



Photodegradation of SF₆ on polyisoprene surface: Implication on elimination of toxic byproducts

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ABSTRACT

Photodegradation of SF₆ was performed on the surface of polyisoprene (PI) based on a brand new mechanism of “controlled release of radicals”. Effective decomposition of SF₆ (60% of SF₆ was degraded in 4 h) was achieved due to the highly reductive radicals (mainly allylic radicals and excited C=C bond) which were generated from the photolysis of PI. No toxic fluoride was detected by FT-IR. The PI irradiated for 200 h in SF₆ circumstance was examined by XPS to be doped with fluorine and sulfur. Fouling due to photoinitiated polymerization on UV lamp was avoided because the radicals were released slowly. Photolysis of SF₆ in pure argon with the presence of irradiated PI showed kinetics of pseudo-first-order reaction and the degradation rate constant was $5.16 \times 10^{-5} \text{ s}^{-1}$. Factors which may affect the photolysis process such as introduction of O₂ and H₂O were also examined.

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1. Introduction

Sulfur hexafluoride has been extensively used in electricity distribution systems and molten metal degassing [1]. Intense infrared radiation absorption in the wave number ranging from 915 cm⁻¹ to 960 cm⁻¹ makes sulfur hexafluoride the second most potent greenhouse gas [2]. Because of the considerable radiative forcing, extremely long life period [3] and rapid annual growth rate [4], SF₆ has been listed as one of the six primarily controlled pollutants in the atmosphere by the Kyoto Protocol.

The degradation of SF₆ had been achieved utilizing combustion, chemical-thermal catalysis and plasma methods [5–7], yet these technologies suffer either from high energy consumption or from the yield of especially toxic byproducts such as SF₄, SF₂, S₂F₁₀, SOF₂, SOF₄, SOF₁₀, SO₂F₂, S₂O₂F₁₀, HF and H₂S [8,9]. Therefore an economically feasible approach that can eliminate SF₆ molecules effectively and generate less toxic products needs to be developed.

Slow electrons attached to SF₆ that dissociate SF₆ subsequently have been investigated for a long time [10–12]. Whether radicals with unpaired electrons excited by UV light have similar effects as slow electrons is yet to be determined. According to reports [3,13], oxidative radicals such as O(¹D) and hydroxyl do not react with SF₆ because of the strong electron affinity of the fluorine atom. On the

other hand, reductive radicals generated from propene that decompose SF₆ have been reported in our previous studies [14], yet the fouling on the surface of UV lamp caused by rapid photoinitiated radical polymerization and formation of toxic SiF₄ were found to hinder possible application of this technology to industry. In this paper, reduction of SF₆ will be investigated in case of the reaction between SF₆ molecules and reductive radicals excited from natural rubber (NR)—a polymer constituted by repeating unit of 1,4-cis polyisoprene (PI). A brand new concept of “controlled release of radicals” (CRR) is employed to explain the degradation mechanism of SF₆.

This paper concentrates mainly on three problems: (a) decompose SF₆ molecules subjected to UV radiation effectively at atmospheric pressure; (b) control the concentration and generation rate of free radicals to inhibit fouling on UV lamp; (c) seek for a method to sweep sulfur and fluorine out of gas phase.

2. Experimental

2.1. Reagents

The source and purity of the Reagents are as follows: SF₆ (purity 99.9%) was obtained from the Shanghai Refrigerant Inc.; argon (>99.99%) and oxygen (>99.2%) were obtained from Shanghai Pujiang Special Gas Corporation. PI was the number 1 unprocessed PI rubbers obtained from Shanghai Butexin Rubber products company. These agents are not further processed before being used.

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2.2. Photodegradation device and procedures

Photochemical degradation was conducted in a homemade PTFE reaction cell (15 cm in length and 5 cm in width). A layer of PI with approximate thickness of 0.4 cm was spread on inner surface of the reaction cell. A low-pressure lamp (power 15 W, Shanghai Huade Lightning Ltd.) emitting both 184.9 nm and 253.7 nm radiation was set through the reaction cell, two ends of the cells were sealed with flanges and rubber “O” ring. Fig. 1 shows the homemade reaction cell and gas-filling vacuum system. Gas storage cylinder and reaction cell were connected to the vacuum system by oil-less stopcocks to avoid possible absorption of byproducts by the oil. The pressure in the vacuum system was measured by a membrane nanometer with a 0.1 mm Hg precision.

To start an experiment, the pressure in the vacuum system was first evacuated to less than 1.5 Pa. Then SF₆ was introduced into the reaction cell. Then the vacuum system was inflated with argon to the pressure of 600 mm Hg. The reaction cell was then disconnected and shaken up long enough for effective mixing of SF₆ and argon before irradiation. The photochemical reactions were performed at 329 ± 1 K due to an enhance of temperature by UV light. For each group of experimental parameters, duplicate experiments were conducted.

2.3. Analysis apparatus

The concentration of SF₆ was quantified by FT-IR spectrometer (Nexus-470IR, Nicolet) operated at a spectral resolution of 1 cm⁻¹ over the range from 625 cm⁻¹ to 4000 cm⁻¹. Gaseous products of the sample were expanded directly into a pre-evacuated gas vessel (infrared path length is 5.0 cm) and then determined by FT-IR. The windows of gas vessel were made of NaCl chips and sealed by fluo-rubber “O” ring between flange and main body. Each spectrum was averaged from 64 interferograms. Based on Beer–Lambert law on the 0–2.14 mol m⁻³ range, the concentration of SF₆ was quantified by monitoring the absorption peak height at 947 cm⁻¹. Then the destruction and removal efficiency (DRE) of SF₆ was calculated.

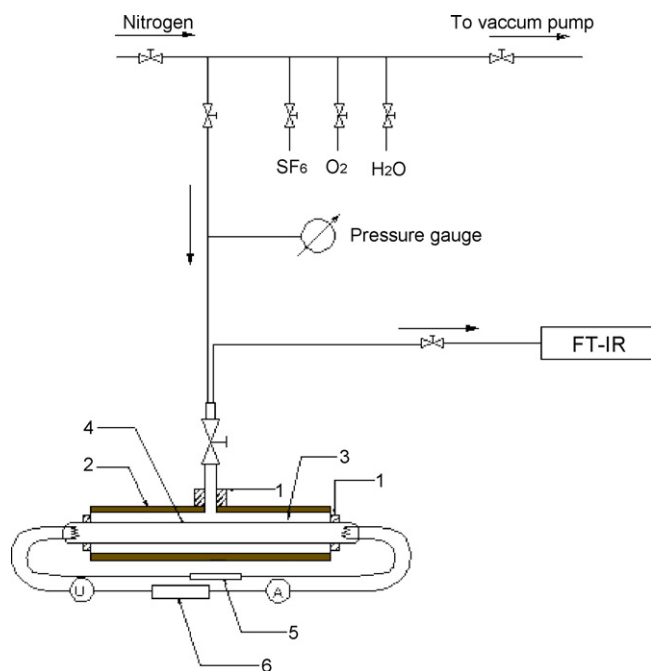


Fig. 1. Sketch map of homemade reaction cell and gas-filling vacuum system. (1) Teflon flange sealed with rubber “O” ring; (2) PI layer; (3) reagents; (4) UV lamp; (5) glow starter; (6) ballast.

The surface PI rubber was investigated by X-ray photoelectron spectroscopy (XPS). The photoelectron was measured at room temperature under a vacuum of 1×10^{-6} Pa using ESCA system (PHI 5000C, PerkinElmer Co.) with a monochromatic Al K α X-ray source (1486.6 eV). The source is working with the power of 250 W. The binding energy is calibrated using C 1s (284.6 eV) as an energy standard. Survey scans were performed with pass energy of 93.90 eV. For the Ag 3d_{5/2} line, these conditions produced a full-width at half-maximum of 0.8 eV.

Samples of PI before and after UV were scraped off PI layer and dissolved in dichloromethane. The solutions were filtrated and then examined by the S-3100 Photodiode Array Detector (PDA, Sinco Co.) over the spectral range between 190 nm and 1100 nm at room temperature. The software version was: LabPro plus Build 342.4.

3. Results and discussions

3.1. CRR process and degradation of SF₆

3.1.1. Discussion about photolysis of isoprene gas (non-CRR process)

The reaction between isoprene gas and SF₆ in the same reaction cell was compared to show the difference between non-CRR process and CRR process. As is shown in Fig. 2, the isoprene monomer has strong UV absorption between 180 nm and 260 nm. Both 184.9 nm and 253.7 nm light lie between this region. The degradation curve of isoprene gas is illustrated in Fig. 3, 80% of isoprene gas was eliminated by UV light after 30 min exposure to UV light and at the same time fouling was observed on the surface of the UV lamp. Because the gas form of isoprene was so prone to degradation that a large quantity of radicals co-existed in the gas phase in a short period. The likely reason of fouling was photoinitiated polymerization upon collision of radicals. Similar phenomenon was reported in our lab's previous works [14]. The fouling on UV lamp will impede the transmittance of UV light and inhibit the DRE largely. Eliminating the fouling calls for the namely “controlled release of radicals” process.

3.1.2. The “CRR” process

Compared to quick releasing of radicals from isoprene gas, UV has been documented to yield radicals with a much slower process on PI surface because of PI's polymerized structure [15]. The release of reductive radicals can be controlled when the isoprene was polymerized into PI. Ultraviolet spectrum of pyrolyzate of natural rubber was studied and the absorption peak attributed to conjugated C=C was found between 180 nm and 260 nm [16]. Energy of 200 nm light

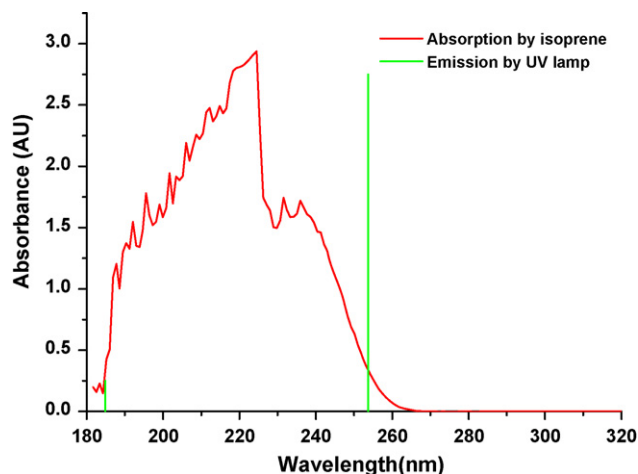


Fig. 2. UV absorption spectrum of isoprene and UV emission by UV lamp.

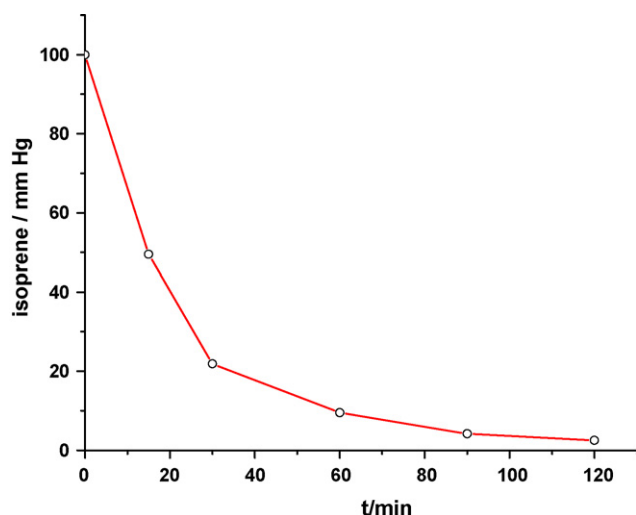


Fig. 3. Photodegradation curve of isoprene.

is sufficient to break up most of the chemical bonds in polymer [17]. Upon absorbing Vacuum Ultraviolet (VUV), PI will decay through break up of double bonds, H abstraction and chain scission paths [15]. Generation of allylic radicals from irradiated PI was well documented in the photodegradation process [17–20]. Basic goal of this research is to expose crude natural rubber to UV and examine the interaction between reductive radicals and SF₆.

In this study, generation rate of these reductive radicals was determined by photolysis rate of PI. The reductive radicals accumulate until a “steady state” between generation of radicals and elimination of radicals through photoinitiated polymerization was achieved. Theoretically, irradiated PI is expected to be an alternative to control the fouling and at the same time achieve more efficient degradation of SF₆. The scheme of “CRR” process is illustrated in Fig. 4.

3.1.3. Destruction and removal efficiency of SF₆

3.1.3.1. DRE of SF₆ in pure argon. Degradation of SF₆ on PI surface is based on the theory that reductive radicals produced by photolysis of PI attract the F atom in SF₆ to form energy-transfer complex and further decompose the molecule upon S–F bond breaking. Two parallel groups of samples were carried out to investigate the relationship between irradiation time and degradation. Initial concentration of SF₆ is 0.054 mol m⁻³. As presented in Fig. 5, the DRE

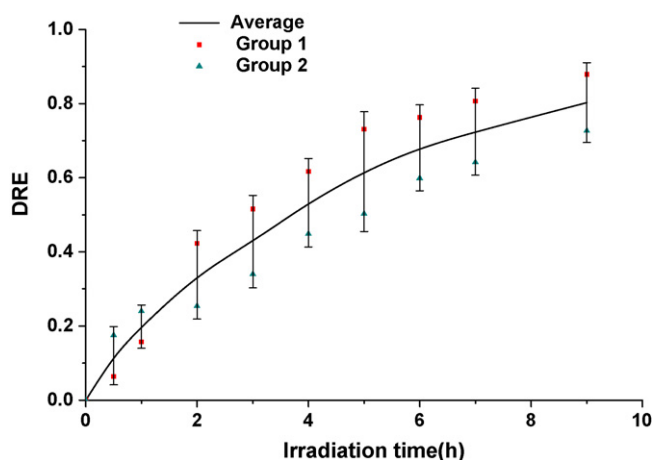


Fig. 5. DRE–time curve of SF₆ in pure argon.

increases with irradiation time. DRE of 40% is achieved in 3 h and the value increased to 80% after 9 h. Blank runs were carried out to assess other possible loss of SF₆ different from photodegradation. Fig. 6 illustrates blank runs with PI + SF₆ but without irradiation and runs under irradiation with SF₆ but without PI. The concentration of SF₆ underwent no big decrease in either case during examined time, thus only photodegradation at the presence of PI is accountable for the degradation of SF₆.

3.1.3.2. DRE of SF₆ with the presence of O₂. In order to simulate the actual atmospheric environment, components of air such as O₂ and H₂O were introduced into the system and the DRE–time curve has been studied.

As is shown in Fig. 7a, DRE at all time range exhibits a slight decrease, compared with no O₂ at all, when the pressure of O₂ in the system is 10 mm Hg. Further, the 3 h–DRE of SF₆ as the function of O₂ content was studied and their relationship is shown in Fig. 7b. 3 h–DRE decreases rapidly as O₂ pressure increases from 0 mm Hg to 20 mm Hg. Thus, the O₂ generally inhibits the photodegradation of SF₆ by reductive radicals. The interaction between O₂ and PI has long been studied. Main product of initial process of the oxidative photoreaction was proved to be RO₂ by ESR study [21]. Excited by UV irradiation, PI–oxygen charge-transfer complex was formed, resulting into a shift of double bond and formation of allylic hydroperoxide groups. This is a mechanism well known as the “ene” process [22–24]. In this manner, the reaction between O₂ competed

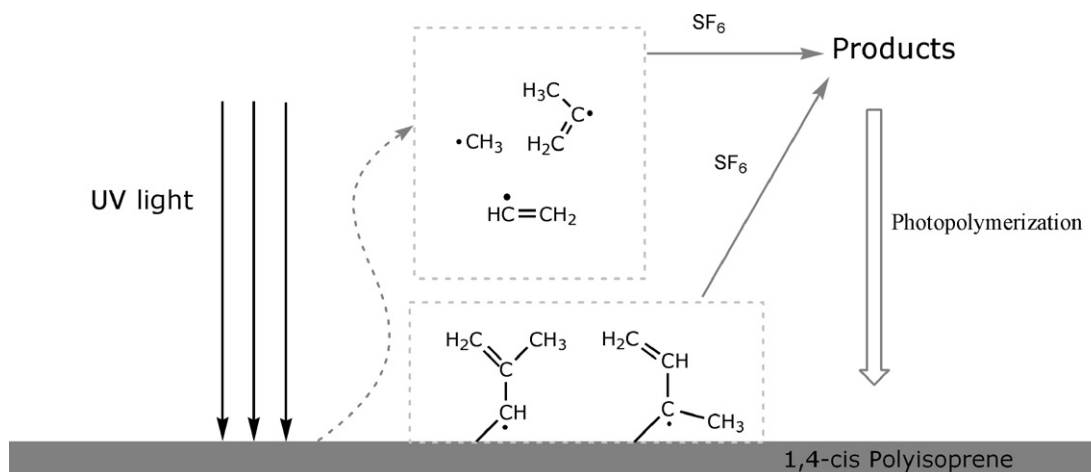


Fig. 4. Scheme of controlled release of radicals on surface of PI.

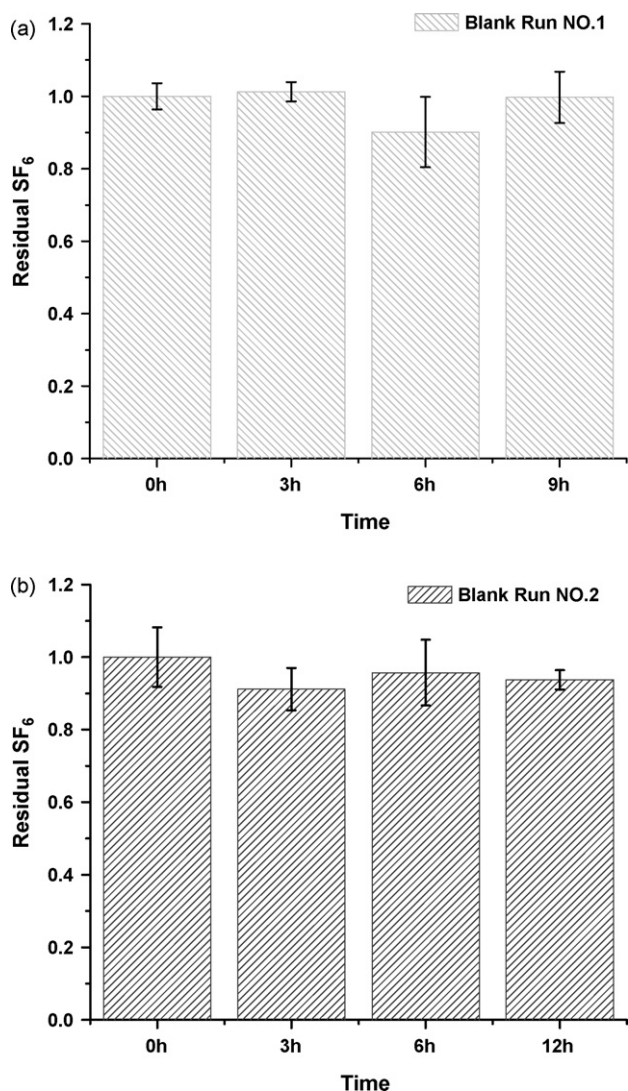


Fig. 6. Blanks runs with PI + SF₆ but without irradiation (a) and runs under irradiation with SF₆ but without PI (b).

with SF₆ for collision with reductive radicals and inhibited degradation of the latter. However, we merely observed a slight decrease of DRE (11% counted in 3 h-DRE) when the pressure of O₂ in the system was 10 mm Hg. A possible explanation is that when the O₂ concentration is comparatively low, the concentration of reductive radicals on PI surface is maintained by continuous UV irradiation at a sufficient level for reactions with both SF₆ and O₂ molecules. But when the O₂ content reaches 20 mm Hg and above, the degradation rate of SF₆ is substantially decreased. The role played by O₂ confines the application of the photodegradation to atmospheric environment because O₂ should be kept less than 20 mm Hg in order to achieve degradation of SF₆.

3.1.3.3. DRE of SF₆ with presence of H₂O. As for the system inflated with water vapor, degradation curves of different H₂O ratios were considered and are shown in Fig. 8. Inhibition of SF₆'s DRE was more obvious when the ratio of H₂O to SF₆ was 10 rather than when it was 1. The H₂O is dissociated into hydrogen atom and hydroxyl while irradiated [25]. Because hydroxyl has a tendency to obtain electrons, it may react with reductive radicals through hydroxylation [26–28]. The inhibition of degradation can be explained by the combined effect of the competition of H₂O for UV energy and the interaction between hydroxyl and reductive radicals. Generally speaking, the

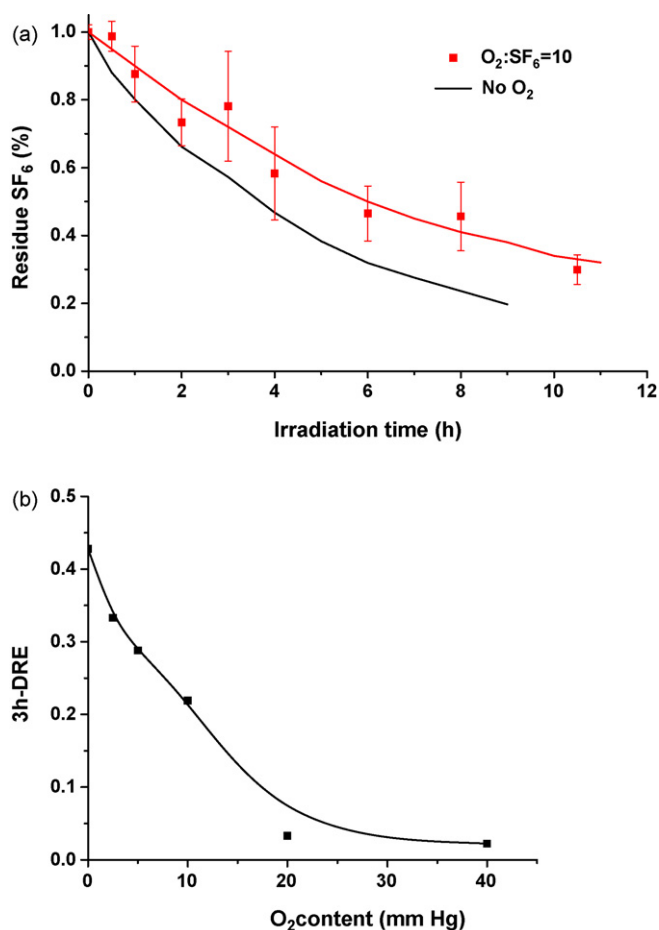


Fig. 7. Degradation curve of SF₆ with the presence of O₂ (a) and dependence of 3 h-DRE on O₂ content (b).

bigger is the percent of H₂O in the system, the more is the decrease in the DRE of SF₆.

During the whole period of this study, no fouling on the surface of quartz lamp was observed even when the system was irradiated for 600 h continuously. This phenomenon was due to the employed "CRR" process and the distance between the quartz wall and PI surface. Because of the controlled release of radicals, a huge amount of radicals cannot be generated simultaneously, thus important photoinitiated polymerization can be avoided. Furthermore, radicals

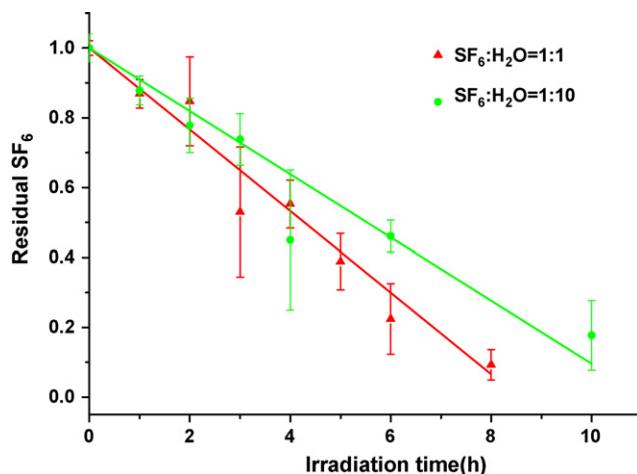


Fig. 8. Degradation curve of SF₆ with the presence of H₂O.

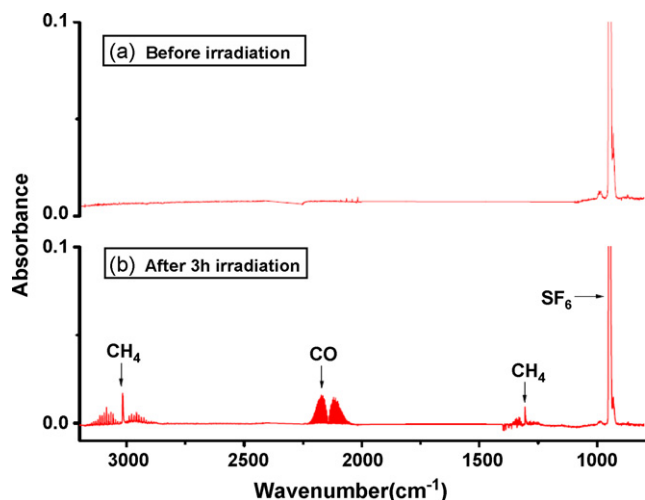


Fig. 9. FT-IR spectra of gaseous substance in the reaction cell before (a) and after (b) 3 h irradiation in pure argon.

need to diffuse through the 1 cm distance before polymerizing and depositing on lamp surface. It is worth noticing that after 600 h irradiation the 3 h-DRE of SF₆ in the system decreased from 43% to 28%, yet the decrease could be attributed to other factors such as UV lamp efficiency decrease.

3.1.4. Determination of photodegradation products

3.1.4.1. Determination of gaseous products by FT-IR. FT-IR spectra of gaseous substance in the reaction cell before and after 3 h irradiation in pure argon are presented in Fig. 9. Main products after irradiation identified from the spectrum are methane and carbon monoxide. No absorption of fluoride other than SF₆ in the gas phase could be detected by FT-IR. Because of big IR absorption cross-section of the fluorides, if fluorine formed gaseous compounds with other elements (S, O, and C), they would have been detected by the

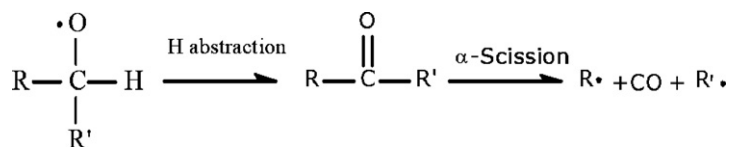
FT-IR. The only reasonable conclusion is that there is hardly any fluorine in the gas phase or the amount is so tiny that it cannot be discerned. Oxygen will be doped into PI while PI was processed [21] and the C=O was formed through “ene” process while irradiated by UV [22–24]. The carbon monoxide was generated through Norrish type I reaction (Scheme 1) [29–31]. The formation of CH₄ will be discussed later.

3.1.4.2. Determination of physical and chemical change of PI surface. Physical and chemical characteristics of PI surface were examined. The amount of SF₆ introduced in each sample was merely 1.6×10^{-5} mol, this was a trace quantity compared to the amount of PI. In order to make the change of NR surface measurable after trace amount S or F is introduced into polyisoprene, the surface of polyisoprene was examined after irradiation of 50 samples (approximately 200 h) in total. The appearances of PI before (a) and after (b) irradiation are shown in Fig. 10a and b.

100 mg of irradiated PI was digested in 10 ml HClO₄–HNO₃ mixed acid at 300 °C until the solution became transparent and colorless. Sufficient drops of BaCl₂ solution were then added into the tubes. As is shown in Fig. 11, much more obvious white precipitate appeared in the tube containing irradiated PI, which indicated the formation of BaSO₄. This suggests that after irradiation the PI has been doped with sulfur from SF₆.

XPS was then employed to analyze F, S, C and O on PI surface. In order to display higher resolution, the narrow spectra according to F region are inserted. Fig. 12 shows the details. The sample of PI (a) suggests a sulfur background value of 0.12%. The peak height of F region was 0, which suggests there was no background element F in NR in this study. After 200 h irradiation, spectrum of PI surface (b) suggests that the comparative content of S is 0.32%, the comparative content of F is 0.37%. Increasing ratio of S and appearance of F peaks indicate that F has been introduced into PI, as a consequence of defluorination of SF₆ in the reaction cell.

Samples of the same weight before and after irradiation were dissolved in dichloromethane for residue analysis. After 24 h, the PI sample before irradiation formed completely dispersed solution



Scheme 1. Pathway of the generation of carbon monoxide.

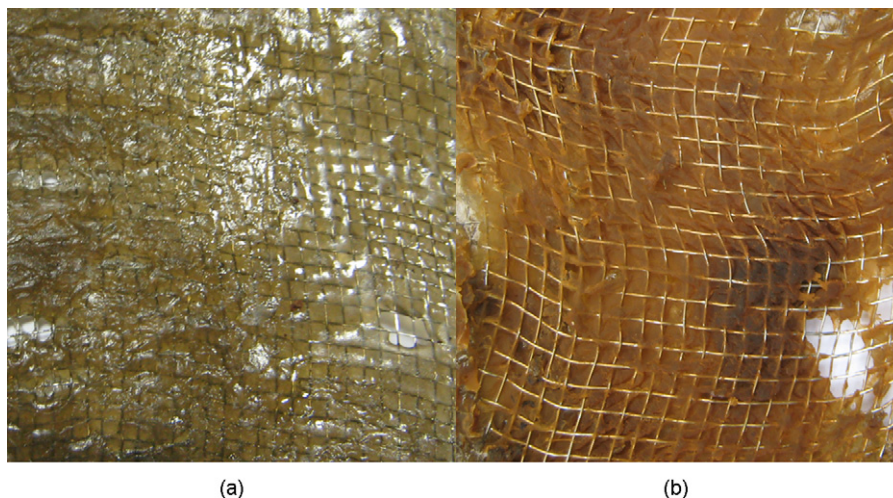


Fig. 10. The appearance of PI before (a) and after (b) irradiation.

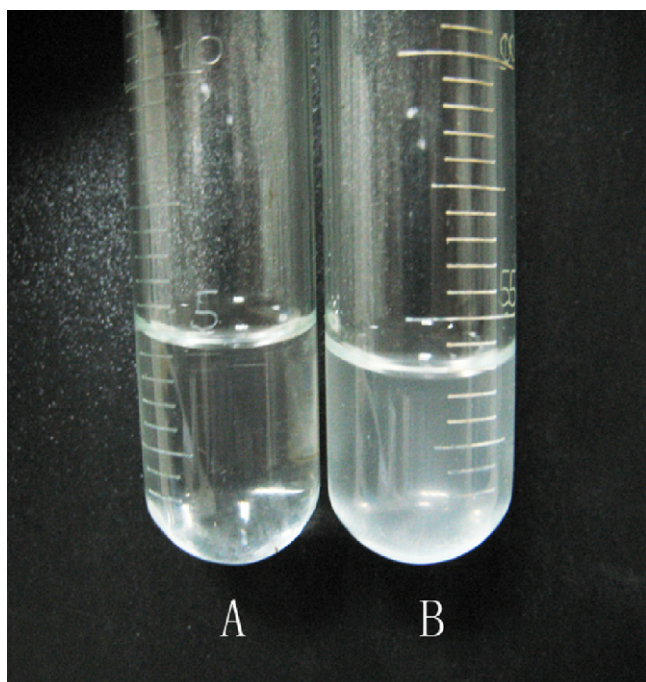


Fig. 11. Comparison of PI before (a) and after (b) irradiation digested in 10 ml $\text{HClO}_4\text{-NO}_3$ mixed acid at 300°C in which excessive drops of BaCl_2 solution were added.

with slight milk white while the irradiated sample contained much brown and ribbon-like insoluble substance. This could be explained by cross-linking of PI main chains while irradiated. PDA UV-vis detector was then employed to examine the dissolved part of two samples; the spectra are compared in Fig. 13. The absorbance of UV decreased a lot after being exposed to UV because a large part of PI cross-linked and could not be dissolved in dichloromethane [32,33]. Main changes in the absorption peaks are that absorption by $\text{C}=\text{C}$ double bonds undergoes a hypsochromic shift of about 2 nm and a new peak appears near 215 nm. These changes can be explained by conjugated double bonds in PI produced by shift of double bonds and new dopants in PI [34,35]. Thus new functional groups are proved to form onto carbon main chain.

3.2. Pathways of degradation of SF_6 in argon

As can be seen from Fig. 14, the degradation reaction displays important feature of pseudo-first-order kinetics during adopted irradiation time. Yet in fact, reaction between SF_6 and PI is in itself fairly complicated. Because SF_6 undergoes no photolysis when irradiated by UV above 110 nm [36], the photoreaction could only possibly be initiated by excited polyisoprene. To interpret the photochemical reactions between PI and SF_6 in this case, FT-IR spectrum was employed to examine the surface of PI before and after degradation through attenuated total reflectance method. See Fig. 15 for details.

Ratios between absorption peaks of different functional groups are analyzed to study major changes of the backbone of PI. Absorption peaks at 2961 cm^{-1} , 1714 cm^{-1} , 1664 cm^{-1} and 1376 cm^{-1} are assigned to CH_3 asymmetric stretching, $\text{C}=\text{O}$ stretching (ketones), $\text{C}=\text{C}$ stretching and CH_3 asymmetric deformation respectively [19]. Degradation of $\text{C}=\text{C}$ had been proved to be one of the main process when PI was exposed to UV irradiation [18]. However, in this study, the ratio of $\text{C}=\text{C}$ stretching to CH_3 asymmetric deformation after UV irradiation is 0.5, which is much bigger than 0.3 before irradiation. This indicates that the elimination rate of $\alpha\text{-CH}_3$ was bigger than that of $\text{C}=\text{C}$. Because the $\text{C}-\text{C}$ bond between two double bonds has

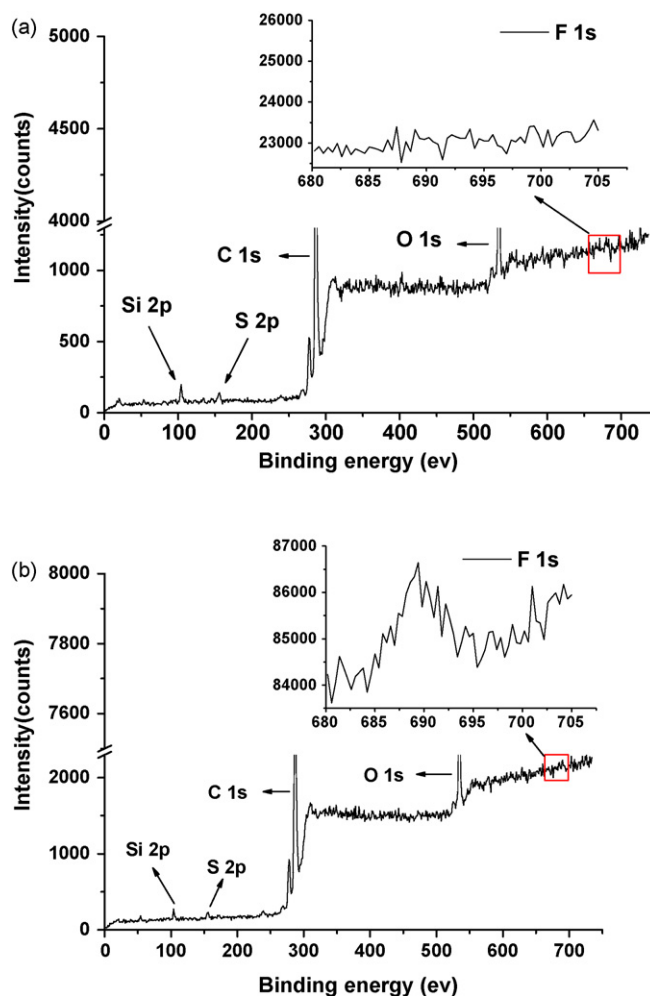


Fig. 12. XPS spectra of PI (a: without irradiation) and PI (b: after 200 h irradiation). Inserted figures are narrow spectra of F region.

the smallest dissociation energy among the bonds in the main chain of PI, it undergoes chain scission to form two kinds of allylic radicals [17,19,20]. The allylic radicals then eliminate $\alpha\text{-CH}_3$ to produce CH_4 [37]. Besides the allylic radicals, when $\text{C}=\text{C}$ bonds absorb UV irradiation and are excited [15], free electrons are generated outside of C atoms to form reductive radicals. Upon approaching SF_6 , these reductive radicals attract electronegative F atom and further

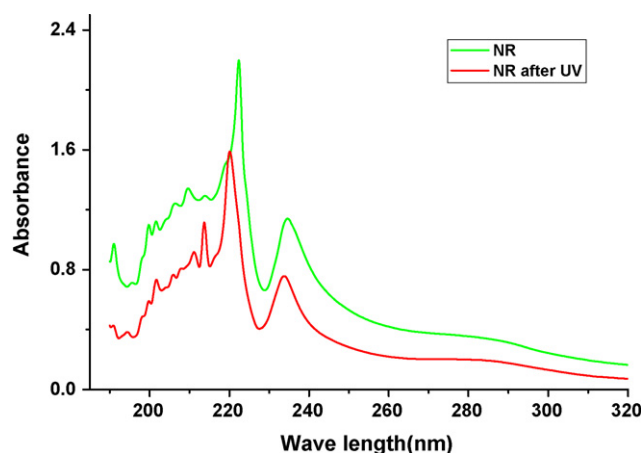


Fig. 13. UV-vis spectra of PI before and after UV irradiation.

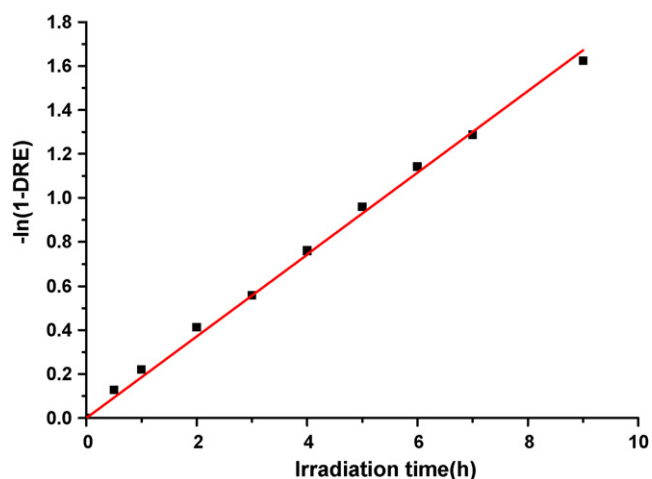


Fig. 14. The linear fitting of DRE–time curve in the atmosphere of pure argon.

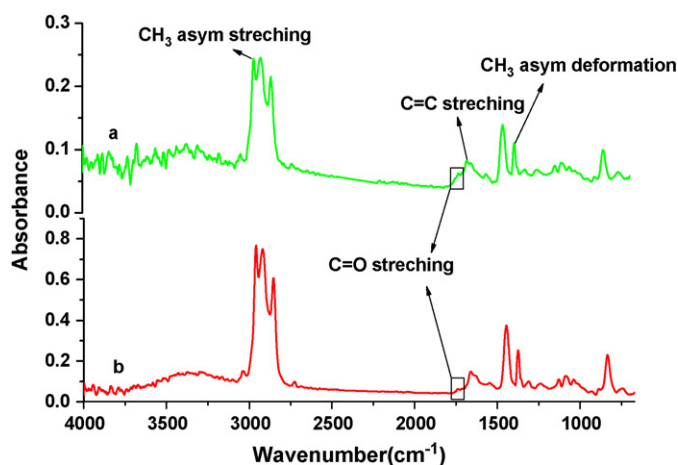


Fig. 15. FT-IR spectra of the surface of PI after (a) and before (b) degradation through attenuated total reflectance method.

abstract it from SF₆. Hence we speculate that allylic radicals and excited C=C bonds are primary species that are responsible for the degradation of SF₆. Assign the allylic radicals and excited C=C bonds with symbols R and R₁ respectively, the rate equation of the initial step of decomposition reaction can be described as following:

$$\frac{-d[\text{SF}_6]}{dt} = (k[\text{R}] + k_1[\text{R}_1])[\text{SF}_6] \quad (k \text{ and } k_1 \text{ are constants}) \quad (1)$$

As irradiation time moves on, [R] and [R₁] accumulates under irradiation by UV lamp. Because of the synergistic effect of the UV light and radical polymerization, [R] and [R₁] eventually reached a steady state. The rate equation can be further described as

$$\begin{aligned} \frac{-d[\text{SF}_6]}{dt} &= k_2[\text{SF}_6] \quad (k_2 \text{ is an approximate constant, } k_2 \\ &= k[\text{R}] + k_1[\text{R}_1]) \end{aligned} \quad (2)$$

This equation explains the pseudo-first-order reaction kinetics exhibited by DRE–time curve. According to Fig. 14, k_2 in this study is calculated to be $5.16 \times 10^{-5} \text{ s}^{-1}$.

4. Conclusion

Based on the theory that reductive radicals can attract fluorine in SF₆ and thus decompose the molecule, this paper has studied the degradation of SF₆ on the surface of polyisoprene. Through the

“Controlled Release Radicals” (CRR) process, effective degradation of SF₆ has been achieved. Toxic fluorides were not detected by FT-IR in the gas phase; fluorine was introduced into the hydrocarbon chain; sulfur was doped into PI surface. No fouling on surface of UV lamp was observed because of the controlled release of radicals. It was found in this study that the degradation curve of SF₆ in pure argon environment shows characteristics of pseudo-first-order reaction, and 60% DRE was achieved in 4 h. A general scheme about initial photochemical processes was proposed in this paper.

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