Formation of Fluorocarbon Films by Ultraviolet Surface Photopolymerization

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Synopsis

The formation of surface-photopolymerized films from six fluorocarbon monomers in the gas phase at low pressure is described. Transparent, low surface-energy films from 250 to 300 Å thick readily formed on glass microscope slides on exposure to an UV source in the presence of the monomer vapor. These films were characterized by water and hydrocarbon contact angles and by surface analysis by x-ray photoelectron spectroscopy (XPS). Although these films strongly adhered to the surface under normal conditions, they could be removed by exposure to an oxygen plasma for a few minutes. Surface analysis by XPS revealed that the fluorocarbon was converted to fluoride ion by plasma treatment.

INTRODUCTION

Organic monomers are well known to deposit polymer films upon photolysis at low pressure.[1-3] For example, the surface photopolymerization of monomers such as 1,3-butadiene,[4,5] C_2F_4,[5,6] and C_4Cl_6[5,7] has been reported. Wright[8] has patented the process and also reported surface photopolymerization of less readily polymerizable monomers such as phenol, cyclohexanol, and ethylbenzene.[9] This paper reports surface photopolymerization of higher molecular weight fluorocarbon monomers known to give fluorocarbon polymers with low surface energies.

EXPERIMENTAL

Materials

Perfluorocyclobutene obtained from the Matheson Company, East Rutherford, New Jersey, was purified by trap-to-trap distillation in a standard high-vacuum system. Hexafluoroisopropyl methacrylate was supplied by Allied Chemical, Specialty Chemicals Division, Morristown, New Jersey, and purified as described above. 1H,1H-pentadecafluoro-octyl acrylate, 3,3,3-trifluoropropyl methyldichlorosilane, and 3-(heptafluoroisopropoxy)propyl-1-trichlorosilane were purchased from PCR Inc., P.O. Box 1466, Gainesville, Florida. These relatively involatile monomers were degassed under vacuum and used without further purification. Glass microscope slides (1 × 3 in.) were used without special cleaning as substrates for film deposition.

Film Thickness

Film thickness was determined mechanically by measuring step heights with a Dek Tak instrument supplied by Sloan Instrument Corp., 535 E. Montecito Street, Santa Barbara, California.

Contact Angles

Liquid-drop contact angles were measured with an NRL contact-angle goniometer (Rame-Hart, Inc.), Drops of liquid were placed on coated slides with a hypodermic syringe. Drops of liquids were always augmented to ensure measurement of advancing contact angles.

X-Ray Photoelectron Spectroscopy

Core electron binding energies were measured with a du Pont 650 electron spectrometer. Coated slides were cut into small squares and attached to the sample probe with double adhesive tape. Binding energies were referenced to the carbon line assumed to occur at 285 eV.

Surface Photopolymerization

A Rayonet photochemical reactor (Southern N. E. Ultraviolet Co., Newfield Street, Middletown, Connecticut) fitted with lamps emitting energy in the region of 3500 Å was used as the light source.

Microscope slides were placed in a cell consisting of a round-bottom quartz tube, 3 cm in diameter, connected to a glass joint and stopcock outlet. A side arm extended out below the stopcock. When monomers of low volatility were used, the monomer was introduced into the side arm of the cell and a slide placed in the quartz tube. The cell was attached to a vacuum manifold and evacuated. When the monomer had been sufficiently degassed, the side arm was maintained at $-78°C$ with a Dry Ice–acetone slush bath while the quartz tube containing the glass slide was heated to $180°C$ with a resistance heater. The cell was constantly evacuated while the quartz cell was heated. After being heated for several hours, the cell was sealed and removed from the manifold. The vapor pressure of these monomers was a few tenths of a torr at room temperature. The cell was put in the photochemical reactor so that only the quartz tube was exposed to light, while the liquid monomer remained in the side arm outside of the reactor.

Volatile monomers were condensed into the side arm of the cell and cooled to $-196°C$ with liquid nitrogen. After the monomer transfer was complete, the quartz tube containing the glass slide was heated while the monomer was maintained at $-196°C$. During photolysis, the side arm was maintained at a temperature such that the monomer vapor pressure was a few tenths of a torr.

RESULTS AND DISCUSSION

The films obtained from all monomers were optically clear and remained intact and adherent after immersion in water for several weeks. The film

was readily detected by the fact that water and hydrocarbons would not wet its surface. The monomers studied and the properties of the films obtained from them are summarized in Table I. Perfluorocyclobutene, hexafluoroisopropyl methacrylate, and 3-(heptafluoroisopropoxy)propyl-1-trichlorosilane repeatedly gave films with the highest liquid contact angles and most uniform coverage. The film deposition rate was quite low under the conditions described. At room temperature, a typical film thickness of about 300 Å resulted after exposure of the monomer vapor to radiation for three days. The water and hexadecane contact angles observed for these three photopolymerized films were similar to values reported for the surfaces of films polymerized from these monomers by conventional means.

Photopolymerized perfluorocyclobutene surfaces gave water contact angles up to 100°; the water contact angle on poly(tetrafluoroethylene) is reported to be 108°.[10] Water and hexadecane liquid contact angles observed for poly(hexafluoroisopropyl methacrylate) ranged up to 106° and 61°, respectively, depending on the degree of polymerization.[11,12] These values can be compared to 103° and 53°, respectively, observed for surface-photopolymerized films from hexafluoroisopropyl methacrylate. The water and hexadecane contact angles obtained for surface photopolymerized 3-(heptafluoroisopropoxy)propyl-1-trichlorosilane are ~98° and 56°, respectively, compared to ~105–113° and 60–66° for surfaces of the conventionally polymerized materials.[11,12]

Liquid contact angles observed for surface-photopolymerized films from 3,3,3-trifluoropropylmethyldichlorosilane, 1H,1H,7H-dodecafluoro-

TABLE I
Properties of Surface Photopolymerized Fluorocarbon Films

Monomer	Average water contact angle	Average hexadecane contact angle	Irradiation time, days	Film thickness, Å	Si 2p binding energy, eV (intensity/10^3)	Fluorine 1S binding energy, eV (intensity/10^3)
Perfluorocyclobutene	95°	43°	5		103.4 (6.0)	688.2 (95)
Hexafluoroisopropyl methacrylate	103°	53°	3	250 ± 50 300 ± 50	103.0 (5.5)	688.9 (95)
3,3,3-Trifluoropropyl-methyldichlorosilane	81°	44°	6		103.7	688.5 (10)
1H,1H,7H-Dodeca-fluoroheptyl acrylate	65°	52°	3			
3-(Heptafluoroisopro-poxy)propyl-1-tri-chlorosilane	98°	56°	3		103.9 (5.5)	689.4 (88)
1H,1H-Pentadeca-fluorooctyl acrylate	52°	30°	3			
Glass slide					103.5	

heptyl acrylate, and 1H,1H-pentadecafluorooctyl acrylate were much lower than those reported for the conventional polymers. Their uniformity of coverage was also much poorer, so that these monomers were not investigated further.

To explore the extent of monomers adsorption on glass, slides were exposed several days to various monomer vapors in the absence of UV radiation. Liquid contact angles measured on these slides were much lower than observed for the photopolymerized films. However, the contact angles did indicate that some fluorocarbon monomer was present on the surface. The thickness, uniformity, and durability of those films were much less than for those prepared by surface photopolymerization.

Attempts to characterize these surfaces by frustrated multiple internal reflectance spectroscopy were repeatedly unsuccessful. However, x-ray photoelectron spectroscopy proved to be particularly convenient for rapid characterization and surface analysis of these films. Core electron lines from silicon, fluorine, and carbon were obtained in less than 10 min per sample. The core electron-binding energies and the number of counts above background for those lines are given in Table I. The carbon, silicon, and fluorine core electron spectra from films from 3-heptafluoroisopropoxypropyl-1-trichlorosilane are shown in Figure 1. No chlorine was detected on the surface of films photopolymerized from the fluorocarbon-substituted chlorosilanes.

All of the silicon chlorine bonds were converted to silicon oxygen bonds by reaction with surface hydroxyl groups or moisture. The weak lines at 293.7 and 290.7 eV in the carbon $1s$ region are presumably due to carbon attached respectively to three fluorine atoms and to one fluorine atom.[13,14] The position of the silicon $2p$ line did not vary more than a few tenths of an electron volt. The $2p$ line for silicon in untreated glass slides occurred at 103.5 eV. Van Wazer et al.[15] reported a value of 103.0 for Si in quartz. The silicon line observed from coatings obtained from silicon-containing monomers was a few tenths of an eV above that value. However, no clear distinction between silicon in the substrate and in the coating was possible. The binding energy of the fluorine line (in the region of 689 eV) varied less than 1 eV among the coatings studied.

To test the durability of these coatings to strong oxidizing agents such as ozone, several surface-photopolymerized coatings were subjected to an oxygen plasma for several minutes. The apparatus has been described.[16] After this treatment, the surfaces were readily wetted by water and hydrocarbons. Surface analysis by XPS revealed that fluorine was present on the plasma-treated surface in the form of fluoride ion. The fluorine $1s$ spectra and silicon $2p$ spectra obtained from oxygen plasma-treated samples are shown in Figure 2. The fluorine line, at 685.7 eV, is somewhat asymmetric. The fluorine $1s$ line in salts containing SiF_5^- occurs at 685.3 eV, while the fluorine $1s$ line from K_2SiF_6 occurs at 687.4 eV. Hayes and Edelstein[17] have reported the fluorine $1s$ binding energy for ten ionic fluorides. The binding energy for fluoride ion in these compounds was
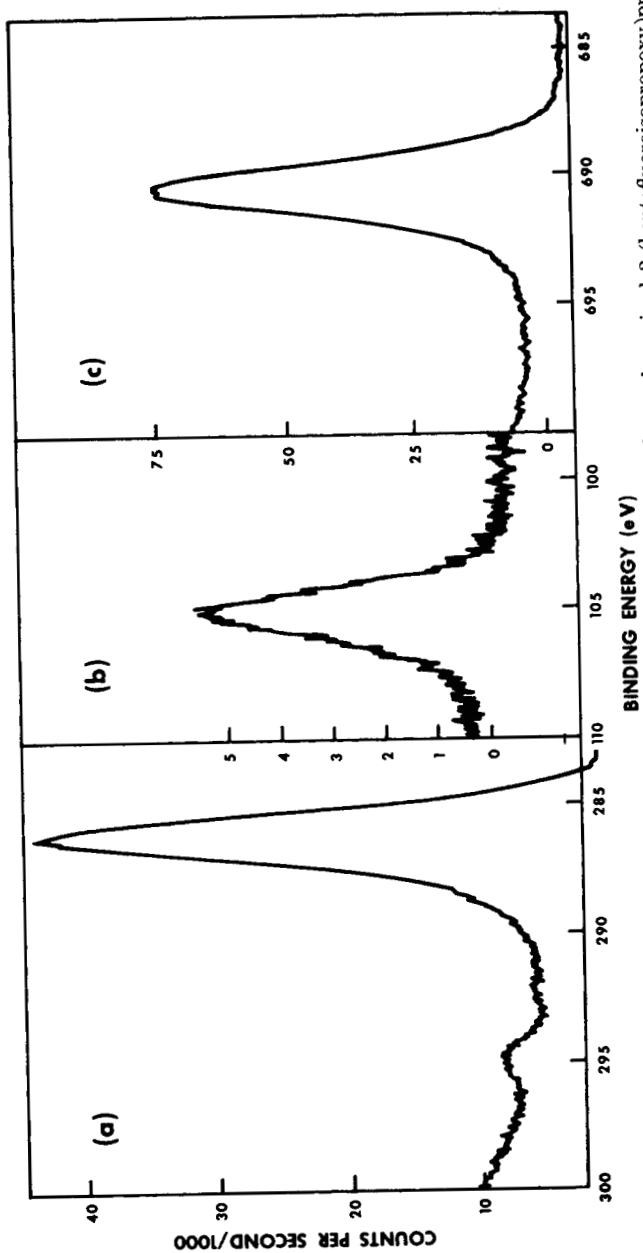
Fig. 1. Carbon 1s (a), silicon 2p (b), and fluorine 1s (c) core electron spectra for surface-photopolymerized 3-(heptafluoroisopropoxy)propyl-1-tri-chlorosilane.
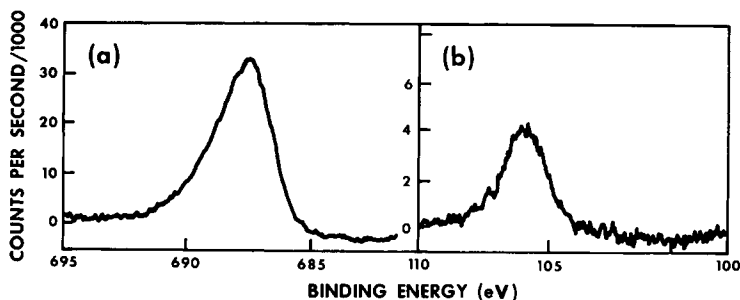
Fig. 2. Fluorine 1s (a) and silicon 2p (b) core electron spectra from plasma-treated hexafluoroisopropyl methacrylate surface-photopolymerized film.

fairly constant, ranging from 685.2 to 686.7 eV. One can conclude that fluoride ion is present after the films have been plasma treated, although the cation associated with the fluoride ion was not identified. Apparently, a fairly complex process takes place at the fluorocarbon–glass substrate interface when the surface is subjected to the oxygen plasma. Reducing species such as electrons[18] are known to exist in the region where active plasmas are formed, so that these possibly could reduce covalently bound fluorine tô fluoride ion. Oxygen plasmas have been used extensively in vacuum technology and the electronics industry for removing organic films and impurities from various substrates. However, little is known concerning the chemical composition of surfaces that remain after plasma clean-up.[19-22]

Discussion of the probable mechanism of forming surface-photopolymerized films is in order. The mechanism[1,2,3] generally postulated for surface photopolymerization begins with adsorption of monomer on the surface followed by photoexcitation of the adsorbed monomer. Chain initiation and propagation steps on the surface then result in forming polymeric films. Kunz and Wright[7] have emphasized the importance of gas-phase reactions that lead to reactive higher molecular weight intermediates that react on the surface to give polymeric films. In this study, mercury atoms were present in the photolysis cell, and the possibility of mercury-photosensitized reactions exists. In the case of perfluorocyclobutene and chlorosilanes, some question exists as to the nature of the energy transfer steps in photoexcitation. These monomers adsorb light at higher energy or lower wavelength than the light emitted by the excitation source used. The actual mechanism in a particular case probably includes both gas-phase and surface reactions. The importance of these depends on the substrate temperature and volatility of the monomer and other species present. It is likely that the higher molecular weight monomers used in these studies are readily adsorbed on the glass surface, so that surface polymerization reactions are relatively important.

Chlorosilanes are known to react at glass surfaces to produce organo-siloxanes at the surface.[23] For this reason, it is even more likely that

surface polymerization reactions are important for the organochlorosilanes used in this study.

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