

ORIGINAL ARTICLE

Degradation mechanism of γ -irradiated polytetrafluoroethylene (PTFE) powder by low-temperature matrix-isolation infrared spectroscopy and chemiluminescence spectroscopy

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In order to elucidate the mechanism of degradation of γ -irradiated polytetrafluoroethylene (PTFE), gases evolved by isothermal heating under vacuum were trapped in low-temperature argon matrices. Infrared spectra of the evolved gases were assigned to COF_2 and CF_4 by comparison with the corresponding literatures. Kinetic analyses of the IR absorbance and chemiluminescence intensity changes against heating time were carried out to determine the rate constants of the thermal reactions, showing that CF_4 was produced more rapidly than COF_2 . By comparison between the rate constants obtained by infrared spectroscopy and chemiluminescence spectroscopy, we propose a new thermal reaction mechanism of γ -irradiated PTFE at the molecular level.

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INTRODUCTION

When hydrocarbon polymers are heated in air at over 100 °C, they frequently exhibit emission because of thermal oxidative degradation in the visible-light region, although the emission intensity is extremely weak. This phenomenon has been known over half a century; for example, Ashby¹ reported thermal chemiluminescence (TCL) from polypropylene in 1961. However, it is difficult to elucidate the emission mechanism of hydrocarbon polymers at the molecular level because various different oxidation reactions occur concurrently during heating in air, and various kinds of luminophores are produced and destroyed, meaning that the emissions due to the various luminophores are superimposed in a complex manner.^{2–4}

On the other hand, polytetrafluoroethylene (PTFE) has excellent thermal and chemical stability⁵ and is widely used in a broad range of high-temperature applications.⁶ In fact, no TCL of PTFE was observed by heating below 200 °C in our previous study,⁷ and no gas was evolved from PTFE below 500 °C.⁸ However, this polymer shows emission due to oxidative degradation upon γ -irradiation,⁹ although the emission mechanism has not been elucidated satisfactorily.

If a small number of luminophores formed by γ -irradiation remains in the sample stored in air at room temperature, TCL spectra should be observable using our highly sensitive multichannel Fourier-transform spectrometer developed recently.^{10,11} We have thus tried to measure and analyze the TCL spectra to identify the luminophore

in γ -irradiated PTFE with the help of quantum chemical calculations.^{7,12} As a result, we concluded that this luminophore could be produced by γ -irradiation but not by thermal oxidation reactions as the TCL emission was observed during heating not only in dry air but also in N_2 . In addition, kinetic analysis of the time-dependent profile of TCL intensity showed that the activation energy determined from the rate constants using an Arrhenius plot corresponded to the dissociation energy of a single O–O bond, suggesting that the luminophore was a peroxide compound.

We initially proposed the TCL reaction mechanism shown in Scheme 1, being based on the thermal reaction mechanism of γ -irradiated PTFE proposed by Oshima *et al.*^{13,14} If this emission mechanism shown in Scheme 1 is correct, OF_2 detached from the main chain by heating should be detected by infrared (IR) spectroscopy. However, Oshima *et al.*^{13,14} claimed that the gas evolved from γ -irradiated PTFE could not be analyzed by Fourier-transform infrared spectroscopy, probably because the amount of OF_2 was too low.

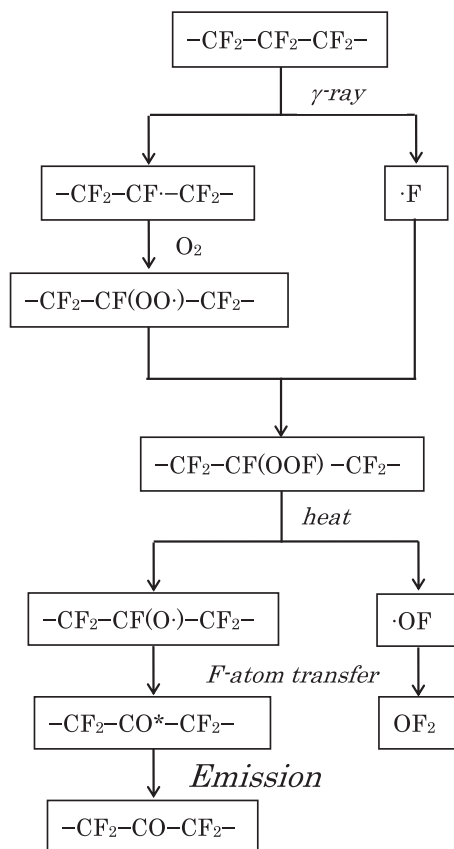
It is well known that the low-temperature noble-gas matrix-isolation IR spectroscopy is one of the most powerful techniques to detect an extremely small amount of an unstable species that can be accumulated and trapped in IR-transparent solid noble gases. This technique, proposed by Norman and Porter¹⁵ and by the group of Pimentel¹⁶ in 1954, has been widely developed by the groups of Pimentel and used in various fields of chemistry and physics.

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Scheme 1 Tentative thermal chemiluminescence (TCL) mechanism for γ -irradiated polytetrafluoroethylene (PTFE) proposed previously.^{7,12}

The species trapped in low-temperature noble-gas matrices can be easily identified by vibrational spectral analyses, because the IR bandwidths measured in low-temperature noble-gas matrices are much sharper than those measured in the gas phase or solution, where the former is broadened by rotational–vibrational lines and the latter by solvent effects.¹⁷

In the present study, we have applied the low-temperature matrix-isolation IR spectroscopy to trap and identify very low amounts of volatile materials released from γ -irradiated PTFE during heating and proposed the thermal reaction mechanism of γ -irradiated PTFE without any inconsistency between the experimental results from TCL and IR spectral analyses. We determine the rate constants of the thermal reactions by kinetic analyses of the time-dependent profiles of IR and TCL intensities and discuss whether or not the thermal reaction mechanism derived from the results obtained by the matrix-isolation IR spectroscopy corresponds to the TCL reaction mechanism proposed previously.^{7,12} We claim that different experimental methods provide different information on the thermal reactions of polymers.

EXPERIMENTAL PROCEDURE

Materials

Additive-free PTFE powder (Product name: F104), supplied by Daikin Industries (Osaka, Japan), was γ -irradiated with a dose of 141 kGy in air at room temperature, which was the same material used in our previous studies.^{7,12} The γ -irradiated PTFE powder is so stable in air at room temperature¹³ that the present experiments were carried out 1 year after storage in air at room temperature.

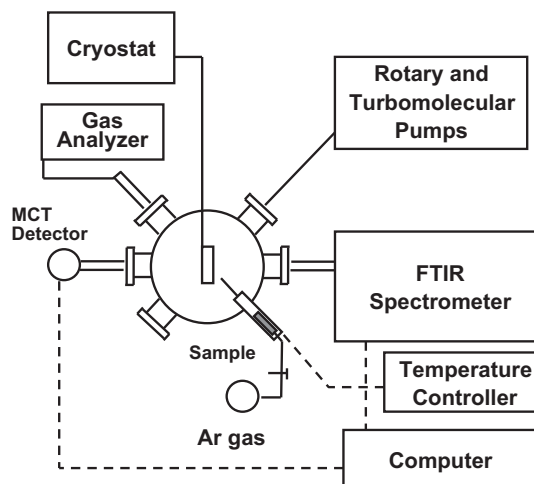


Figure 1 A schematic figure of the instrument for low-temperature matrix-isolation infrared (IR) spectroscopy.

Low-temperature matrix-isolation IR spectroscopy

A powdered sample of γ -irradiated PTFE (~ 50 mg) was placed in a stainless steel sample holder ($\varphi = 4$ mm \times $l = 20$ mm) in a heating nozzle (Figure 1). The sample was heated at 160 °C in a stream of pure argon gas (99.9999% purity; Taiyo Nippon Sanso, Tokyo, Japan). The argon containing gases evolved from the heated sample was deposited on a cesium iodide plate cooled at ~ 20 K in a vacuum chamber.

IR spectra were measured with an Fourier-transform infrared spectrometer (JIR-WINSPEC50, JEOL, Tokyo, Japan). The IR beam of the spectrometer was introduced into the matrix sample through a KBr window and detected with a liquid-nitrogen cooled MCT detector placed on the opposite side of the vacuum chamber. The spectral resolution was 0.5 cm^{-1} , and the number of scans used to accumulate the IR spectra was 50 scans. See previous studies^{18–20} for other experimental details.

Thermal chemiluminescence spectroscopy

A new multichannel Fourier-transform chemiluminescence spectrometer^{7,10,11} was used to obtain extremely weak TCL spectra, based on a similar optical principle as that proposed by Hashimoto and Kawata²¹ in the IR spectral region (Figure 2). In the experiments to obtain TCL spectra, a sample (~ 120 mg) was placed on an aluminum dish and put on a hot sample stage isothermally heated at 200 °C under a dry air stream. The spatial interferogram generated by the interferometer composed of a Savart plate, a quartz lens and two linear polarizers was continuously detected by the CCD sensor. The data accumulated over 30 s were converted to a TCL spectrum by Fourier transform. In the experiments to determine the rate constants of TCL reactions, each sample was isothermally heated at 160 °C. The sum of the signal values at each CCD pixel accumulated over 2 s at an interval of 2 s was used for the kinetic analyses.

RESULTS AND DISCUSSION

Assignments of IR bands of evolved gases

IR bands (1941, 1914, 1274, 1260, 1238 and 1232 cm^{-1}) due to the gases evolved from γ -irradiated PTFE were observed, as shown in Figure 3, where the baseline is computationally corrected. Liu and Davis²² investigated the oxidation of tetrafluoroethylene and reported that the IR bands of COF_2 in an argon matrix appeared at 1942, 1914 and 1238 cm^{-1} , where the splitting bands at 1942 and 1914 cm^{-1} are assignable to the Fermi resonance between the $\text{C}=\text{O}$ stretching mode and an overtone of the symmetric $\text{C}-\text{F}$ stretching mode at 965 cm^{-1} . A similar assignment was also reported by Bettinger and Peng,²³ who heated fluorinated single-walled carbon nanotubes below 300 °C under vacuum and identified the gaseous decomposition products by low-temperature matrix-isolation IR spectroscopy. They assigned the

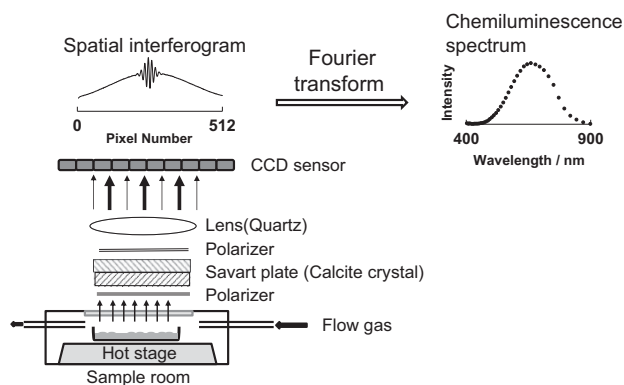


Figure 2 A schematic figure of the instrument and the principle for chemiluminescence spectroscopy.

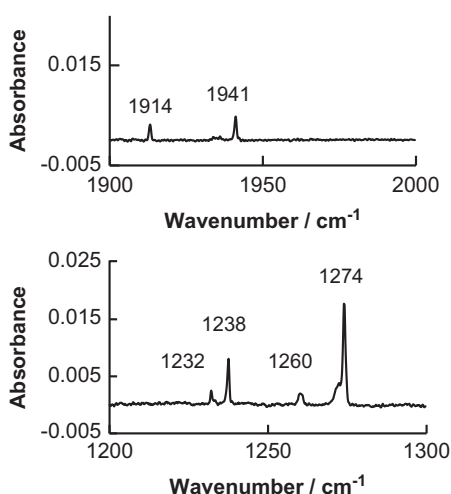


Figure 3 Infrared (IR) spectra of gases evolved from γ -irradiated polytetrafluoroethylene (PTFE) in argon matrices.

bands at 1941, 1914, 1238 and 1232 cm^{-1} observed to COF_2 . As our observed wavenumbers are completely consistent with their results, we conclude that COF_2 is evolved from γ -irradiated PTFE by heating. In addition, Liu and Davis²² and Bettinger and Peng²³ reported that a strong band of CF_4 in an argon matrix appears at 1274 cm^{-1} that has a side band at 1260 cm^{-1} because of the matrix effect.¹⁷ Therefore, we conclude that the bands observed at 1274 and 1260 cm^{-1} are assignable to CF_4 .

One of the purposes of the present use of the low-temperature matrix-isolation technique was to detect the IR bands of OF_2 , which was expected to evolve from the sample by heating, as shown in Scheme 1. Andrews *et al.*^{24,25} reported that the IR bands of OF_2 in an argon matrix appear at 920, 466 and 826 cm^{-1} for ν_1 , ν_2 and ν_3 vibrational modes, respectively. We tried to detect the ν_1 band in our matrix IR spectra, but no bands of OF_2 appeared in the spectral region between 900 and 940 cm^{-1} , as shown in Figure 4. This finding suggests that the amount of OF_2 is too small to be detected even by low-temperature matrix-isolation IR spectroscopy. Another possibility is that OF_2 has no connection with the TCL of γ -irradiated PTFE, as discussed later.

Thermal production mechanism of CF_4 and COF_2

Florin *et al.*²⁶ claimed that the scission of a C–C bond in the main chain of PTFE occurs to produce two carbon radicals by γ -irradiation,

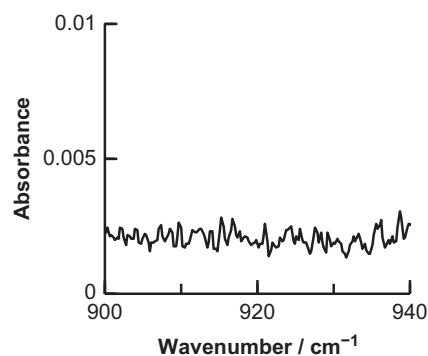
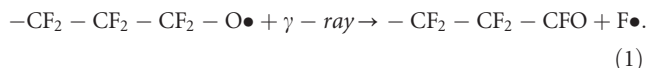


Figure 4 An enlarged infrared (IR) spectrum in the region between 900 and 940 cm^{-1} .

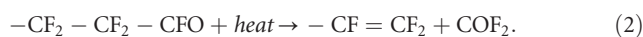
and CF_4 and olefins are produced by transfer of F atoms. They also claimed that a small amount of CF_4 does not diffuse but remains in the crystalline regions of PTFE, resulting in distortion of the crystalline structure. Thus, we assume that an extremely small amount of CF_4 produced upon γ -irradiation remains inside the sample stored for a long time in air at room temperature. This is liberated from the crystalline regions during the early stage of heating without opportunity for the production of luminophores in TCL reaction mechanism.

If two chain-end carbon radicals are produced by the scission in air, one carbon radical immediately combines with an oxygen molecule to produce a chain-end peroxy radical, $-\text{CF}_2-\text{CF}_2-\text{CF}_2\text{OO}\cdot$.^{13,14,27–33} As the counterpart carbon radical, $\cdot\text{CF}_2-\text{CF}_2-\text{CF}_2-$, exists near the peroxy radical, it is possible that it recombines with the peroxy radical before combination with an oxygen molecule, resulting in the production of a peroxide compound $-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{O}-\text{O}-\text{CF}_2-\text{CF}_2-\text{CF}_2-$. Note that this is a minor reaction because strong electron spin resonance signals for peroxy radicals were observed in previous studies.^{13,14,27–33}

Jipa *et al.*⁹ investigated radiation thermoluminescence of PTFE and proposed a thermal reaction mechanism where the O–O single bond of the peroxide compound $-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{O}-\text{O}-\text{CF}_2-\text{CF}_2-\text{CF}_2-$ is broken by heating to produce two alkoxy radicals, $-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{O}\cdot$. They proposed a reaction of the alkoxy radical to produce a fluoroaldehyde group by detaching an F atom during γ -irradiation,



Thus, we assume that the fluoroaldehyde group produces COF_2 by withdrawing an F atom from the main chain so as to make a double bond during heating, as shown in Equation (2),



Kinetic analysis of IR absorbance changes

To confirm that the thermal production mechanism of CF_4 is different from that of COF_2 , we have measured the IR absorbance changes against the deposition time. The absorbance changes for the 1274 cm^{-1} band of CF_4 and the 1238 cm^{-1} band of COF_2 are shown in Figure 5. It is found that the band due to CF_4 appears rapidly at the early stage of heating and is almost constant over 1 h after isothermal heating, whereas the absorbance of the band due to COF_2 increases gradually. As the IR absorbance changes for both species show no

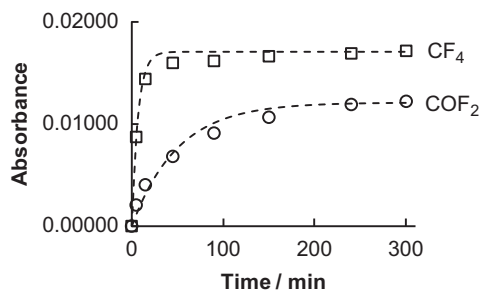


Figure 5 Absorbance changes of the infrared (IR) bands in argon matrices against heating time at the sample heating temperature of 160 °C. Symbols \square and \circ represent the 1274 and 1238 cm^{-1} bands of CF_4 and COF_2 , respectively. The broken line represents the calculated values. The size of the symbols represents the estimated uncertainty.

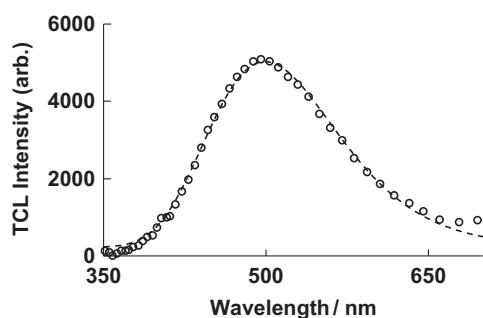


Figure 6 A comparison of thermal chemiluminescence (TCL) spectra measured at 200 °C. The symbol \circ represents the observed spectrum, whereas the broken line represents the corresponding calculated values obtained by a least-squares fitting process using one Gaussian function represented by Equation (4) in the text.

induction period in Figure 5, we assume that the production reactions are due to a first-order reaction; the IR absorbance change for COF_2 or CF_4 can be represented by a function of the heating time t as

$$A_t = A_\infty (1 - \exp(-kt)), \quad (3)$$

where A_t and A_∞ represent IR absorbance at the heating time t and the infinite time, respectively. The symbol k represents the rate constant for the production of CF_4 or COF_2 .

The constants A_∞ and k for the IR bands of CF_4 and COF_2 evolved from γ -irradiated PTFE were determined by a least-squares fitting process using Equation (3). The calculated absorbance values are represented by broken lines in Figure 5 that can satisfactorily reproduce the corresponding observed ones for CF_4 (\square) and COF_2 (\circ). The rate constants k for CF_4 and COF_2 were determined to be 0.145 ± 0.023 and $0.020 \pm 0.007 \text{ min}^{-1}$, respectively. It is found that the rate constant k for CF_4 is ~ 7 times larger than COF_2 . This result supports the assumption that the production mechanism of CF_4 is different from that for COF_2 ; CF_4 produced upon γ -irradiation is trapped in the crystalline regions of PTFE and rapidly evolved by heating, whereas COF_2 is gradually produced by a thermal reaction.

Measurement of TCL spectrum

The conclusion from matrix-isolation IR spectroscopy is that COF_2 is evolved from γ -irradiated PTFE during heating. One may then assume that COF_2 is a final product of the TCL reactions. To confirm this assumption, we have measured the TCL spectra with a multichannel

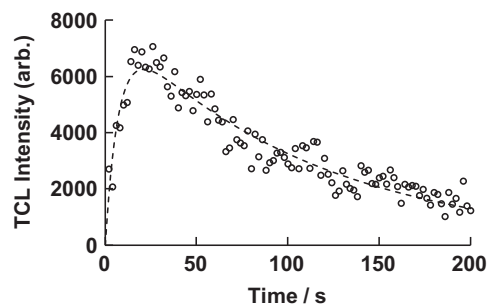


Figure 7 Total thermal chemiluminescence (TCL) intensity changes against the heating time. The sample heating temperature is 160 °C. The symbol \circ represents the observed intensity, whereas the broken line represents the corresponding calculated values.

Fourier-transform chemiluminescence spectrometer. The spectrum obtained is shown in Figure 6.

To determine the peak intensity of the TCL spectra, we performed a least-squares curve fitting to the experimental spectra using one Gaussian function after conversion of the x axis from the wavelength to the wavenumber that is linear with energy:

$$f(x) = y_0 + a \exp(-(x - x_1)^2/w^2), \quad (4)$$

where y_0 represents the baseline mainly due to the dark current in the CCD sensor. The symbols a , x_1 and w represent the peak intensity, peak wavenumber and bandwidth of TCL spectra, respectively. The calculated relative intensities obtained, represented by a broken line in Figure 6, are consistent with the corresponding observed values. Thus, we conclude that only one kind of luminophore exists.

Kinetic analysis of time-dependent profiles of TCL intensities

We have measured the time-dependent profile of the TCL intensity. Details of the analytical processes have been reported in our previous papers.^{7,12} The sample temperature was adjusted to 160 °C so as to make comparable with the rate constants derived from the IR spectral changes. As plotted in Figure 7, the TCL shows the intensity maximum at ~ 25 s and then decreases gradually.

The kinetic analysis of the time-dependent profile of the TCL intensity was performed to determine the rate constants using the following series of first-order reactions:



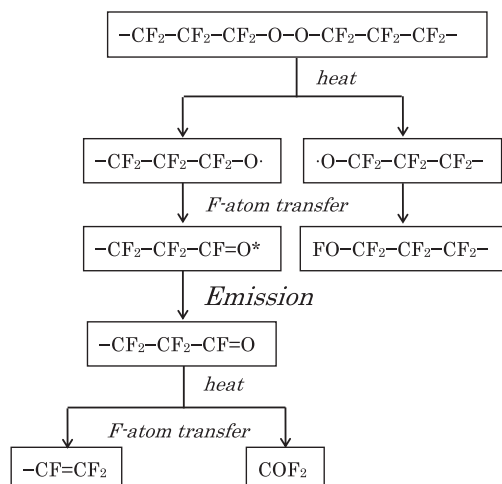
where Luminophore^* represents an unstable state or species to produce an electronically excited carbonyl group. By use of the rate constants defined as k_1 and k_2 for Equations (5) and (6) respectively, the concentrations of Luminophore^* and Product are represented as,³⁴

$$[\text{Luminophore}^*] = A_0 k_1 (\exp(-k_1 t) - \exp(-k_2 t)) / (k_2 - k_1), \quad (7)$$

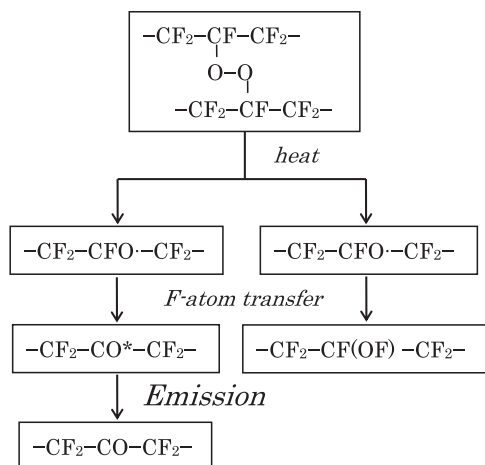
$$[\text{Product}] = A_0 (1 - (k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)) / (k_2 - k_1)), \quad (8)$$

where A_0 and t represent the initial amounts of the luminophore and the heating time, respectively. The rate constants, k_1 and k_2 , and A_0 for γ -irradiated PTFE were estimated by a least-squares fitting process to be $0.009 \pm 0.001 \text{ s}^{-1}$, $0.14 \pm 0.03 \text{ s}^{-1}$ and $(1.1 \pm 0.2) \times 10^5$, respectively. The calculated values obtained by a least-squares fitting process are plotted by a broken line in Figure 7.

The rate constant for the production of COF_2 , 0.02 min^{-1} , is totally different from the rate constants k_1 and k_2 derived from the time-



Scheme 2 Proposed thermal chemiluminescence (TCL) mechanism for γ -irradiated polytetrafluoroethylene (PTFE) with a final product of COF_2 via fluoroaldehyde group.



Scheme 3 Possible thermal chemiluminescence (TCL) mechanism for γ -irradiated polytetrafluoroethylene (PTFE) without the production of COF_2 .

dependent profile of the TCL intensity, 0.009 s^{-1} (0.6 min^{-1}) and 0.14 s^{-1} (8.4 min^{-1}), respectively, strongly suggesting that COF_2 is not the final product of the TCL reactions.

Possible thermal reaction mechanism

Instead of OF_2 , COF_2 was evolved from γ -irradiated PTFE by heating. Thus, we propose a thermal reaction mechanism shown in Scheme 2. The peroxide compound, $-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{O}-\text{O}-\text{CF}_2-\text{CF}_2-\text{CF}_2-$, is yielded by the scission of a main chain followed by the insertion of an oxygen molecule upon γ -irradiation. An extremely small amount of the peroxide compounds remains in the sample stored over a long time in air at room temperature. The peroxides are destroyed by heating to produce two alkoxy radicals. An F atom transfers from one radical to the other radical with visible-light emission because of an electronically excited carbonyl group, resulting in the production of fluoroaldehyde and fluoroalcohol groups. The fluoroaldehyde group, which is treated as a final product of the TCL reactions, gradually evolves COF_2 gas by heating under vacuum with no luminescence.

Another TCL reaction mechanism is also possible. If the peroxy radical in Scheme 1 could be combined with a carbon radical in the other main chain, instead of an F atom detached by γ -irradiation, another peroxide compound, $(-\text{CF}_2-)_2\text{CF}-\text{O}-\text{O}-\text{CF}(-\text{CF}_2-)_2$, would be yielded instead of the fluoroperoxide group in Scheme 1. If the O–O single bond of the peroxide is cleaved by heating, two alkoxy radicals are produced, as shown in Scheme 3. One alkoxy radical transfers an F atom to the oxygen atom in the other alkoxy radical, resulting in the production of an electronically excited carbonyl group and a fluoroalcohol compound. The electronically excited carbonyl group immediately exhibits visible-light emission. This mechanism seems to be reasonable for the explanation of TCL in the visible light region because carbonyl groups show phosphorescence at $\sim 490 \text{ nm}$.³⁵

The TCL reaction mechanism of $(-\text{CF}_2-)_2\text{CF}-\text{O}-\text{O}-\text{CF}(-\text{CF}_2-)_2$ in Scheme 3 is similar to that of $-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{O}-\text{O}-\text{CF}_2-\text{CF}_2-\text{CF}_2-$ in Scheme 2. One important difference between Schemes 2 and 3 is whether or not COF_2 is evolved by heating. Thus, we do not propose Scheme 3 but Scheme 2 as the most probable TCL reaction mechanism of γ -irradiated PTFE. However, we do not remove the possibility of the Scheme 3, because both schemes may occur concurrently during heating. If this is correct, the evolution of COF_2 detected by matrix-isolation IR spectroscopy and TCL measured with a multichannel Fourier-transform chemiluminescence spectrometer can be explained by Schemes 2 and 3, respectively.

CONCLUSIONS

We have observed the IR spectra of gases evolved from γ -irradiated PTFE by heating using the low-temperature matrix-isolation technique. IR bands were assigned to CF_4 and COF_2 . We assume that CF_4 is produced upon γ -irradiation and trapped in the crystalline regions of PTFE and this is removed from the sample by heating under vacuum. On the other hand, COF_2 is gradually evolved from γ -irradiated PTFE by a thermal reaction. We propose Scheme 2 and/or Scheme 3 for visible-light emission, instead of Scheme 1, because no IR band due to OF_2 could be detected in the present study.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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