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Plasma Synthesis of Fluorocarbon Films

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Synopsis

Fluorocarbon films were obtained by introducing perfluorobutene-2 into the afterglow region of an argon plasma. The plasma was generated electrodelessly using plates excited at 13.56 MHz at 70 watts of power. Film deposition rates between 250 Å and 450 Å per minute were obtained during typical operating conditions. The films were light yellow in color, adhered strongly to dry glass substrates, and exhibited liquid contact angles very similar to those reported for poly(tetrafluoroethylene) surfaces. The infrared spectrum of the film was quite similar to that obtained for Teflon. The freshly prepared film contained a high concentration of unpaired spins, and the ESR signal decayed slowly on standing in vacuum. The films could be removed from the glass substrates by immersion in dilute hydrofluoric acid or in brackish water.

INTRODUCTION

The formation of polymeric organic films in plasma systems has been discussed in several review articles.[1–3] In general, polymer films formed in a plasma are highly crosslinked, insoluble, and chemically inert as well as thermally very stable. Prior clean-up of the substrate in the discharge usually results in good film adhesion to the substrate.

Some exploratory work has been reported on the deposition of fluorocarbon films in plasmas.[4,5] Bradley mentions that perfluorobutene-2 could be deposited in a internal electrode plasma system to yield Teflon-like films.[6]

The present work reports a study of the synthesis of fluorocarbon films in an electrodeless flow plasma system and the properties of films obtained from perfluorobutene-2.

EXPERIMENTAL

Materials

Perfluorobutene-2 was obtained from the Matheson Company, East Rutherford, New Jersey, and used as received.

One in. by 3 in. glass microscope slides were used as the substrate for film deposition

Film Thickness

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

Contact Angles

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

Electron Spin Resonance

The ESR spectra were obtained on a Varian E3 EPR spectrometer equipped with a multipurpose cavity and variable temperature accessory. The polymer sample was sealed in a standard 3.0 mm I.D. quartz tube in air. The spin concentration was estimated by comparison with standard Varian pitch sample. The g value was measured by comparison with standard samples of known g value.

Plasma System for Film Synthesis

A schematic diagram of the apparatus used for the synthesis of fluorocarbon polymer films is shown in Figure 1. The fluorocarbon is introduced beyond the plasma zone above the substrate. The film deposition chamber was attached to a small manifold through a large diameter stopcock. The pressure in the system was estimated by a McLeod gauge connected to the manifold. The manifold contained a trap which was maintained at $-196°C$ by liquid nitrogen during film deposition to retain unreacted monomer and plasma-induced decomposition products. The system could be evacuated to 10^{-3} torr prior to introduction of the carrier gas and monomer gas.

The plasma was maintained using a Plasmatics P.G. 100-watt generator operating at 13.56 MHz. Radio frequency energy was coupled into the gas using parallel copper straps, and the generator output was efficiently matched to the load of the gas using a matching network. The power coupled into the gas was estimated by measuring the forward and reflected power.

The flow rate of both gases was estimated using a 150-mm scale rotameter. The system was evacuated and a plasma created with argon flowing through the system. The monomer was introduced into the afterglow of the plasma above the substrate and the monomer flow rate adjusted until the argon discharge was quenched and the deep purple color of the fluorocarbon plasma was established. Typical film deposition conditions were argon flow 5.0 and fluorocarbon flow 0.1, with a pressure of 0.5 torr in the manifold. The film deposition rate was established using typical operating conditions by measuring the thickness of the fluorocarbon film

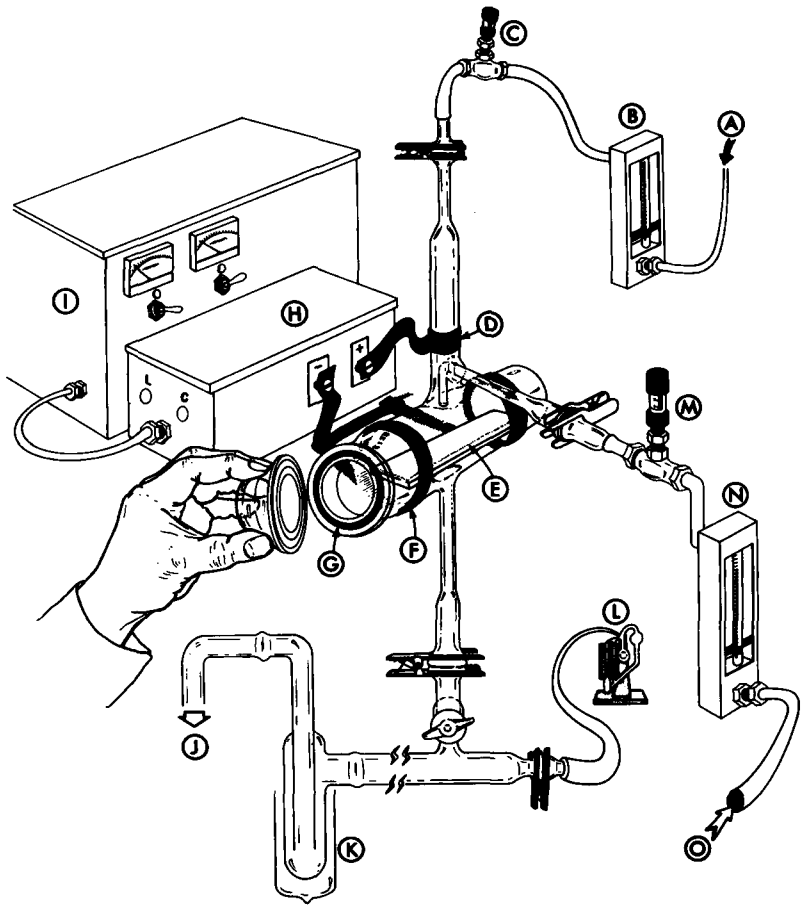

Fig. 1. Flow discharge system used for the synthesis of fluorocarbon films: (A) from gas cylinder; (B) rotometer; (C) flow control valve; (D) high voltage; (E) substrate; (F) ground; (G) O-ring; (H) coupling unit; (I) generator; (J) to pump; (K) −196 trap; (L McLeod gauge; (M) flow control valve; (N) rotometer; (O) from gas cylinder.

deposited for a given length of time. The vacuum system and glass slide substrate were cleaned prior to fluorocarbon film deposition by maintaining an argon plasma in the system for about 10 min prior to introduction of the fluorocarbon. The fluorocarbon films were light amber in color. Low volatile oils and solid products were formed in the cold trap during film deposition. These products were not characterized.

RESULTS AND DISCUSSION

This study was conducted to explore a plasma process for the formation of fluorocarbon films on glass substrates. Optically clear, uniform, pin-hole-free films with good chemical resistance and adherence to glass were required.

TABLE I
Plasma Operating Parameters and Fluorocarbon Film Thickness Values for Perfluorobutene-2

Run	Power, watts	Pressure, torr	Argon flow, cm[a]	Time, min	Perfluorobutene-flow, cm	Film thickness, Å
1	70	0.5	5.5	29	0.1	13,000 ± 1,000
2	70	0.6	5.0	38	quenched discharge	15,000 ± 1,000
3	70	0.5	5.8	42	quenched discharge	13,500 ± 1,000
4	70	0.5	5.5	30	0.1	7,250 ± 1,000

[a] A flow rate of 5 cm corresponded to about 40 cc/min at atmospheric pressure and ambient temperature.

About 20 fluorocarbons were used to form films in the plasma system. Several fluorocarbons were found to yield acceptable films, and perfluorobutene-2 was selected for more detailed study. This monomer was readily converted to a polymer film on exposure to a plasma and the film had the required properties.

Various experimental approaches for deposition of the film in a plasma were explored in order to arrive at the most acceptable procedure. The monomer was excited alone, in the presence of varying partial pressures of argon carrier gas, and introduced into the afterglow region of the argon plasma above the substrate. The latter procedure was found to be the most convenient in that it yielded acceptable films and required the least amount of clean-up after film deposition. Decomposition of the monomer alone or in the presence of argon resulted in the rapid formation of polymer film inside the tube around the electrode area. This film was then dislodged and carried on to the substrate as the film deposition was carried out. Heavy film deposits around the electrode area quickly formed and required frequent and time-consuming clean-up of the apparatus.

After exploratory studies were made to determine process conditions that yielded satisfactory films, a study of the film deposition rate using typical process conditions was conducted. Strips of Teflon tape were placed lengthwise along glass microscope slides and a fluorocarbon film deposited on the slide. The Teflon strips were removed and the step height of the deposited film determined. The film thickness data as well as the values of the discharge papameters used during the film deposition are given in Table I. The deposition rate varied from about 250 Å/min to 450 Å/min.

The films obtained during typical runs were light yellow to amber in color and partially soluble in acetone. The films adhered to the glass in water but were removed by dilute hydrofluoric acid. After 48 hr of immersion in brackish water, the films could be easily wiped from the glass slides.

TABLE II
Water and Hydrocarbon Angles for Fluorocarbon Films Obtained by Plasma Deposition from Perfluorobutene-2

Run	Median	Water range	Dodecane contact angle, degrees	
1	98	93–101		
2	96	92–96	Med 32	28–41°
3	94	90–100		
Teflon	108		42	

Fluorocarbon surfaces are known to be of the low free-energy type and as a result are generally difficult to wet with organic and aqueous liquids.[7] Water and hydrocarbon contact angles are presented in Table II for fluorocarbon films obtained from perfluorobutene-2. The contact angle for water and dodecane on tetrafluoroethylene surfaces is reported to be 108° and 42°, respectively.[8] The contact angles for liquids observed in the case of the fluorocarbon film obtained from the plasma are slightly lower than those reported for tetrafluoroethylene, however, they are similar enough to suggest that the surfaces are quite similar with regard to their liquid wetting properties.

Attempts to obtain the infrared and Raman spectra of these polymer films were not too successful. The films were quite brittle and did not yield a satisfactory mull. The Raman spectra could not be obtained due to the high fluorescence and background scatter that resulted from the film. A poor-quality FMIR spectrum was obtained from a sample prepared by depositing the film on polyethylene. A broad intense band at 1200 cm^{-1} was the only spectral feature of the film.

A FMIR spectrum of Teflon tape was obtained under similar conditions. A single intense band centered at about 1180 cm^{-1} was the only spectral feature between 2000 and 600 cm^{-1}. These two vibrations are probably associated with a C–F stretch mode,[9] and it appears that the film obtained from perfluorobutene-2 is quite similar to Teflon.

The film prepared in the plasma was found by ESR to contain a high concentration of free radicals. The ESR signal is shown in Figure 2 and consists of a single, almost symmetrical line 41.2 G wide, with a g value of 2.0031 ± 0.002. The spin concentration is estimated to be about 10^{20} spin $gram^{-1}$. The line shape is neither Lorentzian nor Gaussian and could not be simulated by superimposing Gaussian or Lorentzian curves. In view of the large line width and high spin density, the line shape probably results from a combination of inhomogeneous broadening and exchange narrowing. The signal decayed slowly, reaching half-intensity in 16 days at ambient temperature. Heating the sample at various temperatures up to 300°C for a total of 35 min caused a decrease of 58% in intensity, but no other change in the signal. These results differ from those found for polymers formed in a discharge from styrene and poly-*p*-xylene in that

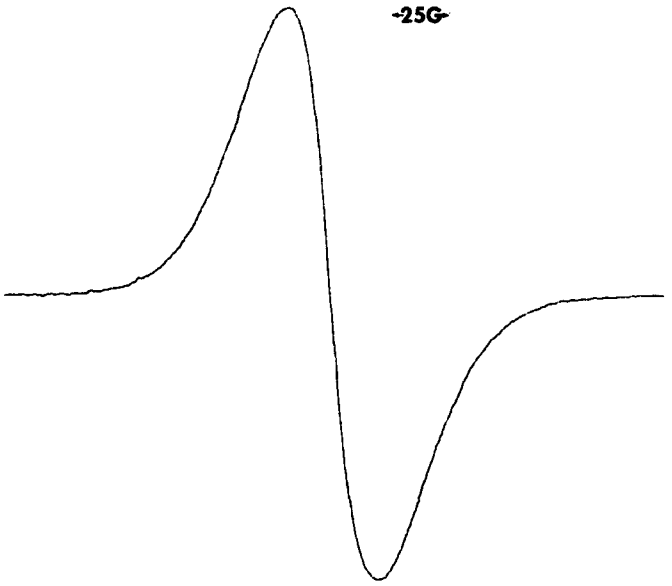

Fig. 2. Typical ESR spectrum obtained for fluorocarbon film.

for these polymers the initial radical signals were only about one half the width we observed, and after heating to 300°C decreased both in intensity and line width.[10] Ten minutes of illumination by a high-intensity mercury lamp filtered to remove wavelengths below 2850 Å had no effect on the perfluorobutene-2 signal.

Perfluorobutene-2 was readily converted into solid polymeric films upon direct exposure to a plasma or introduction into the afterglow region of an argon plasma. The per cent conversion of the monomer into solid film was not determined; however, reasonable deposition rates were easily realized. Some solid material as well as liquid products of varing volatility were found in a trap maintained at −196°C beyond the discharge gone. Lo and Osborn[5] decomposed hexafluoropropene in a ozonizer discharge. They observed a variety of linear, branched, and unsaturated liquid fluoroalkanes as products from this conversion. Some of the liquid products isolated exhibited a strong ESR signal indicating the presence of free radicals.

The properties of the film obtained from the plasma polymerization of perfluorobutene-2 generally support a branched fluorocarbon structure.

The strong ESR signal observed in the film indicates the presence of free radicals. This is a common characteristic of films formed in plasma systems and has been observed by others.[10,11]

The mechanism for the formation of polymer films in a flow discharge system is not known with certainty. Yasuda and Lamaze[12] studied the

formation of polystyrene in a flow electrodeless plasma system. They studied the rate of polymer formation as a function of the pressure, plasma power, and partial pressure of carrier gases in the system. On the basis of their experimental results, they concluded that polymerization occurred in the vapor phase and terminated or partially terminated on the walls of the reactor.

It is known qualitatively that organic substances are converted to free radicals and exited molecules and radicals in a flow discharge system.[13]

Whether these radicals combine in the vapor phase or combine on the sides of the wall with themselves or adsorbed monomer is not known.[1,2] Qualitatively, it is known that the probability of two-body collisions in the gas phase at low pressures is not too great, and it seems unlikely that very long-chain molecules could be formed in this way prior to collision with the wall.

Once radicals formed in the vapor phase collide with the reactor surface, they can react further with adsorbed monomer molecules or other radicals to form a crosslinked polymer.

The relative importance of vapor-phase chain propagation versus propagation on the surface of the reactor is not known, and probably both occur to some extent. The presence of trapped radicals in the film has been observed and seems to further verify that radicals are involved in the formation of films in plasma systems.

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