THERMAL DEGRADATION OF POLYTETRAFLUOROETHYLENE IN FLOWING HELIUM ATMOSPHERE II. PRODUCT DISTRIBUTION AND REACTION MECHANISM

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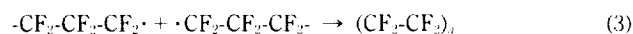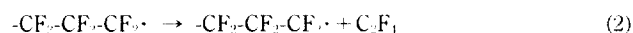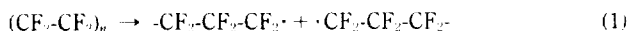P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Abstract — The thermal degradation of polytetrafluoroethylene was studied in the helium flowing atmosphere and the temperature range 510-600°C. The products of the thermal degradation of polytetrafluoroethylene were analyzed by an on-line gas chromatograph and the product distribution was obtained. The products consist of tetrafluoroethylene (TFE), perfluoropropene (PFP) and cyclic-perfluorobutane (c-PFB). Under most conditions the main product was TFE. The c-PFB was regarded as the secondary product formed from TFE because the formation of c-PFB strongly depended upon the degradation rate. However, the production of PFP was not related to the degradation rate, but it was influenced by diffusion limitation of gaseous product in the sample matrix. These phenomena were also verified with Curie-point pyrolyser. The results showed that the production of PFP reached a maximum point under diffusion limitation condition. The degradation mechanism of polytetrafluoroethylene was proposed in terms of unzipping mechanism and other mechanism like radical chain transfer reaction.

Key words: Polytetrafluoroethylene, Thermal Degradation, Product Distribution, Diffusion Effect, Degradation Mechanism

INTRODUCTION

Polytetrafluoroethylene (PTFE) represents the large use of material in commercial production because of its high thermal stability and solvent resistance [Hanford and Joyce, 1946; Renfrew and Lewis, 1946; Lewis and Naylor, 1947]. The thermal degradation of PTFE has become a subject of both practical and theoretical importance and studied extensively during the past decades [Park et al., 1946; Lewis, 1946; Young and Murray, 1948; Madorsky et al., 1953; Florin et al., 1954; Madorsky and Straus, 1960; Florin et al., 1966; Wall, 1972; Choi and Park, 1976; Kim and Rhee, 1980]. In recent years, however, a few researchers have paid attention to the studies of the thermal degradation of PTFE in view of the retreatment and recycling of waste polymer.

Since the monomer, tetrafluoroethylene (TFE), was known to be the major product of PTFE degradation, many efforts were made to obtain the maximum yield of tetrafluoroethylene for the industrial application. The studies on the mechanism of PTFE thermal degradation have been reported by several groups [Lewis and Naylor, 1947; Wall and Michaelson, 1956; Michaelson and Wall, 1957; Errede, 1962; Goldfarb et al., 1962; Siegle et al., 1964; Madorsky, 1964]. Most authors demonstrated the unzipping mechanism, according to which perfluoropropene (PFP) and cyclic-perfluorobutane (c-PFB) were produced by the secondary reaction of TFE, the primary product of the thermal degradation of PTFE. The unzipping mechanism can be briefly described as follows:

$$(CF_2\text{-}CF_2)_n \rightarrow \text{-}CF_2\text{-}CF_2\text{-}CF_2\cdot + \cdot CF_2\text{-}CF_2\text{-}CF_2\text{-} \tag{1}$$

$$\text{-}CF_2\text{-}CF_2\text{-}CF_2\cdot \rightarrow \text{-}CF_2\text{-}CF_2\text{-}CF_2\cdot + C_2F_4 \tag{2}$$

$$\text{-}CF_2\text{-}CF_2\text{-}CF_2\cdot + \cdot CF_2\text{-}CF_2\text{-}CF_2\text{-} \rightarrow (CF_2\text{-}CF_2)_4 \tag{3}$$

Some authors studied the reaction scheme of TFE and c-PFB using TFE monomer at high temperatures (550-1027°C) [Lacher et al., 1952; Atkinson and Trenwith, 1953; Atkinson and Atkinson, 1957; Butler, 1962; Lifshitz et al., 1963; Drennam and Matula, 1968; Simmie et al., 1969; Preses et al., 1977; Buravtsev et al., 1985]. Various reaction mechanisms were suggested by the different methods and conditions and the rate constant values were also quite different.

The present study is based on our earlier work [Jun et al., 1995] and focused on the mechanism of PTFE pyrolysis. We previously reported that the rate of the thermal degradation of PTFE increased with the increase of temperature and significantly influenced by the change of morphology. But the study was limited to gain the mechanistic insight without examining the product distribution. In this research the PTFE thermal degradation was conducted under the inert atmosphere and the gaseous products were analyzed. Curie-point pyrolyser was used to prevent the effect of secondary reaction during the thermal degradation. The reaction mechanism was investigated by the product distribution and the effect of diffusion limitation on the degradation rate was discussed.

EXPERIMENTAL

1. Flow Reactor System

The flow reactor system used in this study has previously been

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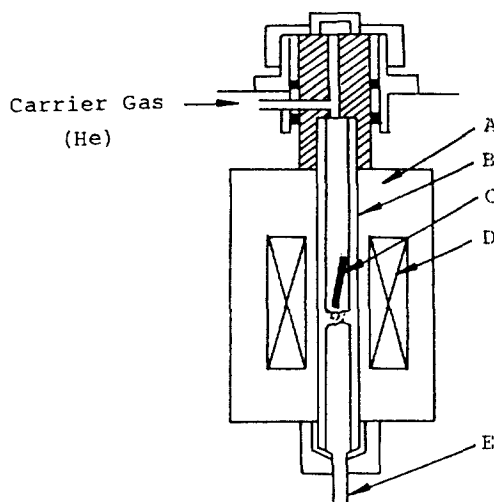[†]To whom all correspondences should be addressed

Fig. 1. Curie-point pyrolyser.

(A) oven (100C); (B) sample holder; (C) sample wrapped in foil; (D) induction coil; (E) connector (100C)
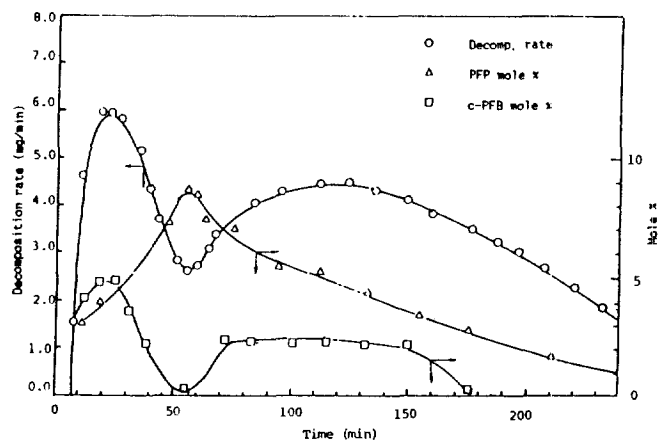

Fig. 2. Product distribution for the decomposition of PTFE (50 ml/min, 515°C).

described in detail [Jun et al., 1995]. The reactor was a nickel tube (2.54 cm dia.×128 cm long). The decomposition products from the reactor were passed through KOH column in order to remove solid particles and HF that might be carried along in the gas stream. Then the pyrolysis products were analyzed by the on-line gas chromatograph.

2. Curie-point Pyrolyser

Curie-point pyrolyser was used for utilizing the fact that ferromagnetic materials and alloys could not exceed a certain limiting temperature (the "Curie-point") when receiving energy from a radio frequency field. This technique was used to obtain the desired temperature (Curie-point) rapidly. The different pyrolysis temperatures were achieved by selecting ferromagnetic alloys of different composition.

The Curie-point Pyrolyser (JHP-2) was obtained from Japan Analytical Industry Co. Ltd. A typical diagram is given in Fig. 1. The Part E was connected to gas chromatograph and the temperature was kept at 100C. No products were detected in this temperature. In order to obtain various Curie-point temperatures, four different foils (500, 590, 650, and 690C) were employed.
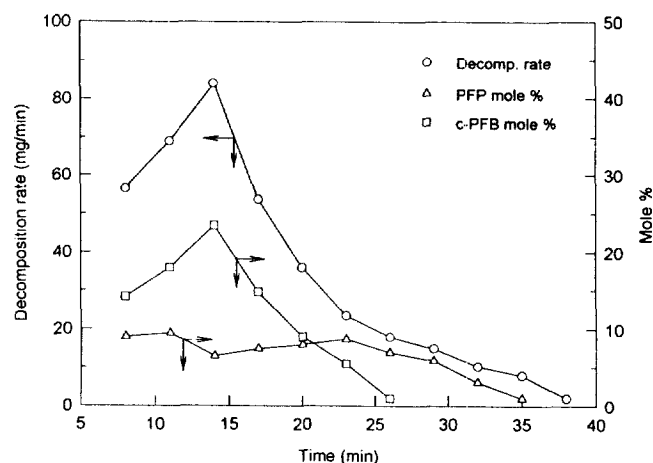

Fig. 3. Product distribution for the decomposition of PTFE (150 ml/min, 564°C).

1 mg of sample was wrapped by Curie-point foil and the sample was in intimate contact with the heating surface of foil. The sample was placed into the sample tube and then the sample tube was purged with helium for a while to flush the hold-up gases. The product gases obtained from the sample tube were detected by the on-line gas chromatograph.

3. Differential Thermal Analysis

The thermal characterization of PTFE were performed by Differential Thermal Analysis (DTA). Du Pont DTA cell-1200 connected to Du Pont Thermal Analyzer 990 were employed. For each experiment 100 ml/min of N_2 carrier gas was used. The experiments were carried out with heating rates of 10, 20, and 50 ℃ /min.

RESULTS AND DISCUSSION

1. Product Distribution in the Helium-Flowing Reactor

In our earlier research the thermal degradation of PTFE was explained on the basis of the diffusion limitation of gaseous products in the polymer matrix [Jun et al., 1995]. The diffusion limitation was strongly influenced on the initial pyrolysis condition. Fig. 2 shows the decomposition rate and the mole percent of degradation products (except for TFE) as a function of time at 515℃ and 50 ml/min of carrier gas flow rate. The mole percent of c-PFB is changed along with the change of decomposition rate, whereas that of PFP is not. The mole percent curve of PFP reached a maximum under diffusion limitation region. The PFP was easily produced at the beginning of diffusion limitation when compared with that at diffusion-limitation-free region. For instance, the decomposition rates at 50 and 180 minutes are nearly same. But the mole percent of PFP at 50 min is much greater than that at 180 min. If we consider that TFE monomer produced from PTFE degradation leads to secondary reaction to produce PFP and c-PFB, then it can be expected that the products of PFP and c-PFB increase with the increase of thermal degradation rate. However, this is not seen in our experimental results. The production of c-PFB depends on the degradation rate while the production of PFP is strongly influenced by the diffusion limitation. This is strong evidence that PFP is produced by a mechanism quite different from the unzipping reaction. Fig. 3 represents a typical decomposition rate at less diffusion limitation and high tempera-

Table 1. Pyrolysis of PTFE by Curie-point pyrolyser

Temp.	Time	Initial weight	Conversion	Composition (mole %)		
(C)	(sec)	(mg)	(wt. %)	TFE	PFP	c-PFB
500	3	1.08	0.1	100	0	0
	4	1.12	0.2	100	0	0
	5	1.07	0.2	100	0	0
590	3	1.04	0.7	69.4	22.2	8.4
	4	0.93	0.9	68.0	23.5	8.5
	5	0.96	1.3	69.7	23.1	7.2
650	3	1.06	53.2	67.6	18.2	14.8
	4	0.99	58.2	67.9	17.3	14.8
	5	1.00	65.8	66.5	17.7	15.8
670	3	0.86	72.2	69.7	16.1	14.2
	4	1.00	77.6	70.7	15.8	13.5
	5	0.86	83.1	69.8	17.2	13.2

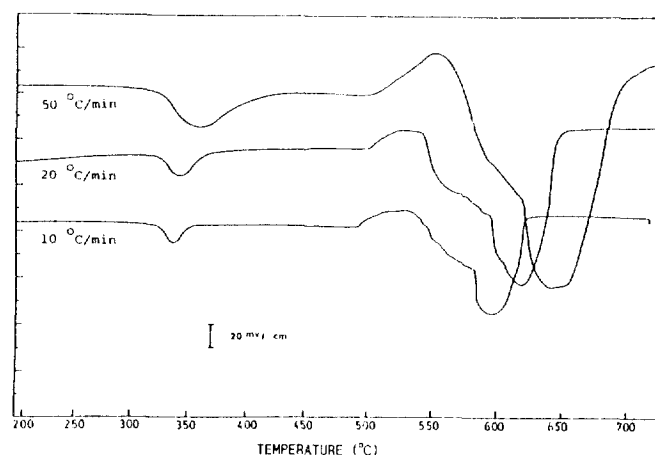**Fig. 4. Differential thermal analysis for PTFE.**

ture (564 C). The mole % of c-PFB varies along with the variation of decomposition rate. However, PFP rises to the maximum mole percent under the strong diffusion limitation condition. From these results we can conclude that PFP is influenced not by the secondary product obtained from TFE but by the diffusion limitation.

2. Curie-point Pyrolyser

The thermal degradation of PTFE was carried out using Curie-point pyrolyser. This technique was used to avoid the effect of secondary reaction because when the temperature reaches the secondary reaction condition it has a possibility that the TFE formed from the degradation could be converted into the PFP and c-PFB. The product distribution obtained from the PTFE degradation is shown in Table 1. Here, the conversion is explained in terms of weight fraction of PTFE degradation.

Buravtsev used the TFE monomer as a reactant to produce PFP and c-PFB products and reported that the production rates of PFP and c-PFB were 2nd and 2/3th order with respect to TFE concentration, respectively [Buravtsev et al., 1985]. He suggested that the production rate of PFP and c-PFB depended upon the concentration of TFE. This differs from our reaction in that no PTFE degradation occurs. If only TFE is produced from PTFE and the reaction of TFE follows Buravtsev's suggestion, then it is expected that the amount of c-PFB obtained from PTFE degradation is larger than that of PFP because the product rate of c-PFB is much faster when compared with that of PFP. However, the noticeable difference in our experiments is that the amount of PFP is much larger than that of c-PFB. These experimental results do not support the proposition of Buravtsev that the PFP and c-PFB are obtained from the secondary reaction of TFE. It shows that the products of PFP and c-PFB are not related to the initial sample weight or conversion. Therefore, it is important to note that the secondary reaction does not occur on the sample surface. It can be explained that the product gases of PTFE degradation is diffused out from the sample surface and that the diffusion rate of PFP is slower than that of TFE but much faster than that of c-PFB [Goldfarb et al., 1962]. Thus the concentration of PFP at the sample surface can be much larger than that of c-PFB.

An effort to obtain more information can be tried in this experiment. The product distribution was considered with various temperatures (Curie-points). At relatively low temperature (500 C) a small amount of TFE was produced. No other products were

found. On the other hand, at higher temperature (above 590 C) the main product was TFE with coproducts PFP and c-PFB. This is quite different from that obtained at 500 C. The production of TFE is predominated at low temperature. But the composition of TFE is not much changed as the temperature increases.

The conversion has some impact on the diffusion of the product gases. For example, the conversion of PTFE at 590 C was as low as 1% and it was considered that the diffusion of the product gases was restricted. Therefore, it has more possibility that the diffusion of PFP is much easier than that of c-PFB. However, when the conversion of degradation increases with the increase of temperature, it is explained that the diffusion limitation is partially restricted. So it is considered that in this condition the amount of c-PFB increases while the amount of PFP decreases. These results are in good agreement with our earlier results [Jun et al., 1995]. Even though the production of PFP was under diffusion limitation, the rate constant in our experiment is much larger than those reported in the literature.. This shows that the results are compatible with those obtained from DTA experiment (see below). It indicates that the bonding of C-F is readily broken to produce F transition product like PFP at high temperatures. It clearly shows that this phenomena occurs under diffusion limitation conditions.

3. Differential Thermal Analysis

The PTFE was analyzed by thermal analysis DTA to observe the behavior of the thermal degradation. DTA curves with various temperature program rates (10, 20, and 50C/min) are shown in Fig. 4. Each curve shows the heat adsorption peaks at near 336C because of its melting point. The melting points are little shifted to the higher temperature with the increase of heating rate. The figure shows that the real thermal degradation occurs at about 492C with a temporal minute exotherm in the beginning of degradation.

As expected the DTA curve irregularity at heating rate of 10 C/min is less than others (20 and 50C). Even though the heating rates are different, the pyrolysis curves are almost identical. In the beginning of degradation the curves represent the slow change which is attributed to the less progress of PTFE degradation whereas at little higher temperatures (above 580C) the curves show the rapid change which is attributed to the much active degradation. It can be expected that the weak bond of PTFE is dissociated at the beginning of degradation while the much strong

Table 2. Kinetic parameters of reactions (11), (12) and (13)

Reaction eq.	Preexponential term (1/mole sec) or (sec-1)	Activation energy (kcal/mole)	Temperature range (C).	Ref.
(11)	16.5×10^7	26.3	288-466	a
	10.3×10^7	25.4	300-590	b
	$10^{7.4}$	24.0	360-560	c
	$10^{8.07}$	25.6	300-455	d
	$10^{7.81}$	25.1	300-455	d
	$10^{8.36}$	26.5	300-455	d
	$10^{9.1}$	31.4	679-1027	e
(12)	8.9×10^{15}	74.1	300-590	b
	$10^{16.0}$	74.3	360-560	c
	2.1×10^{16}	74.3	767-927	f
	$10^{16.0}$	75.5	827-992	g
	$10^{17.0}$	79.4	697-1027	e
(13)	3.9×10^{16}	79.1	300-590	b

a) Lacher et al., 1952; b) Atkinson and Trenwith, 1953; c) Butler, 1962; d) Drennam and Matula, 1968; e) Buravtsev et al., 1985; f) Lifshitz et al., 1963; g) Simmie et al., 1969.
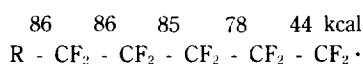
bond of PTFE such as C-F bond is dissociated through the further degradation at the higher temperatures.

4. Mechanistic Implication

The pyrolysis of PTFE has been studied for many years in terms of the unzipping mechanism. However, this is not so clear on the PFP product obtained from these experiments because it has three carbons and the carbon-carbon double bond. Many attempts were made to corroborate and expand the unzipping mechanism.

Goldfarb reported that the reactions occurring during the initial stage involve the scission of the polymer chain and then the large molecules proceed further to smaller molecules which is readily diffused out from the sample surface [Goldfarb et al., 1962]. He mentioned that the pyrolysis of PTFE somewhat involved in the breaking and making of C-F bond. Thus the chain transfer reaction could be a relative importance to understand a detailed mechanism.

Our experimental results have also revealed that the production of PFP could not be explained by unzipping mechanism only. The production of PFP was maximized at strong diffusion limitation region, while that of c-PFB was maximized at quite different condition. In order to gather sufficient evidence and to elaborate further on the degradation, we can generally invoke the radical formation of CF_2 that reacts with another radical or other monomers. According to Errede, CF_2 radical was produced from the pyrolysis of PTFE because it has less bond dissociation energy (44 kcal) in the radical chain and then reacted to produce TFE, PFP and c-PFB [Errede, 1962]. The CF_2 radical is known to be a relatively stable intermediate because of its long lifetime (about 1 sec) [Laird et al., 1950]. He reported that C-C bond dissociation energy of PTFE degradation was 86 kcal/mol and it could be calculated by the bond dissociation energy equation based on radical:

86   86   85   78   44 kcal
R - CF_2 - CF_2 - CF_2 - CF_2 - CF_2 ·

Atkinson et al. reported that at lower temperatures (below 550 °C) TFE produces only c-PFB, whereas at higher temperatures (above 550°C) TFE produces both PFP and c-PFB [Atkinson and

Trenwith, 1953; Atkinson and Atkinson, 1957]. He suggested that the results were explained in terms of the following simplified mechanism:

$$2C_2F_4 \rightarrow C_4F_8 \tag{11}$$

$$C_4F_8 \rightarrow 2C_2F_4 \tag{12}$$

$$C_4F_8 \rightarrow C_3F_6 + :CF_2 \tag{13}$$

$$:CF_2 + C_2F_4 \rightarrow C_3F_6 \tag{14}$$

$$C_3F_6 \rightarrow C_2F_4 + :CF_2 \tag{15}$$

The reaction orders for Eqs. (11) and (12) are second and first, respectively. The reaction parameters for these reactions have been demonstrated by several groups and are given in Table 2. It also supports that the c-PFB is regarded as secondary product formed from TFE.

From our results, the following reaction sequence can be suggested. Initially the degradation undergoes the random scission of the polymer chain to give the formation of radical chain. The radical chain generated may induce smaller radicals such as CF_2 due to the low bond dissociation energy. Then, the CF_2 radical intermediates as reactive species react with another radical or a monomer molecule to form a new radical chain or monomer size products (TFE, PFP, c-PFB). An alternative fate of generated radicals might be an attack on C-F bond in a chain reaction leading to the formation of another radical chains involving $CF_2 = CF-CF_2-$ R. However, it is expected that the radical of CF_2 under the diffusion limitation conditions is captured inside the pore for little longer time and then initiates further radical reaction leading to the more production of PFP. It can be explained that the vacuum pyrolysis of thin samples of PTFE caused mostly tetrafluoroethylene because the radicals are readily diffused out from the sample surface. Thus, the product distribution can be understood on the basis of the CF_2 radical reaction in addition to the unzipping chain transfer reaction.

CONCLUSION

This study suggests that PFP is produced not from the secondary reaction of TFE, but from the CF_2 radical and the chain transfer reaction of PTFE thermal degradation. Our results also reveal that the product distribution is influenced by the gaseous pyrolysis products held inside the sample pores and that the increase of PFP product is strongly related to the diffusion limitation of the gaseous product. From these results, it is expected that the thermal degradation of PTFE at atmosphere pressure can be explained in terms of the involvement of reactions generating radicals in addition to the unzipping chain transfer mechanism.

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