer films. VUV absorbance measurements were then used to determine the absorbance per micrometer.

The 157 nm absorbance per micrometer determined is 5.6 per micrometer. The 193 nm absorbance per micrometer determined is 0.27 per micrometer. The 248 nm absorbance per micrometer determined is 0.12 per micrometer.

**2.2.1.6. Poly(vinylidene fluoride/perfluoropropylvinyl ether) (6): VF<sub>2</sub>/PPVE.** A 210 ml autoclave was loaded with 50 ml of CF<sub>2</sub>CICCl<sub>2</sub>F, chilled to less than –20 °C, and 10 ml of ~0.2 M DP in CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub> added. The autoclave was cooled evacuated and 13 g VF<sub>2</sub> and 53 g PPVE added. After shaking overnight at ambient temperatures (22–26 °C), the autoclave was vented, and solution recovered. Excess solvent was evaporated under nitrogen and the polymer dried 72 h under vacuum at room temperature and then for 28 h at 75 °C, 45 g.

A solution was made by rolling 4 g of this polymer with 16 g of hexafluorobenzene. This solution was passed

through a 0.45 µm glass microfiber syringe filter (Whatman, Autovial™) and the filtrate used to spin coat thick films on optical substrate for absorption measurements. Solutions of 7:5 VF<sub>2</sub>:PPVE were spin coated onto CaF<sub>2</sub> substrates to produce polymer films of 29,874 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

The 157 nm absorbance per micrometer determined is 0.028 per micrometer. The 193 nm absorbance per micrometer determined is –0.003 per micrometer. The 248 nm absorbance per micrometer determined is –0.00074 per micrometer.

**2.2.1.7. Poly(CH<sub>2</sub>=CF<sub>2</sub>/CF<sub>2</sub>=CHO CF<sub>2</sub>CF<sub>3</sub>) (7): VF<sub>2</sub>/PEDVE, VF<sub>2</sub> analogue.** Preparation of perfluoroethyl-2, 2-difluorovinyl ether, CF<sub>2</sub>=CHO CF<sub>2</sub>CF<sub>3</sub> monomer.

- Preparation of 2-chloro-2,2-difluoroethyl trifluoroacetate. A mixture of 2-chloro-2,2-difluoroethanol (132 g) and DMF (15 drops) was charged to a 250 ml flask. Trifluoroacetyl chloride (17 g) was introduced to the flask via a dry ice condenser at about 50 °C. The resulting mixture was refluxed for 4 h. The mixture was distilled to give 234 g of the acetate, bp 79–81 °C, yield 97%. <sup>19</sup>F NMR (CDCl<sub>3</sub>) –62.8 (t, *J* = 8 Hz, 2F), –75.2 (s, 3F) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.79 (t, *J* = 9 Hz) ppm.
- Preparation of perfluoroethyl 2-chloro-2,2-difluoroethyl ether. A mixture of 2-chloro-2,2-difluoroethyl trifluoroacetate (20 g), HF (150 g), and SF<sub>4</sub> (60 g) was heated to 150 °C for 21 h. The mixture was poured into water (300 ml). The bottom layer was isolated to give crude product (16.1 g), yield 73%. It was relatively pure based on NMR analysis. Then the crude product was washed with Na<sub>2</sub>CO<sub>3</sub> until pH = 8, dried over Na<sub>2</sub>SO<sub>4</sub>, and distilled to afford the product, 11 g, bp 54–55 °C, yield 50%. <sup>19</sup>F NMR (CDCl<sub>3</sub>) –63.5 (tt, *J* = 9, 3 Hz, 2F), –86.4 (s, 3F), –91.2 (s, 2F) ppm.
- Preparation of perfluoroethyl-2,2-difluorovinyl ether A mixture of perfluoroethyl 2-chloro-2,2-difluoroethyl ether (69 g), KOH (30.0 g) and DMSO (15 ml) was heated to reflux on a spinning band distillation apparatus. The product was distilled out to give 43 g of perfluoroethyl-2,2-difluorovinyl ether, bp 15 °C, yield 85%. <sup>19</sup>F NMR (CDCl<sub>3</sub>) –86.5 (s, 3F), –91.8 (dd, *J* = 18, 4 Hz, 1F), –92.1 (s, 2F), –109.3 (d, *J* = 18 Hz, 1F) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 6.08 (dd, *J* = 13, 4 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) 98.9 (m), (ddt, *J* = 62, 16, 5 Hz), 116.2 (qt, *J* = 284, 45 Hz), 114.3 (tq, *J* = 275, 42 Hz), 156.3 (d, *J* 295 Hz) ppm.

**Copolymerization of CF<sub>2</sub>=CHO CF<sub>2</sub>CF<sub>3</sub> with CH<sub>2</sub>=CF<sub>2</sub>.** A 75 ml stainless steel autoclave chilled to less than –20 °C was loaded with 10 ml of CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub> solvent and 5 ml of ~0.17 M DP in CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub>. The autoclave was chilled, evacuated and further loaded with 10 g of CF<sub>2</sub>=CHO CF<sub>2</sub>CF<sub>3</sub> and ~4 g of VF<sub>2</sub>. The autoclave was

shaken overnight at room temperature. The resulting fluid was dried under nitrogen, then under pump vacuum, and finally for 4 days in a 77 °C vacuum oven, giving 2.6 g of tacky gum.

**Solution preparation and spinning.** A solution was made by rolling 1 g of polymer with 9 g of Halden™ ZT 85 solvent and passing through a 0.45 µm PTFE fiber microfiber syringe filter (Whatman Autovial™) to remove haze. Solutions of Polymer 5 were spin coated in a conventional atmosphere spinner at spin speeds of 1000 rpm for 30 s onto CaF<sub>2</sub> substrates with a subsequent post apply bake at 120 °C for 2 min to produce polymer films of 10,200 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

**Absorption results.** The 157 nm absorbance per micrometer determined is 0.034 per micrometer. The 193 nm absorbance per micrometer determined is 0.02 per micrometer. The 248 nm absorbance per micrometer determined is 0.01 per micrometer.

2.2.1.8. Poly[CH<sub>2</sub>=CF<sub>2</sub>/(CH<sub>2</sub>=C(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)<sub>2</sub>)] (8): VF<sub>2</sub>/DHB, HFIB analogue

**Preparation of 1,1-dihydro-2,5-bis(trifluoromethyl)-4-oxo-perfluorohex-1-ene, CH<sub>2</sub>=C(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)<sub>2</sub> monomer.** A 250 ml flask was charged with KF (12 g) and diglyme (55 ml) in a dry box. Hexafluoroacetone (40.5 g) was added to the mixture via a dry-ice condenser. The solid was dissolved completely. The HFIB fluorosulfate<sup>1</sup> (49 g) was added dropwise. The resulting mixture was stirred at room temperature for 3 h. The mixture was fresh distilled to give a liquid, which was then spinning band distilled to afford 36.3 g product, bp 84–86 °C, yield 55%. (Less pure fractions were not counted.) <sup>19</sup>F NMR (CDCl<sub>3</sub>) –65.3 (t, J = 8 Hz, 3F), –66.6 (m, 2F), –81.0 (m, 6F), –146.4 (t, J = 23 Hz, 1F) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 6.39 (m) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) 101.5 (d and septet, J = 269, 38 Hz), 117.7 (qd, J = 258, 32 Hz), 118.6 (t, J = 274 Hz), 127.4 (m), 131.2 (m) ppm.

**CH<sub>2</sub>=C(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)<sub>2</sub> copolymerization with CH<sub>2</sub>=CF<sub>2</sub>.** A 110 ml stainless steel autoclave chilled to less than –20 °C was loaded with 26 g of CH<sub>2</sub>=C(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)<sub>2</sub> monomer, 25 ml of CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub> solvent, and 10 ml of ~0.17 M DP in CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub>. The autoclave was chilled, evacuated and further loaded with ~5 g of VF<sub>2</sub>. The autoclave was shaken overnight at room temperature. The resulting viscous fluid was dried under nitrogen, then under pump vacuum, and finally for 88 h in a 75 °C vacuum oven, giving 26.7 g of white polymer.

**Solution preparation and spinning.** A clear, colorless solution was made by rolling 2 g of polymer with 18 g of

Halden™ ZT 85 solvent and passing through a 0.45 µm glass fiber microfiber syringe filter (Whatman Autovial™). Solutions of polymer 7 were spin coated in a conventional atmosphere spinner at spin speeds of 90 rpm for 30 s onto CaF<sub>2</sub> substrates with a subsequent post apply bake at 120 °C for 2 min to produce polymer films of 10,800 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

**Absorption results.** The 157 nm absorbance per micrometer determined is 0.0275 per micrometer. The 193 nm absorbance per micrometer determined is 0.0045 per micrometer. The 248 nm absorbance per micrometer determined is 0.0008 per micrometer.

2.2.1.9. Poly[CH<sub>2</sub>=CF<sub>2</sub>/(CH<sub>2</sub>=C(CF<sub>3</sub>)CF<sub>2</sub>OCH(CF<sub>3</sub>)<sub>2</sub>)] (9): VF<sub>2</sub>/THB, HFIB analogue

**Preparation of 1,1,5-trihydro-2,5-bis(trifluoromethyl)-4-oxo-perfluoro-1-hexene, CH<sub>2</sub>=C(CF<sub>3</sub>)CF<sub>2</sub>OCH(CF<sub>3</sub>)<sub>2</sub> monomer.** A 100 ml flask was charged with tributylamine (15 g), diglyme (15 ml), and hexafluoroisopropanol (13.7 g) in a dry box. HFIB fluorosulfate (see footnote 1) (20.0 g) was added dropwise at 3–12 °C. The resulting mixture was stirred at room temperature for 2 h. The mixture was fresh distilled to give a liquid, which was then spinning band distilled to afford 21.1 g product, bp 92–93 °C, yield 83%. (Less pure fractions were not counted.) <sup>19</sup>F NMR (CDCl<sub>3</sub>) –65.3 (t, J = 7 Hz, 3F), –70.8 (m, 2F), –74.0 (q, J = 5 Hz, 6F) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.99 (septet, J = 5 Hz, 1H), 6.37 (m, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) 69.4 (septet, t, J = 35, 4 Hz), 118.8 (t, J = 269 Hz), 120.2 (q, J = 283 Hz), 120.6 (sextet, J = 5 Hz), 130.9 (sextet, J = 35 Hz) ppm.

**CH<sub>2</sub>=C(CF<sub>3</sub>)CF<sub>2</sub>OCH(CF<sub>3</sub>)<sub>2</sub> copolymerization with CH<sub>2</sub>=CF<sub>2</sub>.** A 75 ml stainless steel autoclave chilled to less than –20 °C was loaded with 11.6 g of CH<sub>2</sub>=C(CF<sub>3</sub>)CF<sub>2</sub>OCH(CF<sub>3</sub>)<sub>2</sub> monomer, 10 ml of CF<sub>3</sub>CH<sub>2</sub>CF<sub>2</sub>CH<sub>3</sub> solvent, and 10 ml of ~0.17 M DP in CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub>. The autoclave was chilled, evacuated and further loaded with ~2 g of VF<sub>2</sub>. The autoclave was shaken overnight at room temperature. The resulting hazy fluid was dried under nitrogen, then under pump vacuum, and finally for 66 h in a 75 °C vacuum oven, giving 12.9 g of white polymer. Fluorine NMR in hexafluorobenzene found 53.4 mol% VF<sub>2</sub> and 46.6 mol% CH<sub>2</sub>=C(CF<sub>3</sub>)CF<sub>2</sub>OCH(CF<sub>3</sub>)<sub>2</sub>. A small sample was purified for DSC measurements by dissolving 0.5 g of polymer in 3 g of Halden ZT 85 solvent [HCF<sub>2</sub>O(CF<sub>2</sub>O)<sub>m</sub>(CF<sub>2</sub>CF<sub>2</sub>O)<sub>n</sub>CF<sub>2</sub>H], filtering the haze off using a 0.45 µm PTFE syringe filter (Whatman Autovial™), evaporating off excess solvent, and drying in a 75 °C vacuum oven for 16 h.

**Solution preparation and spinning.** A hazy solution was made by rolling 2 g of polymer with 18 g of Halden™ ZT 85 solvent. The haze was removed by filtering first through a bed of chromatographic silica in a 0.45 µm glass fiber

<sup>1</sup> Patent pending.

microfiber syringe filter (Whatman Autovial<sup>TM</sup>), centrifuging at 15,000 rpm, and finally filtering again through a 0.2  $\mu\text{m}$  PTFE syringe filter (Gelman Acrodisc CR). Evaporation of 0.1192 g of this solution on a glass slide gave a clear film weighing 0.0085 g (solution  $\sim 7$  wt.% in solids). Solutions of polymer **9** were spin coated in an enclosed vapor can spinner at spin speeds of 800 rpm for 30 s, after an initial 10 s vapor equilibration period onto  $\text{CaF}_2$  substrates with a subsequent post apply bake at 120 °C for 2 min to produce polymer films of 11,700 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

*Absorption results.* The 157 nm absorbance per micrometer determined is 0.011 per micrometer. The 193 nm absorbance per micrometer determined is  $-0.002$  per micrometer. The 248 nm absorbance per micrometer determined is  $-0.002$  per micrometer.

**2.2.1.10. Poly(vinylidene fluoride/2-(difluoromethylene)-2,5,5-trifluoro-5-(trifluoromethyl)-1,3-dioxolane (10): VF<sub>2</sub>/PMD.** A 75 ml autoclave chilled to less than  $-20$  °C was loaded with 5 ml of  $\sim 0.17$  M DP in  $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$ , 15 ml of  $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$ , and 11.6 ml of perfluoro(2-methylene-4-methyl-1,3-dioxolane) (PMD). The autoclave was pressured with 100 psi of nitrogen and evacuated 10 times and then further loaded with 9.6 g of  $\text{VF}_2$ . Shaking overnight at room temperature gave white solid. Evaporation under nitrogen, 16 h under pump vacuum, and 32 h in a 77 °C vacuum oven gave 23 g of resin.

Rolling 1 g of polymer with 19 g of hexafluorobenzene gave partial solution that was passed through a  $\sim 0.25$  in. deep pad of chromatographic silica in a 0.45  $\mu\text{m}$  glass fiber filter (Whatman, Autovial<sup>TM</sup>). A portion of this solution was sent for <sup>19</sup>F NMR which found the composition of the dissolved polymer to be 54 mol% PMD and 46 mol%  $\text{VF}_2$  suggesting that the insolubles were high in  $\text{VF}_2$  content. The remaining filtrate was used to spin coat thick films on optical substrate for absorption measurements. The 157 nm absorbance per micrometer determined is 0.085 per micrometer. The 193 nm absorbance per micrometer determined is 0.002 per micrometer. The 248 nm absorbance per micrometer determined is 0.002 per micrometer.

## 2.2.2. Hexafluoroisobutylene copolymers

**2.2.2.1. Poly(hexafluoroisobutylene/vinyl fluoride) (11): HFIB/VF.** A 400 ml autoclave was loaded with 200 ml water and 0.05 g of Vazo<sup>TM</sup> 56 WSP initiator. The autoclave was cooled and evacuated and then 80 g of hexafluoroisobutylene and 25 g of vinyl fluoride added. After shaking for  $\sim 48$  h at 50 °C, the autoclave was vented, and an opalescent blue emulsion recovered. The emulsion was broken by vigorous agitation in a Waring blender, filtered, and washed four times in the Waring blender with 100 ml of methyl

alcohol. Drying for 6 days under pump vacuum gave 30 g of white powder and lumps.

A solution was made by rolling 10 g of the polymer with 40 g of 2-heptanone and filtering through a 0.45  $\mu\text{m}$  glass microfiber syringe filter (Whatman, Autovial<sup>TM</sup>). The filtrate was used to spin coat thick films on optical substrate for absorption measurements. Solutions of HFIB:VF were spin coated onto  $\text{CaF}_2$  substrates to produce polymer films of 9239 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

The 157 nm absorbance per micrometer determined is 0.005 per micrometer. The 193 nm absorbance per micrometer determined is  $-0.00082$  per micrometer. The 248 nm absorbance per micrometer determined is  $-0.002$  per micrometer.

**2.2.2.2. Poly(hexafluoroisobutylene:trifluoroethylene) (12): HFIB/TrFE.** A 400 ml stainless steel autoclave chilled to less than  $-20$  °C was loaded with 10 ml of  $\sim 0.17$  M DP in Vertrel<sup>®</sup> XF. The autoclave was cooled, evacuated, and further loaded with 50 g of trifluoroethylene and 100 g of hexafluoroisobutylene. The reaction mixture was shaken overnight at ambient, removed from the autoclave, and evaporated down under nitrogen, then for 3 days under pump vacuum, and finally for 22 h in a 75 °C vacuum oven. There was obtained 10.5 g of white solid. A solution was made by rolling 2 g of this polymer with 8 g of 2-heptanone. This solution was passed first through a 0.45  $\mu\text{m}$  glass microfiber syringe filter (Whatman, Autovial<sup>TM</sup>) and then through a 0.45  $\mu\text{m}$  PTFE membrane syringe filter (Whatman, Autovial<sup>TM</sup>). This solution was used to spin coat thick films on optical substrate for absorption measurements.

Solutions of HFIB:TrFE were spin coated onto  $\text{CaF}_2$  substrates to produce polymer films of 12,146 and 1500 Å thicknesses, respectively. VUV absorbance measurements were then used to determine the absorbance per micrometer.

The absorbance per micrometer determined from the thicker polymer film is 0.012 per micrometer. The 193 nm absorbance per micrometer determined is 0.005 per micrometer. The 248 nm absorbance per micrometer determined is  $-0.001$  per micrometer.

## 2.2.2.3. Poly(hexafluoroisobutylene/vinyl alcohol) (13): HFIB/VOH

*Hexafluoroisobutylene/vinyl acetate copolymer (HFIB/VOAc).* A 400 ml autoclave was loaded with 50 ml of  $\text{CF}_2\text{ClCCl}_2\text{F}$ , 27 ml of vinyl acetate, and 50 ml of  $\sim 0.1$  M DP in  $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$ . The autoclave was chilled, evacuated, and further loaded with 49 g of HFIB. Shaking overnight at room temperature gave a viscous pale yellow solution. The polymer was precipitated by addition to 400 ml of methyl alcohol. Filtration, drying under pump vacuum, and drying for 19 h in a 75 °C vacuum oven gave 52 g of poly(HFIB/VOAc) having an inherent viscosity of 0.13 in acetone at 25 °C.

*Hexafluoroisobutylene/vinyl alcohol copolymer.* Fifty grams of the poly(HFIB/VOAc) prepared above, 500 ml of methyl alcohol, and 25 ml of 25 wt.% sodium methoxide in methyl alcohol were refluxed for 6 h. Over this period, additional methyl alcohol was added as ~860 ml of methyl alcohol were distilled off. Addition of resulting polymer solution to water gave a gummy precipitate. The water was decanted off and the precipitate taken back into 200 ml of methyl alcohol and reprecipitated with 500 ml of water in a Waring blender. Vacuum filtration, drying under pump vacuum and then for 24 h in a 75 °C vacuum oven gave 37 g of poly(HFIB/VOH) as off white granules.

*Solution preparation and spinning.* A solution was made by rolling 3.28 g of this polymer with 35 g of 1-methoxy-2-propanol acetate. This solution was passed through a 0.45 µm glass fiber syringe filter (Whatman, Autovial™) giving a slightly hazy pale yellow solution. The solution was treated with 0.4 g decolorizing carbon and filtered again and then with 0.58 g of silica gel and filtered a third time. The solution was still pale yellow but no longer hazy. The filtrate used to spin coat thick films on optical substrate for absorption measurements. Solutions of 1:1 HFIB:VA were spin-coated onto CaF<sub>2</sub> substrates to produce polymer films of 1350 Å thickness.

*Absorption results.* VUV absorbance measurements were then used to determine the absorbance per micrometer. The 157 nm absorbance per micrometer determined is 0.350 per micrometer. The 193 nm absorbance per micrometer determined is -0.047 per micrometer. The 248 nm absorbance per micrometer determined is -0.107 per micrometer.

### 2.2.3. Ethylene copolymers

*2.2.3.1. Poly(ethylene/perfluoropropylvinyl ether) (14): E/PPVE.* A 400 ml stainless steel autoclave chilled to less than -20 °C was loaded with 10 ml of ~0.17 M DP in Vertrel® XF. The autoclave was cooled, evacuated, and further loaded with 133 g of perfluoromethylvinyl ether and 9 g of ethylene. The reaction mixture was shaken overnight at ambient temperature, removed from the autoclave, evaporated down under nitrogen, then for 24 h under pump vacuum, and finally for 31 h in a 72 °C vacuum oven. There was obtained 63 g of white solid.

A solution was made by rolling 2 g of this polymer with 18 g of H Galden ZT 85. This solution was passed through a 0.45 µm glass microfiber syringe filter (Whatman, Autovial™). Solutions of E/PPVE were spin coated onto CaF<sub>2</sub> substrates to produce a polymer film of 23,000 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer. The absorbance per micrometer determined from the film is 0.016 per micrometer. The 193 nm absorbance per micrometer determined is 0.008 per micrometer. The 248 nm absorbance per micrometer determined is <0.01 per micrometer.

*2.2.3.2. Poly(ethylene/hexafluoropropylene) (15): E/HFP.* A 400 ml stainless steel autoclave chilled to less than -20 °C was loaded with 20 ml of ~0.17 M DP in Vertrel® XF. The autoclave was cooled, evacuated, and further loaded with 150 g of perfluoromethylvinyl ether and 7 g of ethylene. The reaction mixture was shaken overnight at ambient temperature, removed from the autoclave, evaporated down under nitrogen, then overnight under pump vacuum, and finally for 6 days in a 75 °C vacuum oven. There was obtained 8 g of thick grease.

A solution was made by rolling 2 g of this polymer with 18 g of H Galden ZT 85. This solution was passed through a 0.45 µm glass microfiber syringe filter (Whatman, Autovial™). Solutions of E/HFP were spin coated onto CaF<sub>2</sub> substrates to produce polymer films of 9760 Å thicknesses. VUV absorbance measurements were then used to determine the absorbance per micrometer. The absorbance per micrometer determined for the film is 0.043 per micrometer. The 193 nm absorbance per micrometer determined is 0.031 per micrometer. The 248 nm absorbance per micrometer determined is <0.01 per micrometer.

### 2.2.4. Perfluorodimethyldioxole copolymers

*2.2.4.1. Poly(ethylene/perfluorodimethyldioxole) (16): E/PDD.* A ~210 ml stainless steel autoclave chilled to less than -20 °C was loaded with 10 ml of ~0.17 M DP in Vertrel® XF and 73.2 g of perfluorodimethyldioxole. The autoclave was cooled, evacuated, and further loaded with 6 g of ethylene. The reaction mixture was shaken overnight at ambient temperature, removed from the autoclave, and evaporated down under nitrogen, then for 24 h under pump vacuum, and finally for 31 h in a 72 °C vacuum oven. There was obtained 59 g of white solid. A solution was made by rolling 4 g of this polymer with 40 g of H Galden ZT 85, centrifuging for 5 h at 14,000 rpm, and filtering through a 0.2 µm PTFE syringe filter (Gelman Aerodisc® CR 26 mm). This solution was used to spin coat thick films on optical substrate for absorption measurements.

Solutions of HFIB:TrFE were spin coated onto CaF<sub>2</sub> substrates to produce a polymer film of 9900 Å. VUV absorbance measurements were then used to determine the absorbance per micrometer.

The absorbance per micrometer determined for the film is 0.019 per micrometer. The 193 nm absorbance per micrometer determined is 0.006 per micrometer. The 248 nm absorbance per micrometer determined is <0.01 per micrometer.

*2.2.4.2. Poly(perfluorodimethyldioxole/tetrafluoroethylene) (17, 18 and 19): PDD/TFE Teflon® AF.* Solutions of Teflon® AF 1200, 1601, and 2400 (12 wt.% in FC-40 solvent) were spin coated at spin speeds of 6000 rpm onto CaF<sub>2</sub> substrates to produce polymer films of 4066, 3323 and 2133 Å thicknesses,

respectively. VUV absorbance measurements were then used to determine the absorbance per micrometer.

For Teflon<sup>®</sup> AF 1200, the absorbance 157 nm absorbance per micrometer determined is 0.64 per micrometer. The 193 nm absorbance per micrometer determined is 0.004 per micrometer. The 248 nm absorbance per micrometer determined is –0.001 per micrometer.

For Teflon<sup>®</sup> AF 1601, the 157 nm absorbance per micrometer determined is 0.42 per micrometer. The 193 nm absorbance per micrometer determined is 0.02 per micrometer. The 248 nm absorbance per micrometer determined is 0.01 per micrometer.

For Teflon<sup>®</sup> AF 2400, the 157 nm absorbance per micrometer determined is 0.007 per micrometer. The 193 nm absorbance per micrometer determined is –0.06 per micrometer. The 248 nm absorbance per micrometer determined is –0.06 per micrometer.

### 2.2.5. Other polymers

**2.2.5.1. Liquid cyclobutanes (20, 21 and 22).** For 1,1,2,2-tetrafluorocyclobutane (TFCB) (**20**), the absorbance 157 nm absorbance per micrometer determined is >0.2 per micrometer. The 193 nm absorbance per micrometer determined is 0.019 per micrometer. The 248 nm absorbance per micrometer determined is 0.0003 per micrometer.

For the propylene/hexafluoropropylene (P/HFP) cyclic adduct mixture **21**, the 157 nm absorbance per micrometer determined is >0.2 per micrometer. The 193 nm absorbance per micrometer determined is 0.07 per micrometer. The 248 nm absorbance per micrometer determined is 0.002 per micrometer.

For hexafluoropropylene/hexafluoropropylene cyclic adduct mixture (HFP<sub>2</sub>) (**22**), the 157 nm absorbance per micrometer determined is 0.1 per micrometer. The 193 nm absorbance per micrometer determined is 0.0001 per micrometer. The 248 nm absorbance per micrometer determined is 0.0003 per micrometer.

**2.2.5.2. Poly(hexafluoropropylene/tetrafluoroethylene) (23): HFP/TFE.** HFP/TFE copolymer was prepared by the method of [15].

Rolling 31.6 g of HFP/TFE copolymer with 986 g of PF-5080 (performance fluid manufactured by 3M, believed to be largely perfluorooctanes) gave solution. Vacuum filtration through a 0.45 μm filter gave clear solution.

Solutions of 1:1 HFP:TFE were spin coated onto CaF<sub>2</sub> substrates to produce polymer films of 1850 Å thickness. VUV absorbance measurements were then used to determine the absorbance per micrometer.

The 157 nm absorbance per micrometer determined is 3.9 per micrometer. The 193 nm absorbance per

micrometer determined is 0.086 per micrometer. The 248 nm absorbance per micrometer determined is 0.073 per micrometer.

## 3. Results and discussion

### 3.1. Optical transparency at 157 nm

Through an extensive program of synthesis and optical characterization of new hydrofluorocarbon polymers we have established structural design principles to guide the development of novel fluoropolymers with reduced optical absorbance and therefore greater 157 nm transparency.

#### 3.1.1. Absorbance of current polymeric materials

At the start of this work, the published literature offered very little encouragement that 0.8 μm thick organic films would even be able to show 98% transparency to 157 nm light. For example, the optical absorbance of Teflon<sup>®</sup> AF and Cytop<sup>™</sup> is shown in Fig. 1. Teflon<sup>®</sup> AF [14] was cited earlier as an breakthrough lead for 157 nm resists because it showed  $A/\mu\text{m} = \sim 0.5$  [1]. An  $A/\mu\text{m}$  of 0.5 is  $\sim 40\times$  too absorbing for pellicles. Cytop<sup>™</sup> [5], another cyclic perfluoroether polymer, is still more absorbing at 157 nm with an  $A/\mu\text{m} = 1.9$ . Lest one think that the problem is the ether functionalities present in both Teflon<sup>®</sup> AF and Cytop<sup>™</sup>, the purely perfluorocarbon polymer 1:1 poly(HFP:TFE) [15] shows a markedly larger  $A/\mu\text{m}$  of 3.9. Perfluorinated polymers are nonetheless better than purely hydrocarbon polymers. For example, poly(acrylic acid), poly(styrene), poly(methylmethacrylate), and poly(vinyl alcohol) all have  $A/\mu\text{m}$  values falling between 4.5 and 11 [3].

#### 3.1.2. Absorbance of normal and perfluoro paraffins

Optical absorption data have been reported for short chain paraffin hydrocarbons  $\text{H}(\text{CH}_2)_n\text{H}$  [16], for fluorocarbons  $\text{F}(\text{CF}_2)_n\text{F}$  [17], and for oligomeric TFE [18]. As shown in Fig. 2, these data demonstrate that the fundamental absorptions moves to longer wavelengths with increasing chain lengths such that 157 nm absorption may set in as early as  $n = 6-10$  [17,18] for linear fluorocarbons and as early as  $n = 1-2$  for linear hydrocarbons. The higher energy and shorter wavelength of the fundamental fluorocarbon absorptions mean that fluorocarbon chains are more resistant than hydrocarbon chains to UV absorption and not surprisingly the industry has been moving increasingly towards perfluorination when seeking high UV transmission. Yet, at the same time, we see from this data that long  $(\text{CH}_2)_n$  or  $(\text{CF}_2)_n$  chains may also, by their very nature, absorb at 157 nm, making transparent polymers seem at first glance an unlikely proposition.

#### 3.1.3. Vinylidene fluoride copolymers

Four out of 10 pellicle candidates having  $\geq 46$  mol% of  $\text{VF}_2$  ( $\text{CF}_2=\text{CH}_2$ ) gave highly transparent polymers having

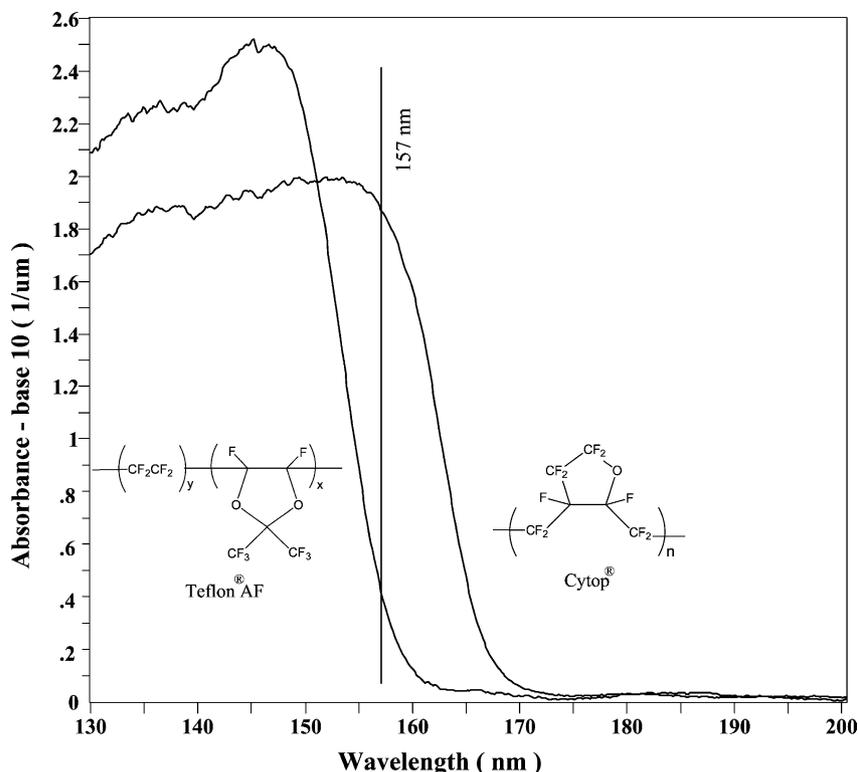


Fig. 1. Optical absorbance in units of 1 per micrometer vs. wavelength for Teflon<sup>®</sup> AF 1601 and Cytop<sup>™</sup>. At wavelengths below 150 and 157 nm, the absorbance spectra show saturation due to the very low transmission of the samples at shorter wavelengths.

an  $A/\mu\text{m} < 0.01$  at 157 nm. The optical absorbance spectra for these polymers are shown in Fig. 3 and the absorbances and VF<sub>2</sub> contents are summarized in Table 2. The one VF<sub>2</sub> polymer here showing a major absorption at 157 nm contained chlorine, a likely chromophore, that had been introduced by a comonomer.

### 3.1.4. Hexafluoroisobutylene copolymers

Hexafluoroisobutylene copolymers present a similar picture. Optical absorbances are presented in Figs. 4 and 5 the

absorbances and HFIB contents are summarized in Table 3. Two out of three candidates containing ~50 mol% of hexafluoroisobutylene [(CF<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub>] gave highly transparent polymers having  $A/\mu\text{m} < 0.01$  at 157 nm. The one HFIB copolymer showing significant absorption was copolymerized with a monomer containing –OH, a likely chromophore. Even with the –OH chromophore, the HFIB/vinyl alcohol copolymer is ~10,000× less absorbing ( $A/\mu\text{m} = 0.3$ ) than the wholly hydrocarbon analog polyvinylalcohol ( $A/\mu\text{m} = \sim 4.5$  [3]).

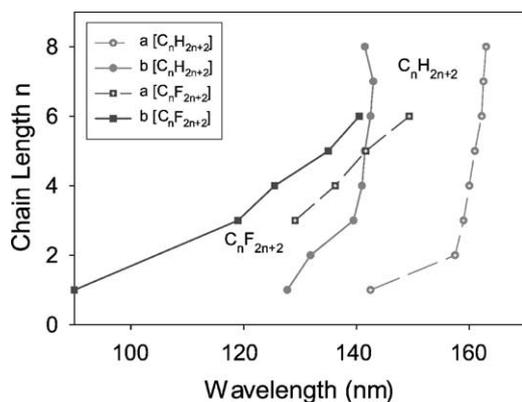


Fig. 2. Literature values [16–18] for the wavelength of the absorption peak for the weak first absorption shoulder (a, dashed line) and the first strong absorption peak (b, solid symbols) about the fundamental absorption edge in normal [C<sub>n</sub>H<sub>2n+2</sub>] and perfluoro [C<sub>n</sub>F<sub>2n+2</sub>] paraffins showing the shift of the absorption to longer wavelengths with increasing chain length for chain lengths from 1 to 8.

### 3.1.5. Intrinsically alternating monomers: CX<sub>2</sub>=CY<sub>2</sub>

VF<sub>2</sub> (CF<sub>2</sub>=CH<sub>2</sub>) and HFIB [(CF<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub>] have one structural feature in common. Both can be structurally classified as CX<sub>2</sub>=CY<sub>2</sub> monomers that force a regular alternation between fluorinated and hydrocarbon chain segments. That is, even though long (CF<sub>2</sub>)<sub>n</sub> and (CH<sub>2</sub>)<sub>n</sub> sequences are absorbing [2–4] as discussed in [1], regularly alternating sequences such as [(CH<sub>2</sub>)<sub>1</sub>(CF<sub>2</sub>)<sub>1</sub>]<sub>n</sub> are not. Perhaps the photochemically excited states involve conjugated sigma bonds and it is easier to mix together bonds of equal energies (all C–F bonds or all C–H bonds) than bonds of different energy (C–H with C–F bonds). This localization of the electrons in the polymer backbone in different CH<sub>2</sub> or CF<sub>2</sub> bonds serves to raise the transition energy for the excitation and thereby shift the fundamental absorption to shorter wavelengths. In any event, the empirical observation is that the fundamental absorption edge shifts to higher energy and shorter wavelengths and the 157 nm transparency

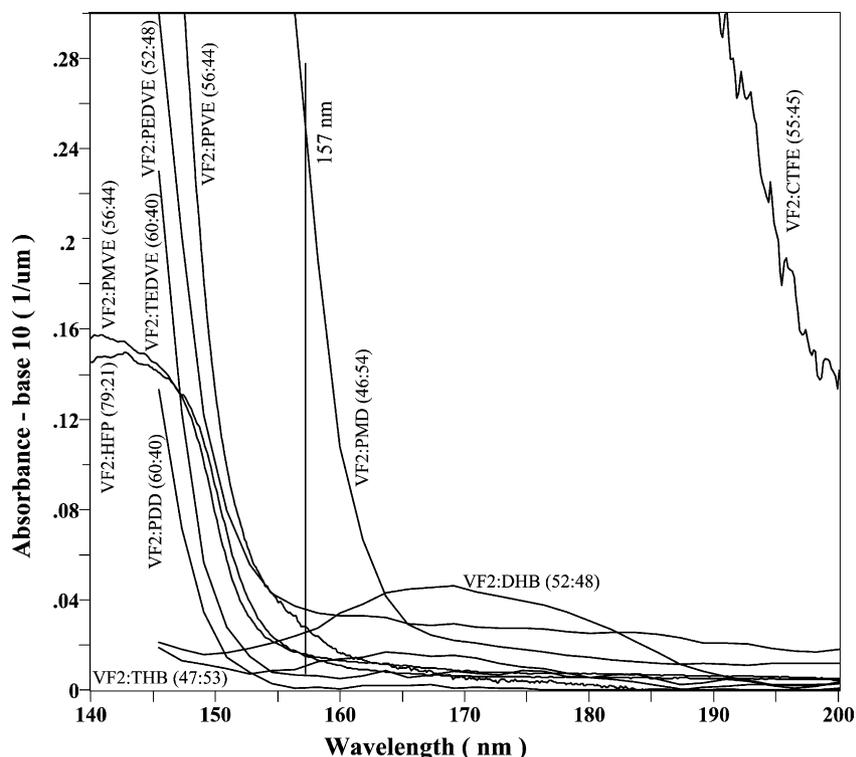


Fig. 3. Optical absorbance in units of 1 per micrometer vs. wavelength for VF<sub>2</sub> copolymers. The effects of saturation of the transmission measurement can be seen as a plateau at higher absorbance values and shorter wavelengths due to the low transmission of the samples at these wavelengths.

often increases as the number of identical adjacent bonds is minimized.

### 3.1.6. Effect of run lengths on transparency: ethylene and TFE copolymers

Given that forced alternation as in [(CH<sub>2</sub>)<sub>1</sub>(CF<sub>2</sub>)<sub>1</sub>]<sub>n</sub> favors high transparency, it is reasonable to ask the extent to which run lengths *x* and *y* in [(CH<sub>2</sub>)<sub>x</sub>(CF<sub>2</sub>)<sub>y</sub>]<sub>n</sub> can be increased without damaging transparency. Table 4 and Fig. 5 show *A*/μm results for three ethylene copolymers. All three copolymers have high transparencies and approximate a [(CH<sub>2</sub>)<sub>x</sub>(CF<sub>2</sub>)<sub>y</sub>]<sub>n</sub> structure for which *x* = *y* = 2.

Transparencies for [(CH<sub>2</sub>)<sub>x</sub>(CF<sub>2</sub>)<sub>y</sub>]<sub>n</sub> when *x* > 2 and *y* > 2 can be probed only indirectly. For example, Teflon<sup>®</sup> AF is a

family of copolymers between PDD and TFE. Increasing TFE content increases the (CF<sub>2</sub>CF<sub>2</sub>)<sub>n</sub> run length with a noticeable increase in 157 nm absorption. Published run lengths [14] are shown in Table 5 and the optical absorbances are shown Fig. 6.

Only Teflon<sup>®</sup> AF 2400 with few (CF<sub>2</sub>CF<sub>2</sub>)<sub>n</sub> runs longer than *n* = 3 gave a low absorbing polymer. This is consistent with the earlier observation that fluoroalkanes F(CF<sub>2</sub>)<sub>n</sub>F may remain transparent up to about only 6–10 carbons atoms [17,18].

Apparently PDD interferes with the absorptive effect of long runs of adjacent (CF<sub>2</sub>)<sub>n</sub> groups. Looking at the structure of PDD it can be seen that the PDD monomer unit adds two adjacent C–F bonds to a polymer chain as shown in Fig. 7.

Table 2

Absorbance at 157 nm for vinylidene fluoride (VF<sub>2</sub>) copolymers listed in approximate order of decreasing VF<sub>2</sub> content

Compound no.	Monomer copolymerized with (CF <sub>2</sub> =CH <sub>2</sub> ): VF <sub>2</sub>	VF <sub>2</sub> (%)	<i>A</i> /μm
1	CF <sub>2</sub> =CFCF <sub>3</sub> : HFP	79	<0.01
2	2,2-bis(Trifluoromethyl)-4,5-difluoro-1,3-dioxole: PDD	60	<0.01
3	CF <sub>2</sub> =CHOFCF <sub>2</sub> CF <sub>2</sub> H: TEDVE	60	<0.01
4	CF <sub>2</sub> =CFOCF <sub>3</sub> : PMVE	56	0.02
5	CF <sub>2</sub> =CFCl: CTFE	55	5.9
6	CF <sub>2</sub> =CFOCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> : PPVE	58	0.028
7	CF <sub>2</sub> =CHOC <sub>2</sub> F <sub>5</sub> : PEDVE	52	0.35
8	CH <sub>2</sub> =C(CF <sub>3</sub> )CF <sub>2</sub> OCF(CF <sub>3</sub> ) <sub>2</sub> : DHB	52	0.026
9	CH <sub>2</sub> =C(CF <sub>3</sub> )CF <sub>2</sub> OCH(CF <sub>3</sub> ) <sub>2</sub> : THB	47	<0.01
10	2-(Difluoromethylene)-2,5,5-trifluoro-5-(trifluoromethyl)-1,3-dioxolane: PMD	46	0.085

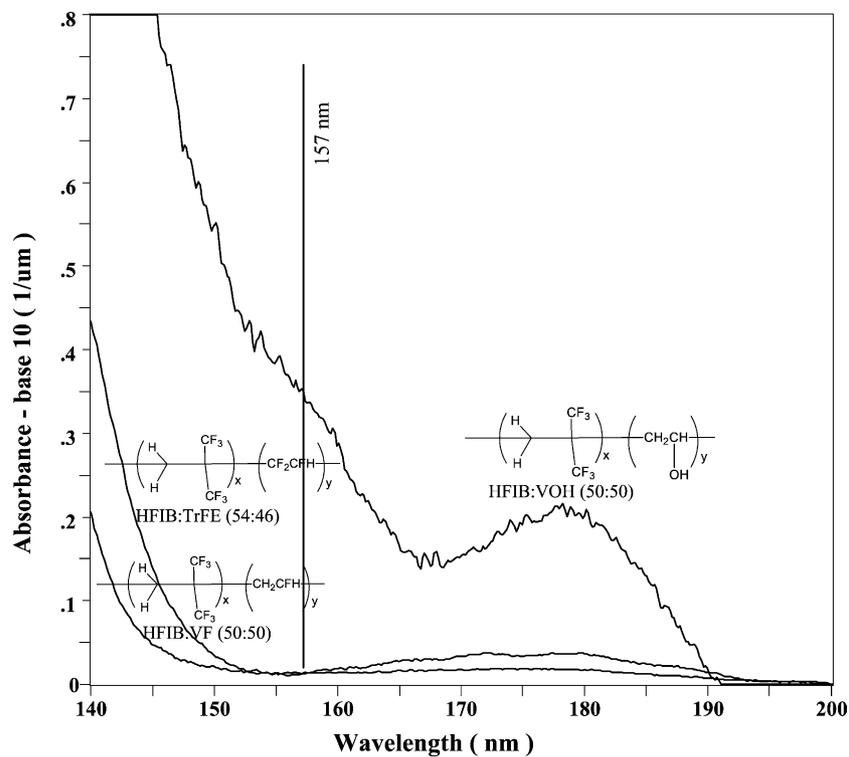


Fig. 4. Optical absorbance in units of 1 per micrometer vs. wavelength for HFIB copolymers. The effects of saturation of the transmission measurement can be seen as a plateau at higher absorbance values and shorter wavelengths due to the low transmission of the samples at these wavelengths.

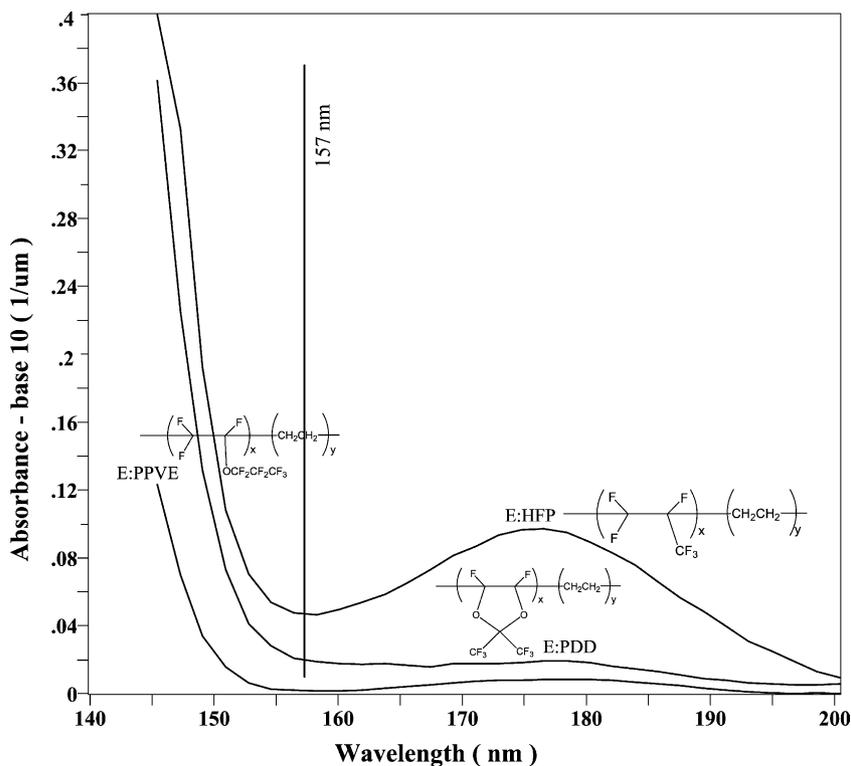


Fig. 5. Optical absorbance in units of 1 per micrometer vs. wavelength for ethylene copolymers.

Table 3  
Absorbance at 157 nm for hexafluoroisobutylene (HFIB) copolymers

Compound no.	Monomer copolymerized with HFIB, $(CF_3)_2C=CH_2$	HFIB (%)	$A/\mu m$
11	$CH_2=CHF$ : VF	50	<0.01
12	$CF_2=CFH$ : TrFE	54	<0.01
13	$CH_2=CH(OH)$ : VOH	50	0.3

In a chain that alternates PDD with TFE as in Teflon<sup>®</sup> AF, this makes for an uninterrupted sequence of C–F bonds down the chain, something we have just argued is bad for absorption. Nonetheless, Teflon<sup>®</sup> AF 2400 is highly transparent. Teflon<sup>®</sup> AF 2400 has a stiff and sterically congested chain as evidenced by its high glass transition temperature (240 °C) [19]. We speculate that the absorption of adjacent

Table 4  
Absorbance at 157 nm for ethylene (E) copolymers

Compound no.	Perfluorinated monomer copolymerized with ethylene	E (%)	$A/\mu m$
14	$CF_2=CFOCF_2CF_2CF_3$ : PPVE	52	<0.01
15	$CF_2=CFCF_3$ : HFP	57	0.043
16	2,2-bis(Trifluoromethyl)-4,5-difluoro-1,3-dioxole: PDD		0.021, <0.022 [20]

C–F bonds is highly dependent upon rotational angle and that the PDD monomer forces conformations unfavorable for 157 nm absorption.

### 3.1.7. Beyond alternation: rotational effects on absorbance

Data for simple fluorocarbon fluids can be interpreted as supporting a rotational dependence for absorption.

Table 5  
Absorbance at 157 nm vs. TFE run length in Teflon<sup>®</sup> AF

Compound no.	Teflon <sup>®</sup> AF grade	TFE in polymer (mol%)	$(CF_2CF_2)_n$ runs having $n$ value shown (%) [7]			$A/\mu m$
			$n = 3$	$n = 4$	$n = 5$	
17	1200	~52	~18	~14	~10	0.64
18	1600	~35	~15	~10	~5	0.42
19	2400	~11	~5	~0	~0	<0.01

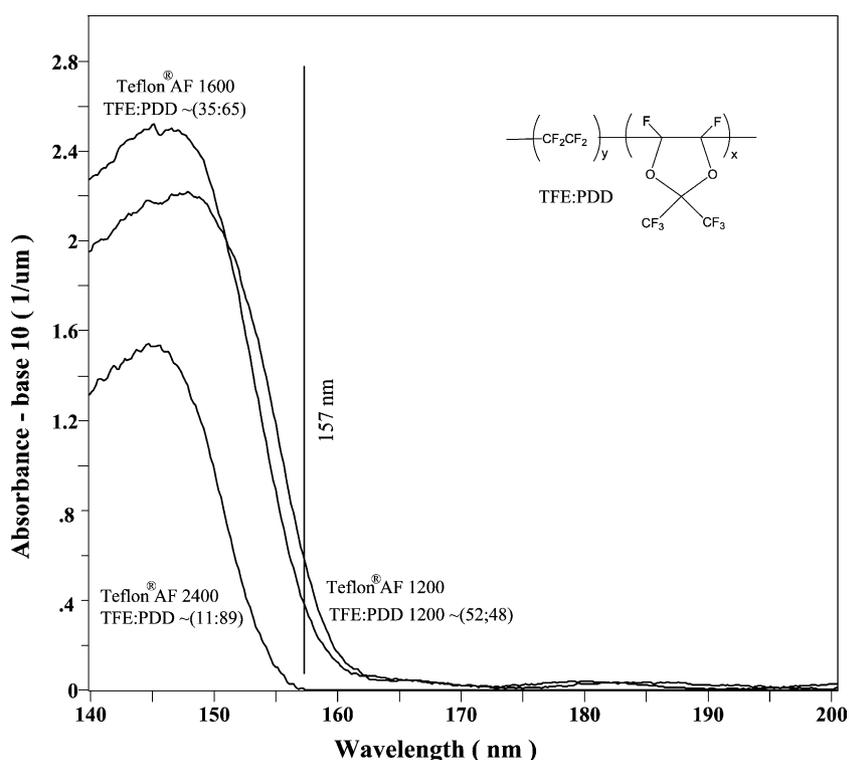


Fig. 6. Optical absorbance in units of 1 per micrometer vs. wavelength for Teflon<sup>®</sup> AF TFE:PDD copolymers as a function of composition. The effects of saturation of the transmission measurement can be seen as a plateau at higher absorbance values and shorter wavelengths due to the low transmission of the samples at these wavelengths.

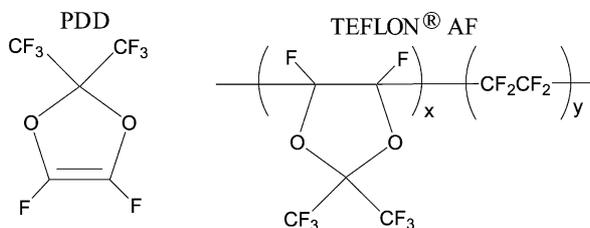


Fig. 7. Comparison of PDD monomer and Teflon<sup>®</sup> AF.

The cyclobutanes of Table 6 are much more strongly absorbing as shown in Fig. 8, than would have been predicted from the ethylene copolymers of Table 4 or sequence length effects of Table 5. Possibly this is because the four-membered rings force eclipsed conformations that are favorable for 157 nm absorption. Other factors may be as important or more important. Cyclobutane rings may, for example, change s and p orbital hybridization around the chain carbons atoms and thereby absorption.

### 3.2. 157 nm lifetime and photochemical degradation

Many of the hydrofluorocarbon polymers in Tables 2–4 meet the transparency specification ( $A/\mu\text{m} < 0.01$  at 157 nm) for pellicles. A second critical requirement for pellicle candidates is that they experience little change in optical characteristics after 75 million exposures to 157 nm light, each exposure having an incident energy of 0.1 mJ/cm<sup>2</sup> (Fig. 9).

Table 6  
The 157 nm absorbances of cyclobutanes

Compound no.	Compound	$A/\mu\text{m}$
20	1,1,2,2-Tetrafluorocyclobutane [21]: TFCB	>0.2
21	Propylene/hexafluoropropylene cyclic adduct mixture [22]: P/HFP	>0.2
22	Hexafluoropropylene/hexafluoropropylene cyclic adduct mixture [21]: HFP <sub>2</sub>	0.1

Unacceptable optical changes include a 10% loss in overall transparency, warping, or, in extreme instances, perforation. Viewed as a cumulative energy dose, 7.5 kJ/cm<sup>2</sup> is equivalent to several days of Florida sunlight which does not sound very impressive. Focusing instead on individual photon energy, 157 nm light has an energy of 182 kcal/mole, an energy roughly twice that of C–C, C–H, and C–F bond strengths. Hitting a 1 μm thick film of poly(TFE) with a cumulative dose of 7.5 kJ/cm<sup>2</sup> of 157 nm light would expose each C–C and C–F bond in the polymer to an average of 740 photons. Even were the poly(TFE) film 98% transparent, each bond in the polymer would still absorb 15 photons. Not surprisingly, none of our pellicle candidates have shown a lifetime anywhere near 7.5 kJ/cm<sup>2</sup>.

When a pellicle candidate is irradiated with 157 nm light, there is first a loss of transparency which at much higher doses is sometimes accompanied by slight visible discoloration. Our primary screen for pellicle lifetime has thus been to

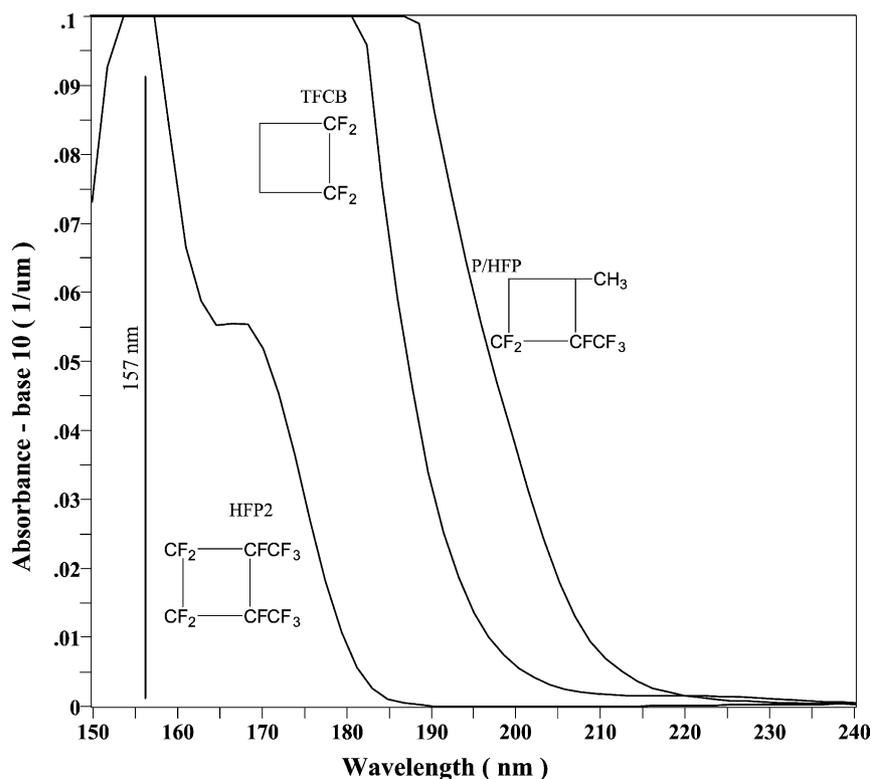


Fig. 8. Optical absorbance in units of 1 per micrometer vs. wavelength for three cyclobutane compounds. The effects of saturation of the transmission measurement can be seen as a plateau at higher absorbance values and shorter wavelengths due to the low transmission of the samples at these wavelengths.

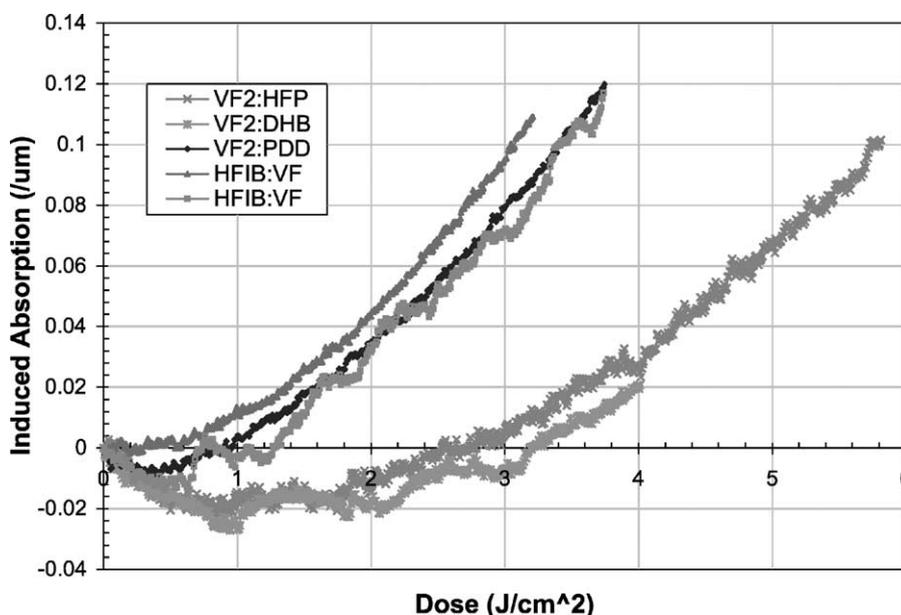


Fig. 9. Induced absorbance of TAFx46P and TAFx4P polymers on CaF<sub>2</sub>.

measure the exposure in J/cm<sup>2</sup> needed to produce a 10% loss in transparency at 157 nm. Results [7] for some of the polymers discussed here are shown in Fig. 9 and summarized in Table 7. The best of our pellicle candidates lose 10% of their transparency after a dose of only 2–6 J/cm<sup>2</sup> versus the industry goal of 7.5 kJ/cm<sup>2</sup>.

To a first approximation, the polymers that have lower 157 nm optical absorbance also tend to show the longest lifetimes. But there is the occasional exception as for example polymer 8 (VF<sub>2</sub>/DHB) which has a relatively high  $A/\mu\text{m}$  of 0.026 and yet one of the longest lifetimes observed (6 J/cm<sup>2</sup>). It is interesting to compare the 10% PCD lifetime and optical absorbance of VF<sub>2</sub>/DHB, to that of VF<sub>2</sub>/THB. There is only one atom difference between the DHB and THB monomers, and this change leads to apparently better alternation in the THB monomer. The optical absorbance of

the VF<sub>2</sub>/THB polymer is substantially smaller than that of VF<sub>2</sub>/DHB as shown in Table 2, yet the lifetime of VF<sub>2</sub>/THB is not increased due to this lower optical absorbance. Instead, VF<sub>2</sub>/THB has a substantially reduced lifetime when compared to VF<sub>2</sub>/DHB. These results imply that quantum yield, or the extent to which the polymer structure can harmlessly dissipate the energy, can be important as well. To make further progress, a better understanding is needed of what are the chromophores, how the energy is dissipated, what bonds are broken, and what if any role adventitious impurities or structural irregularities play.

#### 4. Conclusions

For application as pellicles for 157 nm photolithography, membrane forming polymers with low optical absorbance and high radiation durability are required. It has been found that polymers such as  $-(\text{CH}_2\text{CHF})_x\text{C}(\text{CF}_3)_2\text{CH}_2]_y-$ , or  $-(\text{CH}_2\text{CF}_2)_x[2,2\text{-bis}(\text{trifluoromethyl})\text{-}4,5\text{-difluoro-}1,3\text{-dioxole}]_y-$  with chains that alternate fluorocarbon segments with either oxygen or hydrocarbon segments frequently show >98% transparency at 157 nm, if amorphous.

These polymers are made from monomers, such as VF<sub>2</sub> and hexafluoroisobutylene, which themselves exhibit good alternation of CH<sub>2</sub> and CF<sub>2</sub> in their structures. Ether linkages also can serve to force alternation. In addition we find that fluorocarbon segments shorter than six carbons, and hydrocarbon segments less than two carbons or less than three carbons if partially fluorinated, also promote 157 nm transparency. Even with these design principles, it is advantageous to avoid small rings, as arise in the cyclobutanes. These results suggest a steric component to transparency in addition to the importance of alternation.

Table 7  
10% PCD lifetime: exposure dose required to reduce 157 nm transparency of a 0.8  $\mu\text{m}$  thick membrane by 10%

Compound no.	Polymer	Dose (mJ/cm <sup>2</sup> )
1	Poly(vinylidene fluoride/hexafluoropropylene): VF <sub>2</sub> /HFP	4.8
2	Poly(vinylidene fluoride/perfluorodimethyldioxole): VF <sub>2</sub> /PDD	3.3
3	Poly(CH <sub>2</sub> =CF <sub>2</sub> /CF <sub>2</sub> =CHOFCF <sub>2</sub> CF <sub>3</sub> ): VF <sub>2</sub> /PEDVE	2.0
8	Poly[CH <sub>2</sub> =CF <sub>2</sub> /(CH <sub>2</sub> =C(CF <sub>3</sub> )CF <sub>2</sub> OCF(CF <sub>3</sub> ) <sub>2</sub> ): VF <sub>2</sub> /DHB	5.2
9	Poly[CH <sub>2</sub> =CF <sub>2</sub> /(CH <sub>2</sub> =C(CF <sub>3</sub> )CF <sub>2</sub> OCH(CF <sub>3</sub> ) <sub>2</sub> ): VF <sub>2</sub> /THB	1.8
10	Poly(hexafluoroisobutylene/vinyl fluoride): HFIB/VF	3.5

However, upon irradiation these polymers undergo photochemical darkening and therefore none has demonstrated the kilojoule radiation durability lifetimes required to be commercially attractive. This is likely because these exposure lifetimes require every bond to absorb  $\sim 10$  photons, each photon having an energy roughly twice common bond energies.

To a first approximation, the polymers that have lower 157 nm optical absorbance also tend to show the longest lifetimes. These results imply that quantum yield, or the extent to which the polymer structure can harmlessly dissipate the energy, can be important as well.

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