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Infrared Laser-Induced Reactions of Difluorovinylidene with 1,2-Polybutadiene

MARCUS W. THOMSEN* AND BARBARA F. KIMMICH†

Chemistry Department, Franklin and Marshall College, Lancaster, Pennsylvania 17604-3003

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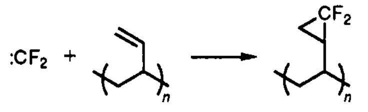
Laser-induced gas–solid heterogeneous reactions are important because they provide insight into mechanisms of heterogeneous processes and hold promise of technical innovations for practical applications.[1] Most work has involved nonmetal and non metal oxide surfaces (e.g., Si, Ge, SiO_2) or metal and metal oxide surfaces (e.g., Pt, Zn, TiO_2, ZnO); however, only a small number of studies have been conducted in order to examine the analogous reactions involving polymers. Chemical alterations of polymer surfaces performed without affecting the bulk of the polymer have potential for producing low-cost polymers for specialty applications. Previously, we have reported on our investigations of the infrared laser-induced reactions of difluorocarbene with 1,2-polybutadiene (PBD).[2] In this paper we report the results of our study of the infrared laser-induced reactions of difluorovinylidene with PBD.

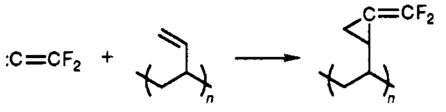
When chlorodifluoromethane (FC-22) is irradiated by the output of a pulsed CO_2 TEA laser, it absorbs energy and decomposes to difluorocarbene and HCl (reaction 1).[3-5] Once it is formed, the carbene migrates to the surface of a PBD film and reacts with the π-bonds to form *gem*-difluorocyclopropanes at the surface of the polymer (reaction 2).[6] In a similar manner, difluorovinylidene can be generated from 2-chloro-1,1-difluoroethene (FC-1122) by the elimination of HCl (reaction 3).[7] However, because FC-1122 does not exhibit a suitably intense infrared absorption band in the region accessible with the CO_2 laser, silicon tetrafluoride (SiF_4) was used as a sensitizer for the reaction. The SiF_4 absorbs infrared radiation from the laser and then activates the 2-chloro-1,1-difluoroethene via collisional energy transfer. The activated FC-1122 eliminates HCl to yield the carbene. Once the difluorovinylidene is produced, it may migrate to the polymer surface and react to produce methylenecyclopropane groups (reaction 4). Additionally, the difluorovinylidene may suffer a successive reaction to yield difluorocarbene and free carbon (reaction 5),[7] and the resultant difluorocarbene can migrate to the polymer surface and react with the π-bonds (reaction 2).[2] Two known reactions could compete with this process (reactions 6 and 7); however, these reactions do not occur with appreciable rates at the pressures employed for this research.[7]

$$HCClF_2 \xrightarrow{nh\nu} :CF_2 + HCl \qquad (1)$$



(2)

$$HClC{=}CF_2 \xrightarrow{SiF_4,\ nh\nu} :C{=}CF_2 + HCl \qquad (3)$$



(4)

$$:C{=}CF_2 \longrightarrow :CF_2 + C \qquad (5)$$

$$:C{=}CF_2 + HCl \longrightarrow F_2C{=}CHCl \qquad (6)$$

$$2\,:C{=}CF_2 \longrightarrow F_2C{=}C{=}C{=}CF_2 \qquad (7)$$

Experimental Section. The experiments were performed using a grating-tuned Lumonics TEA 101 CO_2 laser which was operated at 0.5 Hz and was tuned to the P(40) line of the 001–020 transition (1027.4 cm^{-1}), which corresponds to a strong infrared absorption band of the sensitizer (SiF_4). The laser beam was collimated using ZnSe lenses in order to obtain qualitatively reproducible beam profiles which were checked using thermally sensitive paper. The average beam diameter was 0.50 cm. In all cases the laser fluence was 0.9 ± 0.1 J/cm^2. The power was monitored with a Scientech Model 362 power-energy meter. Frequencies were determined using an Optical Engineering 16A CO_2 spectrum analyzer.

The photolysis cell was a 250-mL round-bottomed flask which was modified with a gas inlet port and a cylindrical side arm (i.d. 25 mm) and fitted with KCl or NaCl windows. The PBD films were mounted in the cylindrical arm of the cell. The photolysis cell was filled with 6.00 ± 0.03 Torr of FC-1122 and 11.40 ± 0.03 Torr of silicon tetrafluoride using standard gas-transfer techniques on a vacuum line equipped with an MKS Model 122 capacitance manometer.

Reactions were performed by positioning the cell within the laser beam path so that the geometric relationship of the PBD film to the beam was uniform and parallel. Typically, between 100 and 1600 pulses were delivered to a given sample prior to analysis of the reacted PBD. The PBD was analyzed by multiple internal reflectance infrared spectroscopy (MIR-IR) using a Perkin-Elmer Model 983. Changes in IR absorbances of the PBD were determined by standard spectral subtraction techniques.[8] Electron spectroscopy for chemical analysis (ESCA) experiments were done by an independent laboratory at the University of Missouri—Rolla.

The 2-chloro-1,1-difluoroethene (FC-1122, SCM Specialty Chemicals) and the silicon tetrafluoride (Matheson) were used without further purification. However, the gas samples were always subjected to freeze–pump–thaw cycles before use in an experiment. The 1,2-polybutadiene films were prepared from solutions of the polymer (Scientific Polymer Products, Inc.) in distilled chloroform. The solutions were poured over smooth, level pieces of aluminum foil, which had been previously cleaned with acetone, and the solvent was allowed to evaporate. Samples of the polymer film were used with the aluminum backing because the foil backing facilitated handling of the PBD films.

Results and Discussion. The ESCA results for the various PBD films are provided the Table I. The unreacted PBD film exhibited peaks that correspond to carbon (284 and 1008 eV), oxygen (532 and 756 eV), and silicon (106 eV). The use of silicone grease on the glassware employed to distill chloroform and to prepare polymer solutions accounts for the silicon and oxygen. Additionally, some oxygen may be attributed to the slow oxidation of the PBD samples. The reacted PBD film (Table I, column 2) possesses these same binding energies and three new ones at 202, 610, and 691 eV. The ESCA bands which were centered at 610 and 691 eV indicated the presence of fluorine. The fluorine/carbon ratio as determined by ESCA increases with extended photolysis of the freon (Figure 1). When ~30 Å of the PBD surface is removed by sputtering, the fluorine peak intensity decreases relative to the carbon peak intensity and is eventually eliminated (Table I, column 3). This result indicates that fluorine is

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† Hackman Summer Research Scholar.

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Table I
ESCA Results for Polybutadiene Films (Electron Binding Energies in eV)

PBD			
pure	reacted	sputtered	assignment
106	105	107	silicon (2p)
207	202	202	chlorine (2p)
275	273	275	chlorine (2s)
284	287	287	carbon (1s)
532	535		oxygen (1s)
	610		fluorine (Auger)
	692		fluorine (1s)
756	756		oxygen (Auger)
1008	1008	1007	carbon (Auger)

primarily at the surface of the PBD film. The incorporation of fluorine into the PBD surface is rationalized by the reaction of difluorovinylidene with the polymer (reaction 4). The fluorine in the reacted PBD samples cannot be attributed to absorption of FC-1122 by the polymer. The ESCA profile of PBD subjected to all experimental conditions except laser photolysis (i.e., mounting in the photolysis cell, evacuation, and exposure to FC-1122 and silicon tetrafluoride for 90 min) does not exhibit peaks at 610 or 691 eV. Indeed, the ESCA results for the polymer simply exposed to FC-1122 are identical to those results obtained for completely untreated PBD.

All samples of PBD exhibited ESCA bands near 202 and 275 eV, which are indicative of chlorine. The sputtering experiments indicate that the chlorine is present in the bulk of the polymer, and therefore its presence is primarily an artifact associated with the occlusion of chloroform by PBD during the formation of the films. Previous research has shown that hydrogen chloride does not react with PBD at a detectable rate under the conditions of the experiment.[2]

The MIR-IR spectra of PBD exposed to difluorovinylidene showed measurable changes relative to the MIR-IR spectra of unreacted PBD. For example, the intensity of the absorption associated with the π-bond at 1639 cm^{-1} decreased with increasing exposure of the polymer to difluorovinylidene. This result is consistent with the hypothesis that difluorovinylidene is reacting with the π-bonds of PBD. The rate law for this reaction is

$$\text{rate} = k[:\mathrm{C{=}CF_2}][\pi\text{-bonds}]$$

However, since only $\approx 1\%$ of the FC-1122 in the volume subtended by the laser beam reacts with each laser pulse to yield difluorovinylidene, the $[:\mathrm{C{=}CF_2}]$ is small and essentially constant for the conditions of these experiments. Therefore, the rate law for the reaction can be approximated as

$$\text{rate} = k'[\pi\text{-bonds}] \quad \text{and} \quad k' = k[:\mathrm{C{=}CF_2}]$$

and the extent of this reaction can be described by a relationship analogous to a first-order kinetic analysis; i.e., $A_0/A_t = e^{kn}$ in which n is the number of laser pulses, k is the fraction of π-bonds of PBD reacted per laser pulse, and A is the absorbance at 1639 cm^{-1} at time zero (no pulses) and after n pulses. This relationship is represented in Figure 2 (slope = 9.6×10^{-5}, $r = 0.95$). Similar results were obtained by analysis of other infrared bands, e.g., the absorptions between 900 and 1000 cm^{-1} which are assigned to the out-of-plane C–H motions of monosubstituted alkenes. Additionally, an absorption at 1160 cm^{-1} appeared after exposure of the polymer to difluorovinylidene. This absorption may be evidence for the presence of the difluoromethylene moiety produced via reaction 4; however, more sensitive probes of the polymer surface are necessary in order to complete the structural characterization of the polymer surface.

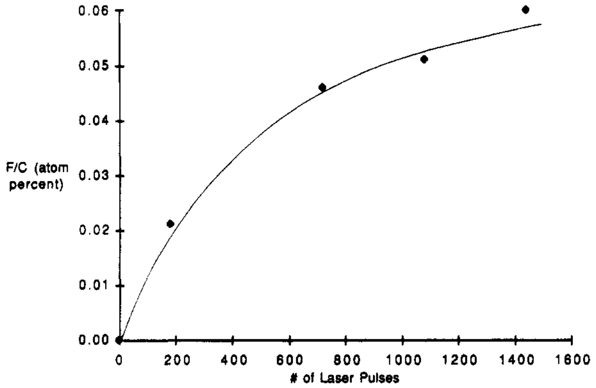

Figure 1. Fluorine-to-carbon ratio on the PBD surface as a function of the extent of laser photolysis.

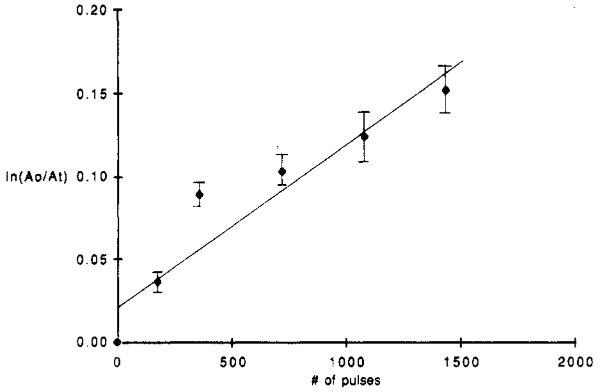

Figure 2. Fraction of PBD π-bonds reacted as a function of the number of laser pulses. Plotted as a first-order process.

During the course of IR laser photolysis experiments, small quantities of soot were produced. This result, which is consistent with results of an earlier study,[7] indicates that some of the difluorovinylidene is decomposing to difluorocarbene and carbon (reaction 5). Therefore, some of the fluorine incorporation on the PBD must be attributed to the addition of $:\mathrm{CF_2}$ to the π-bonds of the polymer.

In a set of control experiments the laser was tuned to the R(20) line of the 001–020 transition (1078.6 cm^{-1}). The FC-1122 did not react at this laser frequency. The PBD samples subjected to these control experiments showed no significant changes in IR absorption bands associated with the π-bonds of PBD. Therefore, IR laser-induced decomposition of the FC-1122 is necessary to produce the observed changes in PBD. This observation is consistent with the ESCA results, which indicated that simple exposure to FC-1122 did not alter the PBD.

The results of the ESCA and MIR-IR studies support the hypothesis that difluorovinylidene, which is generated by sensitized IR laser photolysis of FC-1122, reacts with 1,2-polybutadiene. In addition, the results suggest that difluorocarbene, which is produced by a successive reaction of difluorovinylidene, is another intermediate that reacts with the polymer. Further studies on the effect of gas pressures and laser power on this reaction are in progress. Infrared laser-induced reactions of carbenes (e.g., dichlorocarbene[9]) with 1,4-polybutadiene and carbenes with other polymers (e.g., polystyrene, poly[styrene-*co*-butadiene]) are planned.

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