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The photochemical formation of a Titan haze analog. Structural analysis by X-ray photoelectron and infrared spectroscopy

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Abstract

The photochemical flow reactor (D.W. Clarke et al., 2000, *Icarus* 147, 282–291) has been modified to minimize the incorporation of oxygen and other impurities in the photoproducts. A mixture of gases that approximate their mixing ratios on Titan (N_2 , CH_4 , H_2 , C_2H_2 , C_2H_4 , and HC_3N) (0.98, 0.018, 0.002, 3.5×10^{-4} , 3×10^{-4} , 1.7×10^{-5} , respectively) was irradiated in the flow photochemical reactor using a 185-nm source to give a Titan haze analog as a solid product. X-ray photoelectron spectroscopy (XPS) gave a composition of 93.3% C, 5.3% N, and 1.4% O. Of the 93.3% carbon, high-resolution XPS revealed that 81.2% was present as C–H, C–C, and C=C groups, 12.1% may be C–O, C–N, C=N, $-C\equiv N$, and/or C≡N groups, 5.3% as a $-C\equiv N$ group. The peak for N was symmetrical and was assigned to the $-C\equiv N$ while that for oxygen was assigned to the C=O and/or the C–O group. Some of these assignments were confirmed by FTIR spectroscopy. The polymeric product had a C:N ratio of 17.6, which is significantly greater than that for Titan haze analogs prepared in discharge reactions. When the polymer was exposed to air for seven days the oxygen content increased by 6% along with an increase in the infrared absorption at 1710 cm^{-1} assigned to the C=O group of a ketone. The oxidation is attributed to the reaction of oxygen with free radicals trapped in the polymer matrix. It is proposed that the photochemical initiation of Titan haze formation from compounds formed from starting materials formed high in Titan's atmosphere is a more plausible model than haze formed in reactions initiated by solely by discharges. These data will be helpful in the interpretation of the data returned from the Huygens probe of the *Cassini* mission.
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Keywords: Photochemistry; Titan haze; Huygens; Atmospheres; Evolution

Introduction

Titan is the largest satellite of the planet Saturn and one of the few satellites in the Solar System with an atmosphere (Kuiper, 1944). The *Voyager 1* images showed an optically thick haze in the stratosphere completely obscuring the surface at visible wavelength (Rages and Pollack, 1983; Samuelson and Mayo, 1991). The presence of CH_4 and the reddish color of this hazy material led to the proposal that it was an organic aerosol on Titan produced in situ from the major atmospheric constituents (Sagan and Khare, 1979; Chyba and Sagan, 1989). The discovery of olefins, acety-

lenes, and nitriles in Titan's atmosphere prompted the investigation of the photochemical transformation of these compounds to the polymeric products that may constitute the haze layers observed (Hanel et al., 1981; Kunde et al., 1981; Maguire et al., 1981; McKay et al., 1989).

Laboratory simulations have been carried out in an effort to reproduce the solid organic material thought to compose the Titan haze. In these laboratory simulations, gas mixtures with constituents present in Titan's atmosphere were irradiated with UV light (Bar-Nun et al., 1988; Clarke and Ferris, 1995, 1996), or bombarded with spark and plasma discharges (Khare and Sagan, 1973; Khare et al., 1981; Sagan et al., 1992; Coll et al., 1999; McKay et al., 2001). Although simulated polymers have been investigated for many years since the initial studies of Khare and Sagan (1973), their exact structures are not known.

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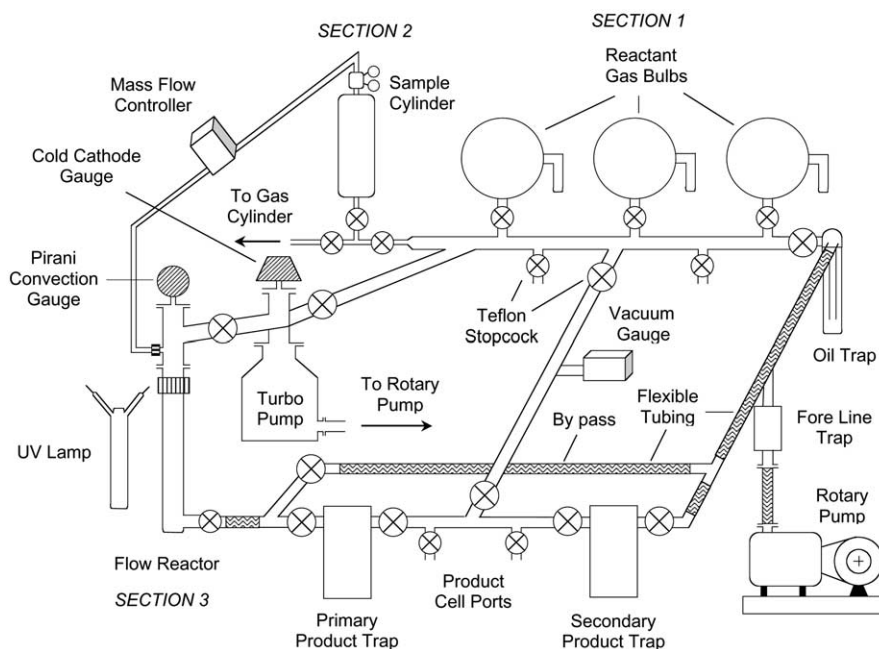


Fig. 1. Photochemical flow reactor.

The present research provides a detailed study of the composition and structures of the polymers generated photochemically using mixtures of gases that approximate the composition of Titan's atmosphere using a photochemical flow reactor (Clarke et al., 2000). UV light was chosen because the solar ultraviolet light is the predominant energy source driving the atmospheric chemistry on Titan (Sagan and Thompson, 1984; Clarke and Ferris, 1997a; Clarke et al., 2000; McKay et al., 2001). Thus photochemical reactions more closely simulate the atmospheric chemistry occurring on Titan than do discharge studies. A current list of proposed photodissociation processes has been published (Lebonnois et al., 2001).

Experimental

A. The photochemical flow system

1. System construction

The photochemical flow reactor described previously was modified (Clarke et al., 2000). It is composed of three sections (Fig. 1). The first is a standard glass vacuum rack that allows for trace gases to be introduced into the second section. In the second, a stainless steel section, the reactant gas is mixed with a carrier gas. The gas mixture is then introduced into the third section using a mass flow controller, where the photochemistry is performed. After passing through the photolysis cell, gases are collected in cryogenic traps downstream. A Varian model V-70D turbo molecular pump and two Welch model 1402 rough pumps were used to evacuate the system. It provides an oil-free system and

high vacuum in the range 10^{-7} – 10^{-8} Torr with a capacity of pumping 60 L/s. Low-pressures are measured by a MKS Cold Cathode Sensor Model 423 I-Mag and a MKS Convection Pirani Sensor model 317 with a MKS 937A Multi-sensor Controller. Pressure measurements in the range of 1–1000 Torr are made by a MKS Baratron model 390-HA 1000 with a model 270C Signal Conditioner. Gas flow was controlled by a MKS 1159B mass flow controller (0 – 100 standard $\text{cm}^3 \text{min}^{-1}$ capacity) connected to a MKS type 246B single-channel readout. The sample cylinder was constructed with stainless steel valves and tubing (#318 steel) capable of withstanding 1800 psi and holding 10^{-4} Torr vacuum. Fluoroelastomer (FETFE) o-rings were used in the vacuum line and greaseless stopcocks, and they were changed after every flow run.

Reactant gas preparation. The gas mixture was prepared and stored in a sample cylinder (Fig. 1). Cyanoacetylene was synthesized by the procedure of Moureu and Bongrand (1920) as modified by Miller and Lemmon (1967) and then distilled five times at a cold bath temperature of -50°C . Acetylene (Matheson, purified, 99.6%) was trapped at liquid nitrogen temperature (-196°C) and then distilled five times at -70°C using an ethanol/ CO_2 ice cold bath. Hydrogen (Matheson, UHP grade, 99.999%) was trapped at liquid nitrogen temperature (-196°C) for 1 h to remove water before filling the sample cylinder. Other gases such as ethylene (Praxair, Research grade, 99.99%), methane (Matheson, Research grade, 99.99%), and nitrogen (Air Products, Built-In-Purifier grade, 99.9999%) were used without purification. The nitrogen contains 10 ppb molecular oxygen and 20 ppb water.

Table 1
Comparison of reaction conditions to those on Titan

Conditions	Titan ^(a)	This work
Total pressure (Torr)	7.6–76	700
Mixing ratio:		
HC ₃ N	1.7×10^{-7}	1.7×10^{-5}
C ₂ H ₄	3.0×10^{-6}	3.0×10^{-4}
C ₂ H ₂	3.5×10^{-6}	3.5×10^{-4}
Hydrogen	0.002	0.002
Methane	0.018	0.018
Nitrogen	0.98	0.98

^a Averaged values reported for altitudes corresponding to pressure of 0.1 and 1.5 mbar (Coustonis et al., 1993).

Photochemistry. A gas mixture containing Titan mixing ratios of N₂, CH₄, and H₂ (0.98, 0.018, and 0.002, respectively) and 100-fold higher mixing ratios of HC₃N, C₂H₄, and C₂H₂ (1.7×10^{-5} , 3×10^{-4} , and 3.5×10^{-4} , respectively) was used to collect sufficient polymer for a total of 82 h of irradiation (Table 1). The gas mixture flowed through a quartz tube past the UV source at a rate of 15 cm³/min. at a pressure of 700 ± 20 Torr. The total gas pressure of 700 Torr was used to facilitate obtaining sufficient polymer for analysis rather than the 7.6 to 76-Torr pressure expected at the 100-km altitude in Titan's atmosphere. The mixture was irradiated with a low-pressure mercury lamp with principal emissions at 185 and 254 nm (Clarke and Ferris, 1997b). The photolyses were carried out at room temperature (298 K) and not at 160–180 K in Titan's atmosphere. The higher temperature will have little effect on the initial photochemical reactions (Clarke et al., 2000) but the product mixture may change at lower temperatures if products volatile at 298 K condense from the atmosphere and do not undergo further photochemical reactions.

2. Collection of polymer samples

The solid product was collected as a film on quartz and 1×1 cm² silicon plates (type P, Silicon Quest International). These were placed on a Pyrex plate located at the lower part of the flow cell (Fig. 2).

To minimize the incorporation of oxygen compounds bound to the interior surface of the vacuum line into the products the flow reactor, including Si wafer, was baked out at 150°C for 24 h and purged three times with high-purity nitrogen gas. Then the whole system was evacuated again using a turbo molecular pump for 24 h before each photochemical flow run. After the photolysis was terminated the silicon wafer was rapidly transferred to a special glass-sample-collection cylinder, which had been purged and slightly over pressurized with pure nitrogen to prevent atmospheric oxygen and water vapor entering the chamber. The whole sample-collection system was evacuated and over pressurized again with high-purity nitrogen before transporting to General Electric Corporate Research and Development Center, Schenectady, NY, for XPS analysis.

B. Analysis instruments

1. XPS analysis

X-ray photoelectron spectroscopy measurements were obtained using a Physical Electronic, Inc. 5500 system with monochromatic Al-*k*_α source, operated at a power of 200 W. An analyzer pass energy of 187 eV was used for survey scans, and 12 eV for high-resolution scans of the individual core levels. Surface charging was controlled using a low-energy electron flood gun at 3 eV, and the spectra were shifted to align the C–H component of the C 1s line at 284.6 eV. Data massage was implemented using PHI PC Access software Version 7.1A and PHI sensitivity factors. Gaussian/Lorentzian line shapes were employed for curve fitting high-resolution scans, after subtraction of linear baseline. Atomic compositions were computed from the survey scans; peak areas were derived after subtraction of a linear baseline, and corrected for sensitivity factors supplied in the software. The photoelectron take-off angle (TOA) was 15° and 45° with respect to the sample plane, which provides an integrated sampling depth of approximately 19 and 53 Å, respectively.

2. FT-IR analysis

A very thin polymer film formed on the silicon substrate so it was not possible to directly analyze the film by reflection-absorption infrared spectroscopy (RAIR). The poly-

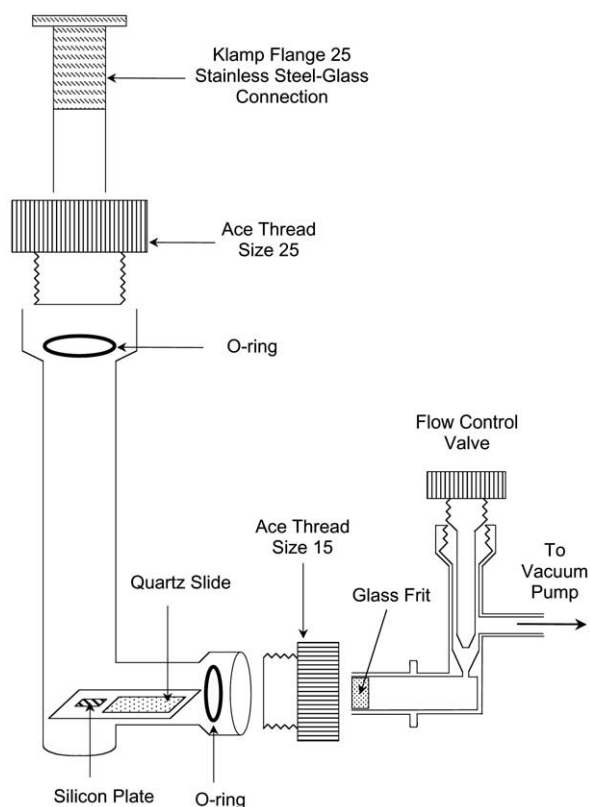


Fig. 2. Flow reactor irradiation chamber.

mers were removed from a silicon wafer using a scalpel and a Cambridge Instruments microscope, and then were transferred to a pie-shaped wedge of a NaCl disk for a transmission FTIR measurement. The FTIR spectrum of polymer powder, deposited on a NaCl disc, was recorded in transmission mode from 4000 to 650 cm^{-1} using a NICOLET FTIR, Model Magna 560, equipped with a microscope attachment by Spectra-Tech. The IR beam was focused on the sample with a 100- μm diameter circular aperture using a microscope. Oxidation of the polymer was minimized prior to the measurement of its FTIR spectrum by scraping it rapidly from the silicon plate and immediately measuring its spectrum.

Results and discussion

A. Modification of the photochemical flow reactor

It has been shown that a flow reactor has many advantages in laboratory simulations of the atmospheric photochemistry of Titan. First, measurable amounts of minor constituents can be mixed with a large amount of carrier gas, such as nitrogen, to obtain the mixing ratios that approximate those in Titan's atmosphere. Second, the flow time and flow rate could be varied to obtain enough products for analysis. Third, it minimizes wall reactions and the formation of secondary photoproducts (Clarke et al., 2000).

In this study we use mixtures that approximate the composition of Titan's atmosphere. The mixing ratios of the components of Titan's atmosphere differ by a factor of 10^7 (Table 1). A flow reactor was employed to permit long term photolyses that generate sufficient material for characterization purposes. Since about $10^{-2}\%$ of the light is absorbed by reactant gas, only a small amount of polymer is formed in the photochemical flow reactor (Clarke et al., 2000). Thus it is not possible to analyze these small amounts using macroscopic techniques. In this paper we report the use of X-ray photoelectron spectroscopy (XPS) and microscopic Fourier transform infrared spectroscopy (FTIR) to investigate the structure of the polymers generated from such gaseous mixtures. These polymers simulate the haze formed in Titan's atmosphere and the studies will suggest the structures of the materials likely to be encountered by the *Huygens* probe during its transit down through Titan's atmosphere in 2005 (Israel et al., 1999).

The design and use of the photochemical flow reactor was described previously (Clarke et al., 2000). This reactor design was used to investigate the photolysis of mixtures of gases with a composition that simulates the atmospheric composition of Titan (Joseph, 1999). Subsequent XPS studies revealed that the solid polymeric products formed contain about 8–12 atom percent oxygen even though no oxygen-containing reactants were used.

The flow line was modified to reduce the water and molecular oxygen levels in the system and thus diminish the

Table 2
XPS composition of photochemically generated polymers using different vacuum systems

Element	Composition (%)	
	Oil diffusion pump	Turbo molecular pump
C	85.3	93.3
N	5.7	5.3
O	9.0	1.4

levels of oxygen in the photoproducts. First, the installation of a turbo-molecular pump proximate to the site where the gas mixture is to be irradiated warranted low levels of oxygen and other impurities and a pressure in the range 10^{-6} – 10^{-7} Torr. In order to avoid the contamination due to absorption of organics by grease and o-rings, all ground glass stopcocks have been replaced by Teflon ones. The fluoroelastomer (FETFE) o-rings used were changed after every flow run. The vacuum system can be baked out at 150°C and purged with high-purity nitrogen gas to remove gases bound to the inside of the vacuum line. The glassware manifold was built from two main vacuum lines (Fig. 1) connected with a rotary pump on one side and with a turbo-molecular pump and a rotary pump on the other. This design makes it possible to work at two different pressure levels in each section of the line: 10^{-3} Torr and 10^{-6} – 10^{-7} Torr when the turbo-molecular pump is used.

The XPS analysis of a sample obtained from the previous design of the flow reactor (Clarke et al., 2000) contained 9% oxygen based on the C, N and O analysis (hydrogen cannot be analyzed by XPS). A sample prepared in the modified flow system contained only 1.4% oxygen (Table 2). This oxygen presence may be due to trace amounts of residual oxygen compounds in the flow reactor as well as oxygen in the nitrogen used. Nitrogen has the highest mixing ratio in the mixture of gases used to simulate Titan's atmosphere so the 10 ppb of molecular oxygen and 20 ppb water present in it may be incorporated in the products.

B. Elemental and structural analysis of the polymer film by XPS

The polymeric film was collected on a plate of silicon placed at the bottom of the quartz tube where the flowing gas is irradiated (Fig. 2). The coated plate was transferred rapidly from the flow line to a vacuum desiccator filled with nitrogen to minimize the polymers contact with air.

Localized bonding information about the chemical environments of the carbon, nitrogen, and oxygen atoms in the polymer can be determined from the differences in the binding energy required to excite their core 1s electrons. Fig. 3 shows the XPS survey spectrum of polymer film collected on silicon substrate. The films consisted mostly of carbon, nitrogen, and small amounts of oxygen with trace impurities of fluorine and silicon. The silicon (101.9 eV) is

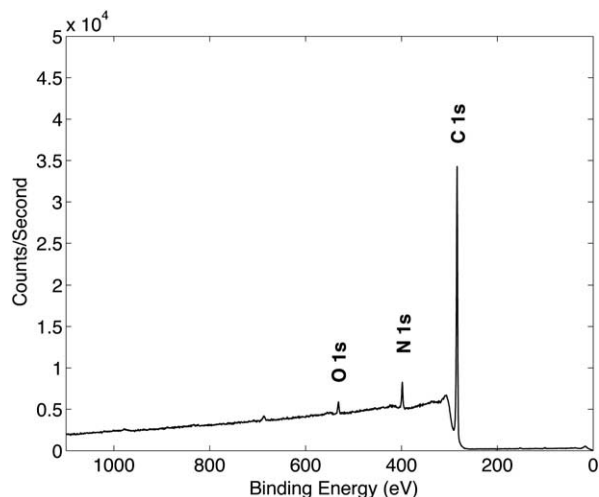


Fig. 3. XPS survey spectrum of polymer film deposited on Si substrate.

present as siloxane and the fluorine as fluorocarbon (Table 3). The peak areas of these contaminants were subtracted to deduce the composition of the polymer (Table 3a).

The small differences in binding energies are determined by curve fitting of the high-resolution XPS spectra and comparing the energies measured to reference energy values (Beamson and Briggs, 1992). The C 1s peak of the polymer resolves into two peaks (Fig. 4a). The main peak at 284.6 eV corresponds to hydrocarbons containing C–C, C–H, and C=C bonds. The 286.0-eV peak is related to C–N, C=N, C≡N, and C–O groups. The 286.0-eV peak is also assigned to the α carbon of a nitrile group C–C≡N, because the nitrile group is very polar. This inductive effect made the α signal shift to a binding energy of about 1.4 eV, which is higher than the signal of a normal C–C grouping (Burrell and Chera, 1999). A small signal due to the C=O group at about 287.4 eV may also be present in this peak. The N 1s peak at 399.0 eV, which was not resolvable into additional

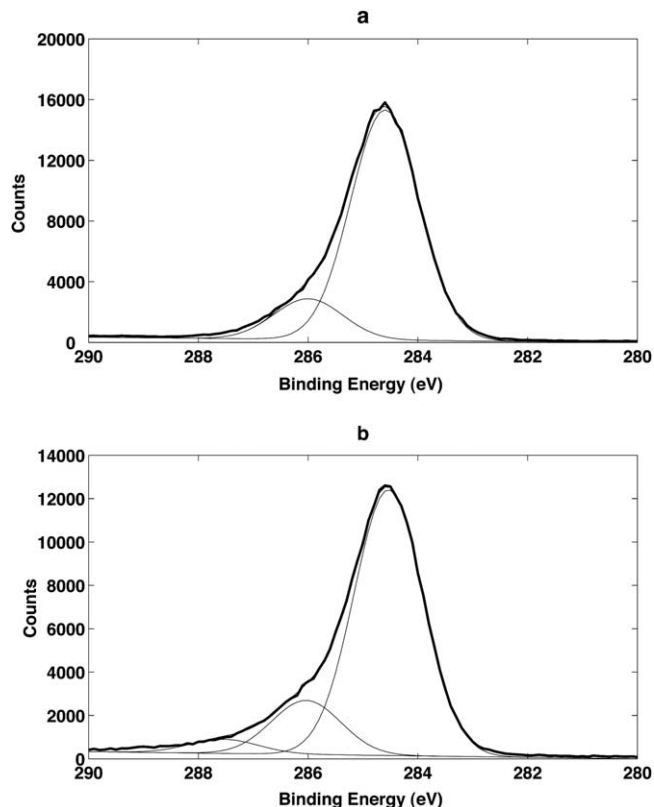


Fig. 4. High-resolution C (1s) XPS spectra of polymer (a) as deposited on Si substrate and (b) after 7 days air exposure.

peaks, can be assigned to a variety of nitrogen species such as –C–N–C– , –C–N=C– , –C–NH_2 , and $\text{–C}\equiv\text{N}$ (Fig. 5a). It is assigned to the nitrile functional group because the infrared spectrum of the polymer (discussed below) has an absorption band characteristic of this group. The weak (1.4%) O 1s peak centered at 532.1 eV was attributed to the C=O and C–O species (Fig. 6a). The peak's areas were calculated using Scienta data system software. The estimated percent errors are less than 5% for the main components and might be higher for the minor ones. The data are summarized in Table 4a.

The main change in the high-resolution spectrum of the polymer after it was allowed to stand in air for 7 days was in the intensities of the C 1s peak at 287–288 eV and the O 1s signal at 532–533 eV (Table 4b). It was possible to resolve the O 1s signal into two peaks at 532.0 and 533.0 eV. These energies could be due to C=O and C–O groupings, respectively but it is not possible to make more specific assignments on the basis of published data (Polzonetti et al., 1991; Tsai et al., 1994; Tsai and Boerio, 1998).

The infrared spectrum of the polymer, to be discussed below, suggests the presence of double bonds. It is expected that the XPS spectra would exhibit “shakeup” satellite bands at slightly higher energies than the main C 1s band. These bands are due to the two-electron excitation of the π electrons of the double bonds (Briggs and Riviere, 1990). The bands are weak in the acetylenic polymers that were

Table 3
XPS composition of photochemically generated polymers

Element	Binding energy (eV)	Composition (%)	
		As analyzed	After subtracting Si and F impurities
(a) Polymer			
C	284.6	92.0	93.3
N	399.0	5.1	5.3
O	532.1	1.8	1.4
Si	101.9	0.4	—
F	688.0	0.7	—
(b) Oxidized polymer			
C	284.6	87.0	87.8
N	399.1	4.9	5.0
O	532.0	7.6	7.2
Si	101.9	0.5	—

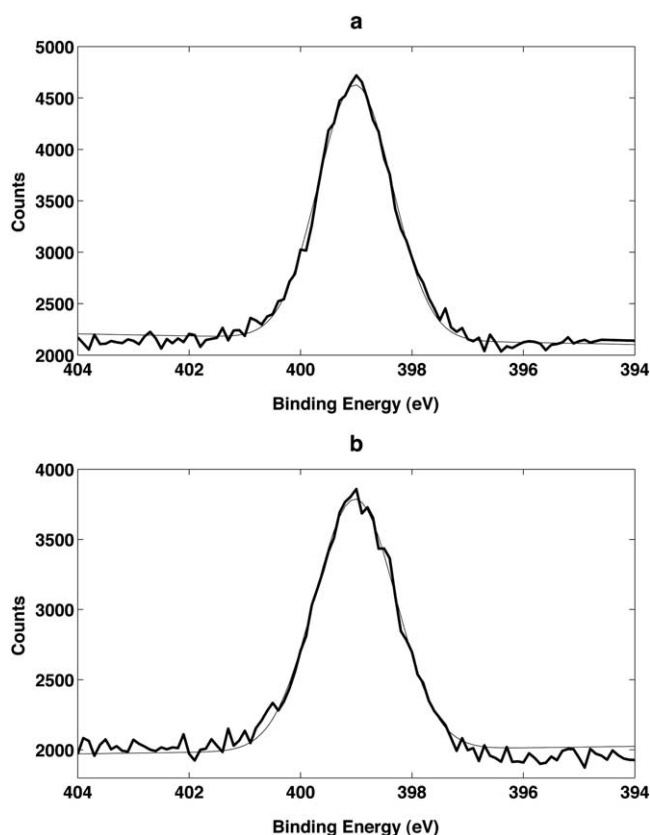


Fig. 5. High-resolution N (1s) XPS spectra of polymer (a) as deposited on Si substrate and (b) after 7 days air exposure.

initiated by plasma discharges (Tsai et al., 1994; Tsai and Borerio, 1998) and may be of such low intensity in the polymers prepared in this study that they were not detected.

XPS provides elemental composition data on the polymer film that did not contain enough material for a conventional combustion analysis. The polymer film was analyzed at two different TOAs, 15° and 45° , corresponding to sampling depths of 19 and 53 Å, respectively. Little difference in the composition was observed, indicating that the polymer was homogeneous and the oxygen observed was not due to surface adsorption but was uniformly distributed throughout the film (Table 5).

C. Infrared spectral measurements on the polymer

It was possible to measure the infrared spectrum of the polymer film after scraping the polymer from the silicon disk with a scalpel and placing it on a NaCl salt plate. The spectrum was measured as quickly as possible to minimize its oxidation by atmospheric oxygen (Fig. 7, Table 6). It was not possible to assign the weak band at 3640 cm^{-1} but the band at 3400 cm^{-1} may be due to an N–H stretching frequency. Strong bands characteristic of the asymmetric and symmetric stretching and bending modes, respectively, for CH_3 groupings were observed at 2960, 2870, and 1380

cm^{-1} and bands at 2920 and 1460 cm^{-1} were assigned to the CH_2 stretching and bending modes, respectively (Colthup et al., 1990).

An absorption band at 2210 cm^{-1} is assigned to the $-\text{C}\equiv\text{N}$ stretching frequency of an α,β -unsaturated nitrile stretching frequency at $2215\text{--}2235\text{ cm}^{-1}$ (Colthup et al., 1990; Tsai et al., 1994). This absorption is assigned to the α,β -unsaturated nitrile group on the basis of arguments outlined previously (Clarke and Ferris, 1997b). A very weak absorption at 2116 cm^{-1} may be due to some $-\text{C}\equiv\text{C}-$ groupings in the polymer.

A strong and broad adsorption at 1600 cm^{-1} was assigned to the $\text{C}=\text{C}$ stretching of double bonds conjugated with $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, or/and $-\text{C}\equiv\text{N}$ groupings (Fresenius et al., 1989). Attempts to obtain further structural data using laser (1064 nm) FT-Raman spectroscopy were unsuccessful due to the thermal destruction of the polymer. This destruction may be due to the light absorption by conjugated double bonds present.

A very weak band at about 1700 cm^{-1} as a shoulder on the 1600 cm^{-1} absorption may be due to the presence of the carbonyl group of a ketone (Colthup et al., 1990). This assignment is consistent with the conclusion from the XPS data that this functional group is present.

The presence of CH_3 and CH_2 groupings suggests that reduction processes are an important part of polymer for-

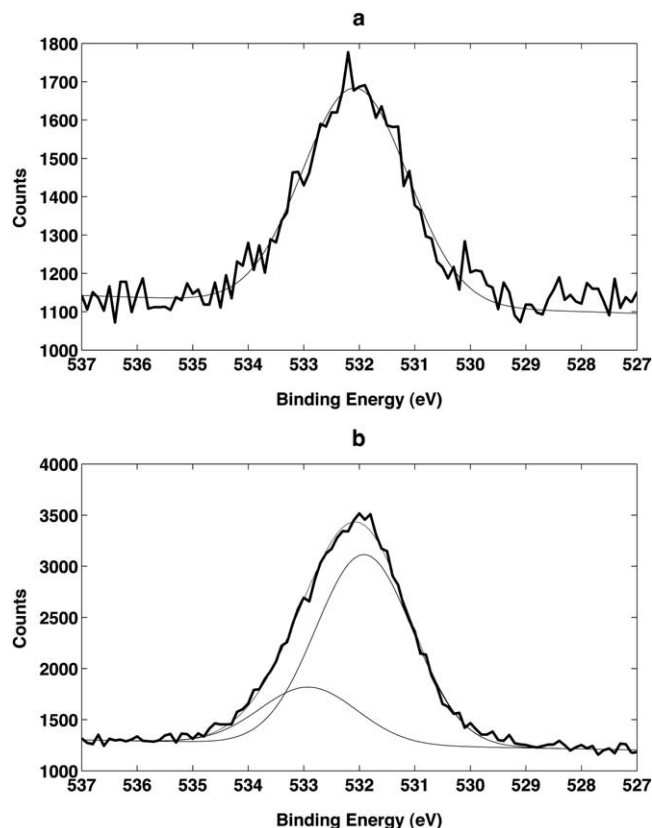


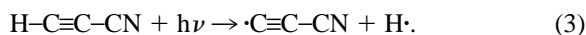
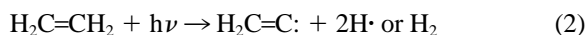
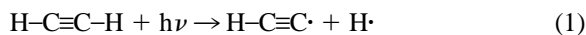
Fig. 6. High-resolution O (1s) XPS spectra of polymer (a) as deposited on Si substrate and (b) after 7 days air exposure.

Table 4
XPS binding energies and relative intensities of polymers

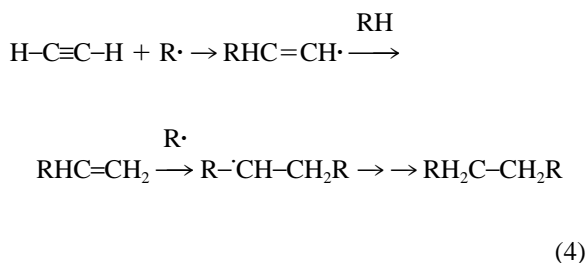
Element transition	Binding energy (eV)	Peak width (eV)	Atom (%)	Peak assignment
a. Polymer				
C 1s	284.6	1.48	81.2	C–H, C–C, C=C
C 1s	286.0	1.54	12.1	C–O, C–N, C=N, C≡N, C–C≡N, C=O
N 1s	399.0	1.58	5.3	C≡N
O 1s	532.1	2.07	1.4	C=O, C–O
b. Oxidized polymers				
C 1s	284.6	1.46	70.2	C–H, C–C, C=C
C 1s	286.1	1.54	14.1	C–O, C–N, C=N, C≡N, C–C≡N
C 1s	287.5	1.70	3.5 ^a	C=O
N 1s	399.1	1.71	5.0	C≡N
O 1s	532.0	1.95	5.8 ^a	C=O
	533.0	2.00	1.4	C–O

^a The values of 3.5 and 5.8% for C and O, respectively, are within error limit for XPS analysis.

mation. The reductions could have resulted from the addition of the hydrogen atoms formed by photolysis of acetylene, ethylene, and cyanoacetylene to the polymer:



The virtual absence of the $-\text{C}\equiv\text{C}-$ group strongly suggests that the polymerization of acetylene proceeds by the addition of radicals to the triple bond of acetylene to form a double bond. The double-bonded product and ethylene may both undergo alkyl radical or hydrogen atom addition to give saturated units in the polymer chain:



The absence of the C–H stretching of the C=C–H grouping at frequencies at 2980–3130 cm^{-1} is not consistent with the presence of a C=C stretching frequency at 1600 cm^{-1}

(Colthup et al., 1990). The broad C=C absorption suggests that the double bonds are in a variety of environments in the polymer so that the absorption feature due to a hydrogen attached to a double bond is expected but not observed. There are frequencies at 970, 880, and 825 cm^{-1} that can be assigned to C–H bending in the C=C–H groupings. The C=C–H stretching band was observed in the products of the photolyses of the cyanoacetylene–hydrocarbon mixtures in static systems (Clarke and Ferris, 1997b) so its absence in the polymer formed in the flow reactor remains to be explained.

When the polymer is allowed to stand in the presence of oxygen under ambient fluorescent lighting there is an increase in the absorption band at 1710 cm^{-1} indicative of a ketone (Fig. 8) (Tsai et al., 1994; Tsai and Boerio, 1998). A new band is also observed at 1220 cm^{-1} that may be associated with the proposed ketone function or with the C–O stretching frequency of an ester (Colthup et al., 1990). An ester seems less likely because the carbonyl stretching frequency is not in the range 1750–1720 cm^{-1} for saturated and α,β -unsaturated esters (Bellamy, 1975; Colthup et al., 1990).

D. The oxidation of the polymers

It was observed that a sample of the polymer that had an infrared band at 1710 cm^{-1} as a shoulder on the broad 1600 cm^{-1} absorption developed much stronger absorption at 1710 cm^{-1} when the sample was allowed to stand on the laboratory bench in a closed container in the presence of air (Fig. 8). This increase infrared at 1710 cm^{-1} was accompanied by a 5.8% increase in the oxygen content of the polymer to 7.2% (Figs. 4b, 5b, 6b, Table 6b). The oxygen is distributed throughout the polymer as shown by the observation that the XPS oxygen analysis did not change with different TOA.

Table 5
Composition of polymer sample at different depths

TOA angle/depth	Composition (%)		
	C 1s	N 1s	O 1s
15°/19 Å	93.0	5.5	1.5
45°/53 Å	93.3	5.3	1.4

Note. TOA = take off angle.

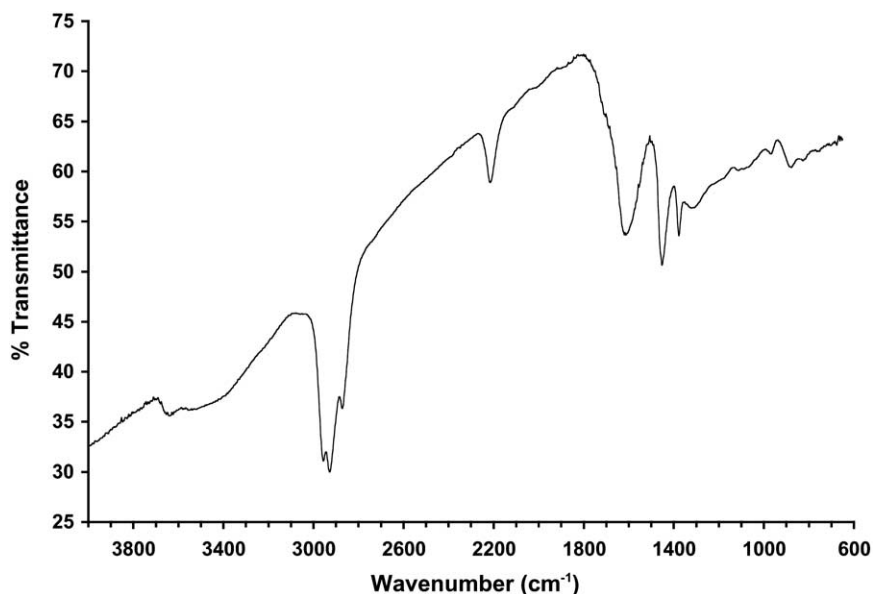


Fig. 7. Transmission FTIR spectrum of polymer powder.

The uptake of oxygen by the sample probably reflects the presence of free radicals trapped in the polymer matrix. The reaction of oxygen with the polymeric products formed by the plasma-initiated polymerization of acetylene has been reported (Tsai et al., 1994; Tsai and Boerio, 1998). The action of a plasma discharge passing through a 9:1 nitrogen–methane mixture was used to simulate the atmospheric chemistry on Titan and also generated photoproducts that reacted with oxygen (Raulin et al., 1994; McKay, 1996).

A possible reaction pathway for the reaction of oxygen with the polymers is given in Eqs. (5)–(9) (Gugumus, 1990;

Commereuc et al., 1997). The radicals combine with the oxygen diradical when exposed to air to form a peroxy radical:



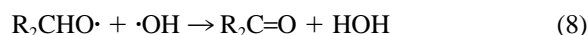
That radical abstracts a hydrogen from the polymer matrix to form a hydroperoxide:



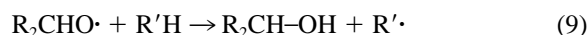
Hydroperoxides are readily photolyzed by ambient light in the laboratory to cleave the peroxide into two radicals



that in turn react to form carbonyl-containing products



that have infrared absorption in the 1700 cm^{-1} region (Tsai et al., 1994). Hydrogen abstraction yields alcohols



which together with the hydroperoxide groups, contribute to the weak, broad band in the 3400 cm^{-1} region.

E. Comparison with polymers formed in other simulations

Solubility studies show that the materials formed by plasma discharges differ markedly from those formed photochemically. The plasma-discharge materials are soluble in polar solvents such as water, ethanol, methanol, glycol, and dimethylsulfoxide and less soluble in nonpolar solvents such as ethane, hexane, and benzene (McKay, 1996). Our photopolymer was not soluble in a broad range of polar and nonpolar organic solvents as well as inorganic acids and bases (Joseph, 1999).

Table 6
Assignment of absorption features in the infrared spectra

Frequency ν (cm^{-1})	Wavelength λ (μm)	Intensity ^a	Vibrational groups identity
3640	2.7	w, b	?
3400	2.9	w, b	N–H stretching
2960	3.4	s	C–H asymmetric stretching (CH_3)
2920	3.4	s	C–H out-of phase stretching (CH_2)
2870	3.5	s	C–H symmetric stretching (CH_3)
2210	4.5	m	$\text{C}\equiv\text{N}$ stretching
1710	5.8	w,sh	C=O stretching
1600	6.3	s,b	C=C and C=N stretching
1460	6.8	m	C–H deformation (CH_2)
1380	7.2	m	C–H deformation (CH_3)
1320	7.6	b	C–H wagging (CH_2)
1220 ^b	8.2	w	C–O stretching
1120 ^b	8.9	w	C–O stretching (in O– CH_2)
970	10.3	w	CH out-of-plane wagging (CH=CH, trans)
880	11.4	w	CH_2 out-of-plane wagging (C= CH_2)
825	12.1	w	CH out-of-plane wagging (C=CHR)

^a Intensity code: b = broad, m = medium, s = strong, sh = shoulder, w = weak.

^b Bands appeared during exposure of the polymer to the atmosphere.

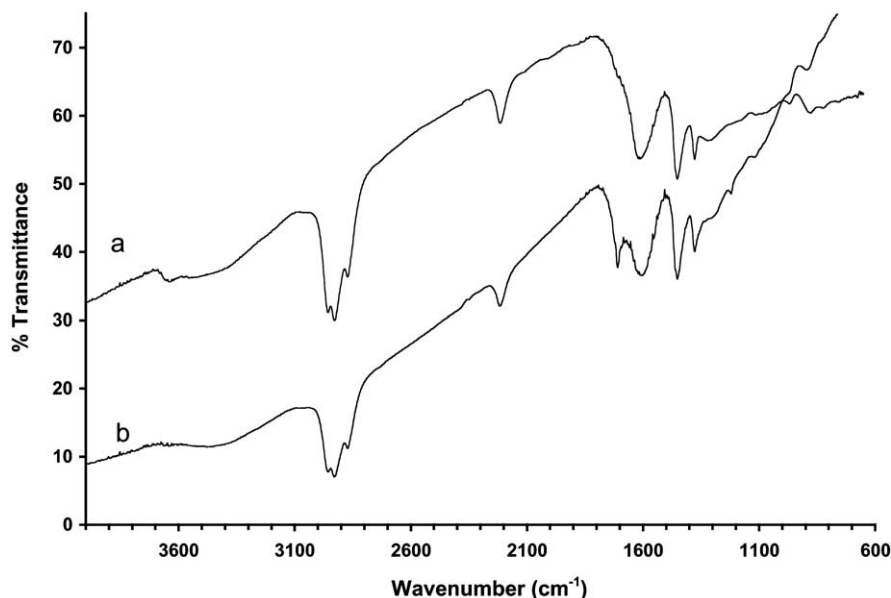


Fig. 8. FTIR spectra of polymer (a) after exposure to air for 1 h, and (b) after exposure to air for 7 days.

The C/N ratios for the photopolymer were determined from the analytical data and compared with the analyses of the materials obtained in other simulations of Titan haze (Table 7). The C/N ratio of 17.6 for the photopolymer is greater than any of those reported previously. This ratio reflects our use of 20-fold less cyanoacetylene than acetylene and ethylene in the light-absorbing reacting gases on Titan and in gas mixtures used in the simulation. The lower C/N ratios were observed from plasma discharge reactions in a nitrogen–methane atmosphere that dissociate molecular nitrogen into nitrogen atoms (Khare et al., 2001). These radicals combine with radicals formed from methane to form HCN, cyanoacetylene, and the subsequent products formed from these compounds. The plasma discharge serves as a model for the action of Saturn's magnetospheric electrons and the solar UV of wavelengths less than 100 nm on Titan's upper atmosphere. These energy sources are absorbed at the level 500–1300 km while haze formation occurs below 500 km (McKay et al., 2001; Ramirez et al., 2001). Our photochemical model is based on the formation of the unsaturated compounds by magnetospheric electrons

and by UV at wavelengths less than 100 nm. Acetylene and ethylene are also formed by methane photolysis at wavelengths less than 150 nm. The subsequent photolysis of acetylene, cyanoacetylene, and ethylene by UV at wavelengths greater than 150 nm penetrates to the levels of 100 km and generates Titan haze.

Laboratory studies of the atmospheric chemistry of Titan using spark or plasma discharges simulate chemical processes high in the atmosphere of Titan where the reactions are initiated mainly by magnetosphere electrons and UV light of wavelengths less than 100 nm. The products of these reactions will contain a much higher proportion of nitrogen because the high mixing ratio of atmospheric nitrogen results in a higher concentration of nitrogen atoms that initiate these processes. This energy does not penetrate down to the levels where haze is being formed so the use of laboratory processes that mainly generate nitrogen atoms is an incomplete model for haze formation on Titan. The C:N ratio on Titan may decrease with altitude since the reactive nitrogen atoms only form at high altitudes (Tanguy et al., 1990). The nitrogen-containing organics diffuse down into the more dense regions of the atmosphere where their mixing ratios decrease to 10^{-7} and those of acetylene and ethylene are 10^{-6} . Thus, the haze formed on Titan is expected to contain 10- to 20-fold less nitrogen than carbon.

Table 7
Comparison of elemental composition of Titan haze analogs

References	Stoichiometry	C/N ratio
Sagan and Thomson (1984)	$C_8H_{13}N_4$	2
Coll et al. (1999)	$C_{11}H_{14}N_4$	2.8
McKay (1996)	$C_{11}H_{11}N_2$	5.5
Clarke and Ferris (1997b)	$C_{6.4}H_{3.9}N$	6.4 ^a
Coll et al. (1995)	$C_{11}H_{11}N$	11
This work	$C_{17.6}H_xN$	17.6

^a Static photochemical experiment where a mixture of C_2H_2 and HC_3N was irradiated.

Conclusions

The laboratory simulation of Titan haze formation has resulted in the formation of a solid polymeric product containing CH_3 , CH_2 , $C=C$, $C=C-C\equiv N$, and possibly N–H functional groups. The C:N ratio in the polymer was determined to be 17.6:1 by XPS analysis. These data will be useful in

analyzing the data from the *Huygens* probe as it passes through the atmosphere of Titan in 2005. Free radicals trapped in the polymeric matrix react with molecular oxygen on exposure to air. XPS and microscopic FTIR have been demonstrated to be effective methods for the determination of the composition and structural units in the polymer.

It is proposed that the use of a flow system that utilizes UV light as its energy source provides a more accurate simulation of Titan haze formation than does a static system or a plasma discharge energy source. The flow system more closely models the composition of gases in Titan's atmosphere, and the UV light of wavelengths greater than 150 nm is the energy source that initiates haze formation on Titan.

Future studies will focus on the development of analytical techniques for the structural analysis of the solid and gaseous products, the determination of the reaction pathways and the incorporation of other components of Titan's atmosphere into the reactant gases.

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