

Thermal Degradation of the Polyimide Synthesized From 4,4'-(Hexafluoroisopropylidene) Diphthalic Dianhydride and 4,4'-Diaminodiphenylmethane

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ABSTRACT: The thermal degradation of polyimide PIF2 synthesized from 4,4'-(hexafluoroisopropylidene) diphthalic dianhydride and 4,4'-diaminodiphenylmethane was systematically and thoroughly investigated by high-resolution pyrolysis gas chromatography/mass spectrometry, thermogravimetric analysis, and Fourier transform infrared spectroscopy. The pyrolyzates of PIF2 were dependent on the pyrolysis temperature. Two weight-loss peaks were observed in the derivative thermogravimetric analysis of PIF2 and the first peak was related to the fluorine-containing

segment (hexafluoroisopropylidene). The overall activation energy and preexponential factor were calculated through dynamic TGA with Ozawa's method. Based on the results, a thermal degradation mechanism of the PIF2 was proposed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2295–2301, 2004

Key words: 4,4'-(hexafluoroisopropylidene) diphthalic dianhydride; 4,4'-diaminodiphenylmethane; polyimide; pyrolysis gas chromatography/mass spectrometry; thermal degradation

INTRODUCTION

Polyimide has been intensively studied since the 1960s because of its good thermal stability. Thermogravimetry analysis (TGA) is one of the major characterization techniques for such a study; the samples were mostly commercial polyimide products such as Kapton film.¹ Polyimides are increasingly used in the electronic and telecommunication industry. However, the commercially available polyimides contain some disadvantages, such as low optical transparency and high dielectric constant. Considerable attention had been drawn to the synthesis and application of fluorine-containing polyimides because of their unique properties. Hence, the incorporation of fluorine groups, such as hexafluoroisopropylidene moieties, into the polyimide structures has been explored extensively in past decades.^{3–9} However, their thermal degradation mechanisms have been investigated less often. A fluorine-containing polyimide PIF2 was synthesized from 4,4'-(hexafluoroisopropylidene) diphthalic dianhydride and 4,4'-diaminodiphenylmethane in our lab.

In this study, the thermal degradation mechanism of PIF2 was investigated by using TGA, FTIR, and high-resolution pyrolysis gas chromatography/mass spectrometry (HRPy-GC/MS), which is the most efficient and direct technique to study thermal degradation of polymers.¹⁰

EXPERIMENTAL

Materials

The chemical structures of PIF1 and PIF2 are shown in Figure 1. Pyromellitic dianhydride (PMDA, Shanghai Chemical Reagents) was sublimed before use. 4,4'-(Hexafluoroisopropylidene) diphthalic dianhydride (6FDA), 4,4'-diaminodiphenylmethane (DDM, Aldrich Chemical Co.), and *N*-methyl-2-pyrrolidinone (NMP, BASF Co.) were used as received. The poly(amic acids) (PA) and the polyimide films were prepared by the technique described in ref. 11.

Characterization

The pyrolysis was carried out with a JHP-3S Curie Point pyrolyzer (Japan Analytical Industry Co., Ltd.) interfaced with a Hewlett–Packard 6890 gas chromatograph system with 30 m × 0.25 mm HP-5 capillary column, which was held at 50°C for 2 min and heated up to 280°C with a ramp of 5°C/min. The 0.15–0.25

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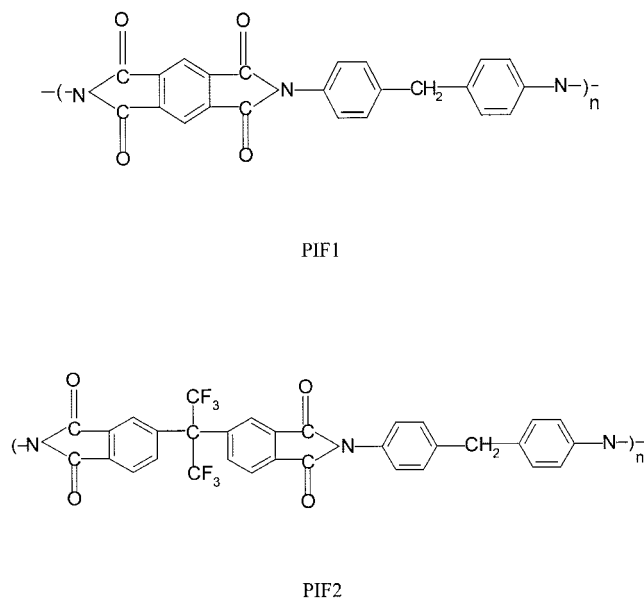


Figure 1 The chemical structures of PIF1 and PIF2.

mg sample was pyrolyzed at 590, 670, 740, and 920°C, respectively, for 5 s at a column rate of 1 ml/min and a split ratio of 50 : 1 in a helium atmosphere. The pyrolysates were identified by using an HP 5973 quadruple mass spectrometer with an electron impact ion source at 70 eV attached to the gas chromatography system.

TGA and derivative thermogravimetric analysis (DTG) were carried out on a TGA 2050 thermal analyzer (TA Co.) in a dry nitrogen atmosphere at a flow rate of 80 ml/min. The dynamic TGA measurements were made at different heating rates of 5, 20, 30, and 50°C/min. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet 760 FTIR (Nicolet Co.).

RESULTS AND DISCUSSION

DTG in Figure 2 showed that PIF2 had two weight-loss peaks, whereas PIF1 exhibited only one weight-loss peak. They should have different thermal degradation mechanisms. It is believed that the first weight-loss peak in DTG of PIF2, which ranges from 485.42 to 621.23°C, was associated with fluorine. To systematically study the thermal degradation mechanism of PIF2, HRPy-GC/MS was used. The total ion chromatograms (TIC) of the PIF1 and PIF2 pyrolysis at 740°C were shown in Figure 3. Their pyrolysates were listed in Table I and the chemical structure of each pyrolysate was shown in Figure 4. The pyrolysates of PIF2 are different from the pyrolysates of PIF1. Some pyrolysates such as aniline, *p*-aminotoluene, 9-phenyl-9H-fluorene, and [1,1'-biphenyl]-4,4'-dicarbonitrile could be found in the pyrolysates of PIF1, while they could not be found in the pyrolysates of PIF2. It was found that the fluorine-containing pyrolysates were

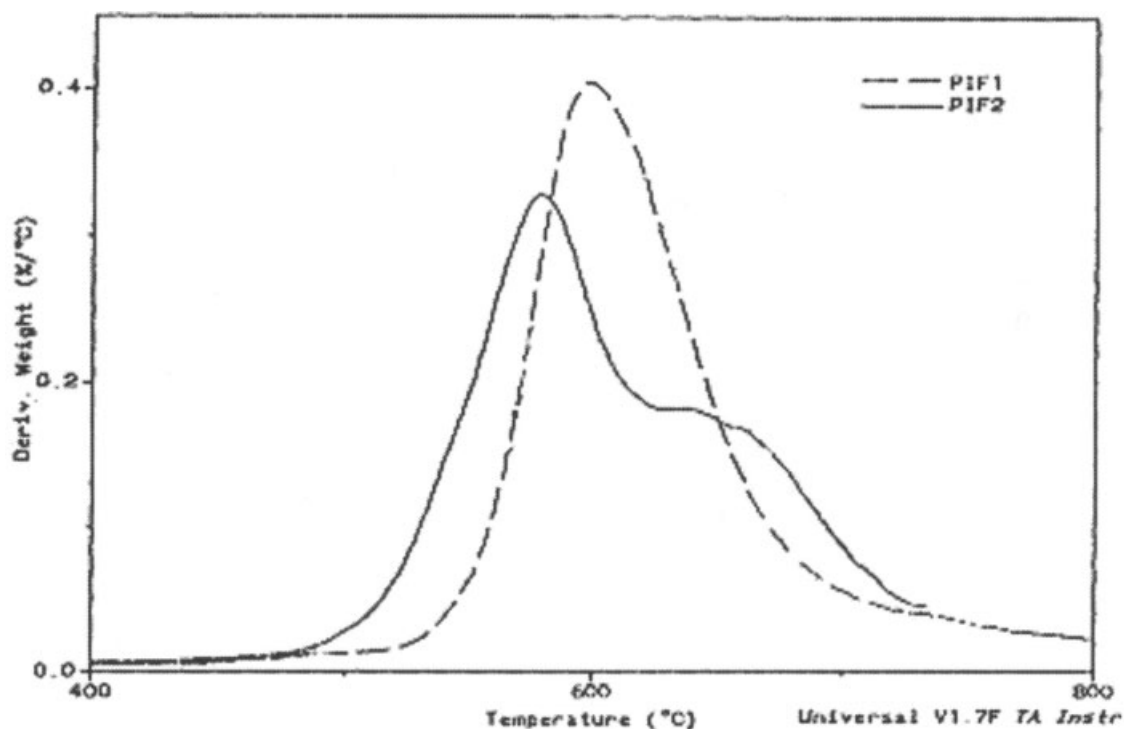


Figure 2 DTG of PIF1 and PIF2.

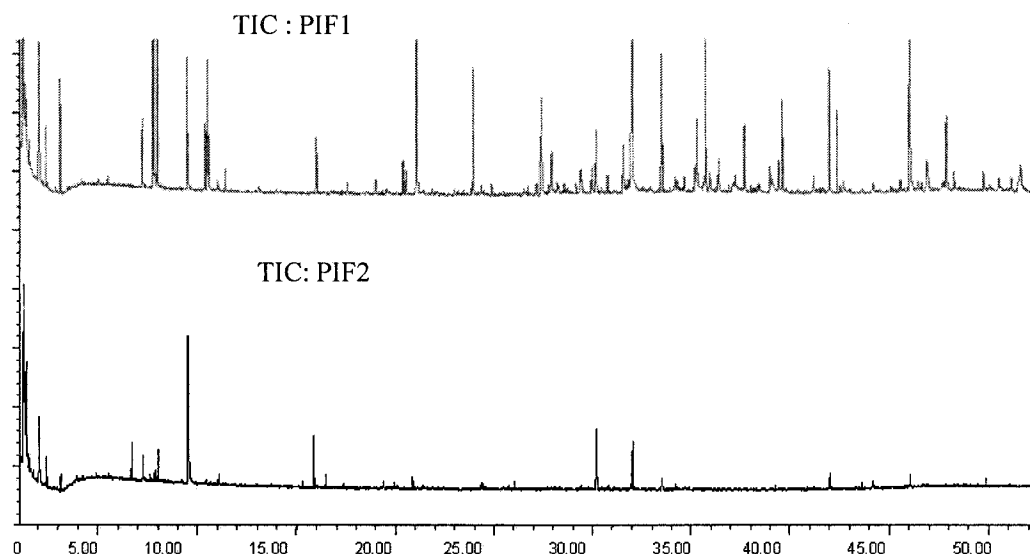


Figure 3 TIC pyrograms of PIF1 and PIF2 at 740°C.

HCF_3 and $\text{C}_6\text{H}_5\text{CF}_3$. In general, it can be proposed that there are three classes of pyrolysates in Table I. The first class of pyrolysates is low boiling-point products such as CO , CO_2 , and HCF_3 . The second class of pyrolysates, which is directly formed from the polymer backbone, has the characteristic structure of the main chain, such as compounds 13, 14, 16, and 18 in Figure 4. The third class is formed through the rearrangement reaction or cyclization reaction such as compound 15 in Figure 4. Multistep pyrolysis was used to clearly study the thermal degradation process and the two weight-loss peaks of DTG of PIF2. The sample was first pyrolyzed at 590°C for 5 s. Subsequently, the residue of the pyrolysis was gathered and pyrolyzed at 920°C for 5 s. Their TICs are shown in Fig. 5. HCF_3 and $\text{C}_6\text{H}_5\text{CF}_3$ were found in the first pyrolysis at 590°C. Their MS spectra are shown in Figures 6 and 7. However, they were not found in the

pyrolysis of the residue at 920°C. It indicates that the C—C bond of the $\text{CF}_3\text{—C—CF}_3$ in PIF2 should be broken in the first pyrolysis. In addition, it was found that the pyrolyses at 670, 740, and 920°C are the same, although different from the pyrolysis at 590°C. The pyrolysis of PIF2 is dependent on the pyrolysis temperature.

A fragment TGA was employed to further investigate the thermal degradation mechanism of PIF2. TGA was performed from 30 to 580°C with a ramp of 50°C/min when the first weight-loss peak of the DTG curve disappeared and the second still had not appeared. The PIF2 residue after being heated at 580°C was characterized by HRPy-GC/MS and FTIR. The fluorine-containing pyrolysates, HCF_3 and $\text{C}_6\text{H}_5\text{CF}_3$, cannot be found in pyrolysis of PIF2 residue. FTIR spectra of PIF2 and the PIF2 residue were shown in Figure 8. The peaks at 1255 and 980 cm^{-1} are attributed to the C—F bond in PIF2 spectrum. It was found that they disappeared from the FTIR spectrum of the PIF2 residue. Hence, it was verified that the first weight-loss peak in the DTG curve was associated with the fluorine because of the weaker bond energy of the C—C bond in $\text{CF}_3\text{—C—CF}_3$. The strong electron affinity of fluorine could result in the weaker bond energy of the C—C bond in $\text{CF}_3\text{—C—CF}_3$.

In addition, the thermal degradation data of PIF2 were studied by using dynamic TGA with Ozawa's method. The overall activation energy (E) and preexponential factor (A) were 249.23 kJ/mol and $4.226 \times 10^{15} \text{ min}^{-1}$, respectively. Based on all of the information, the thermal degradation mechanism of PIF2 pyrolysis at 740°C was proposed in Figure 9.

TABLE I
Pyrolysates of PIF1 and PIF2 at 740°C

No.	m/z	PIF2	PIF1	No.	m/z	PIF2	PIF1
1	28	+	+	11	117	+	+
	44	+	+				
	70	+	—				
2	78	+	+	12	128	+	+
3	146	+	—	13	168	+	+
4	92	+	+	14	147	+	+
5	104	+	+	15	166	+	+
6	119	+	+	16	223	+	+
7	93	—	+	17	242	—	+
8	103	+	+	18	237	+	+
9	133	+	+	19	204	—	+
10	107	—	+				

+, Observed; —, not observed.

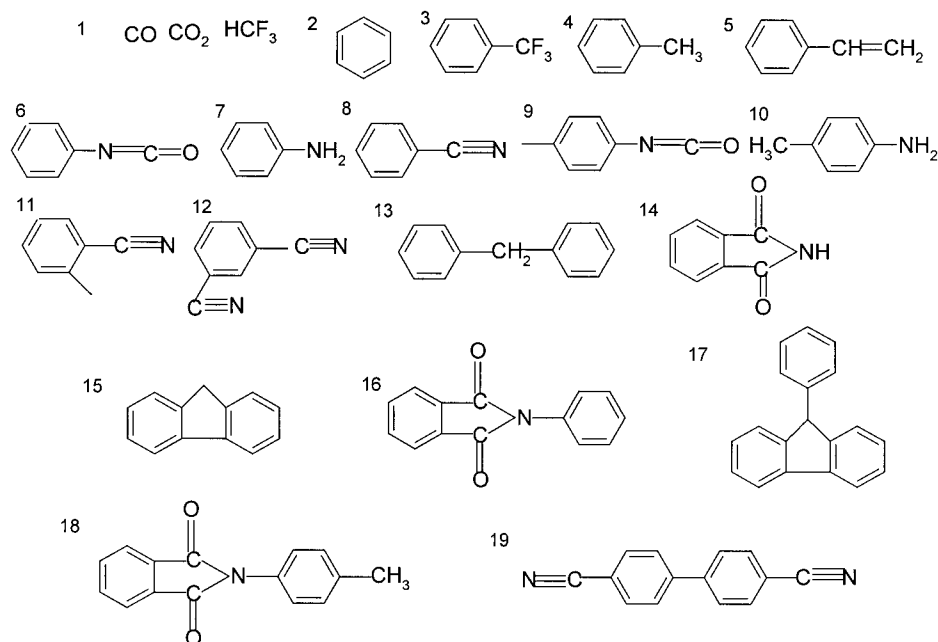


Figure 4 The chemical structures of pyrolysates in Table I.

CONCLUSIONS

The thermal degradation mechanism and kinetics of PIF2 were studied by HRPyGC/MS, TGA, and DTG.

There are two weight-loss peaks in the DTG of PIF2. The C—C bond of $\text{CF}_3\text{—C—CF}_3$ in PIF2 was broken during the first weight-loss peak because of the

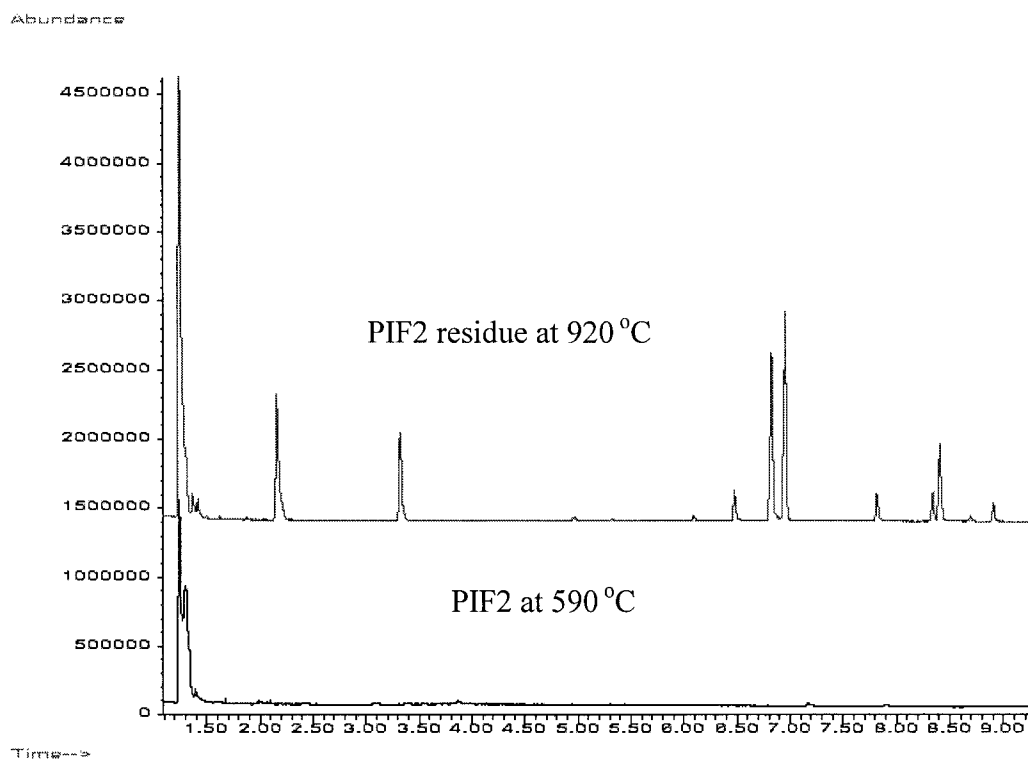


Figure 5 TICs of the PIF2 pyrolysed at 590°C and the PIF2 residue pyrolysed at 920°C.

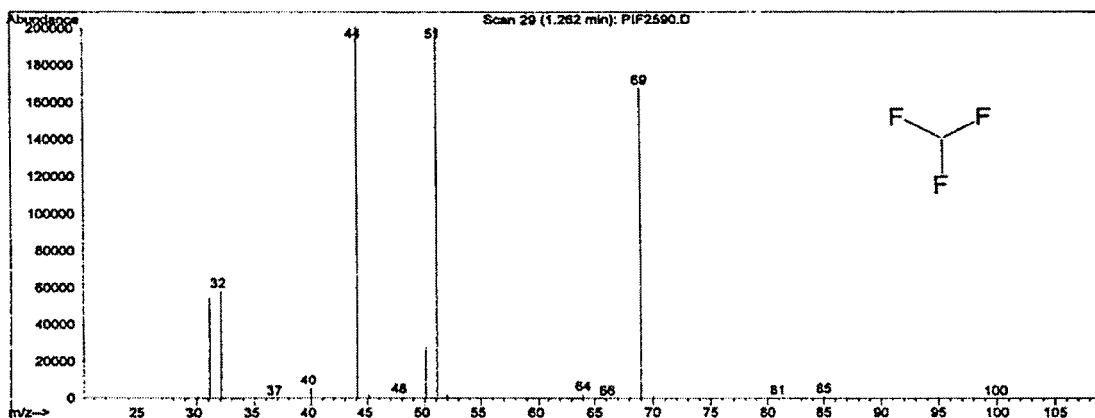


Figure 6 1.26 min MS of PIF2 pyrolysed at 590°C.

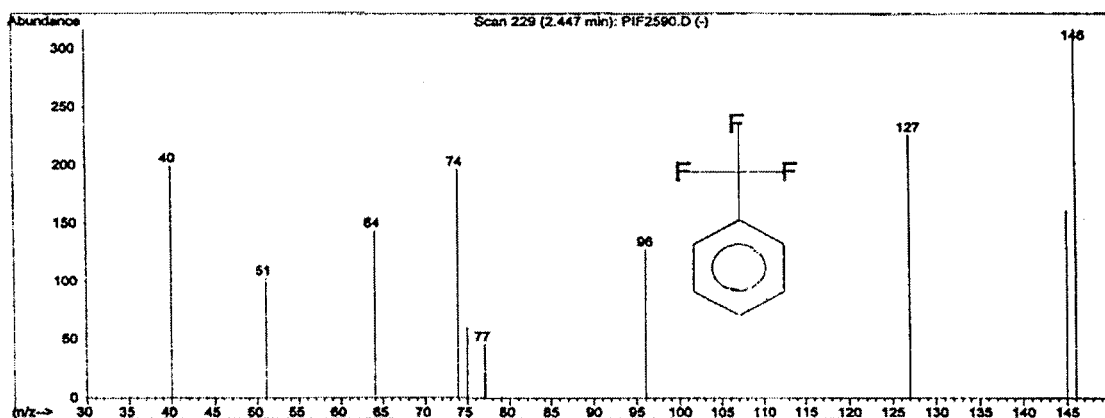


Figure 7 2.45 min MS of PIF2 pyrolysed at 590°C.

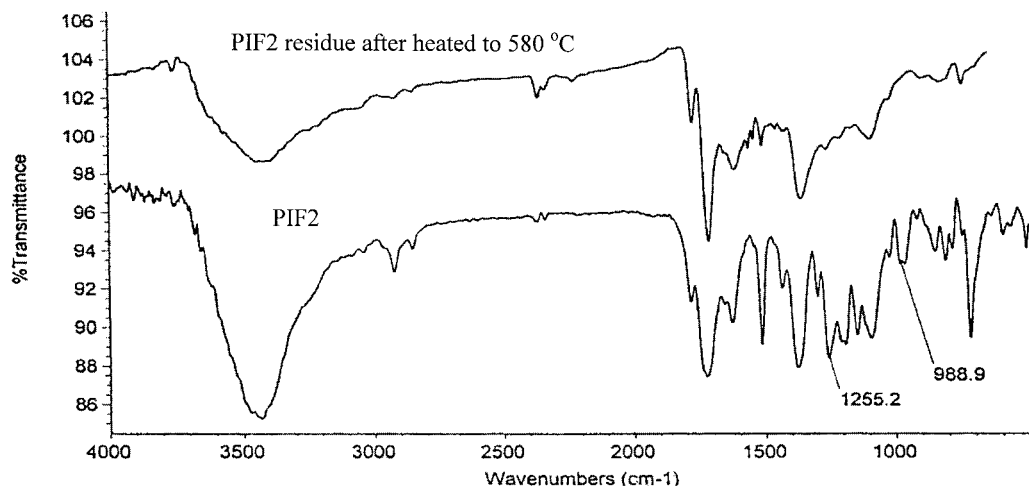


Figure 8 FTIR spectra of PIF2 and PIF2 residue after heated to 580°C.

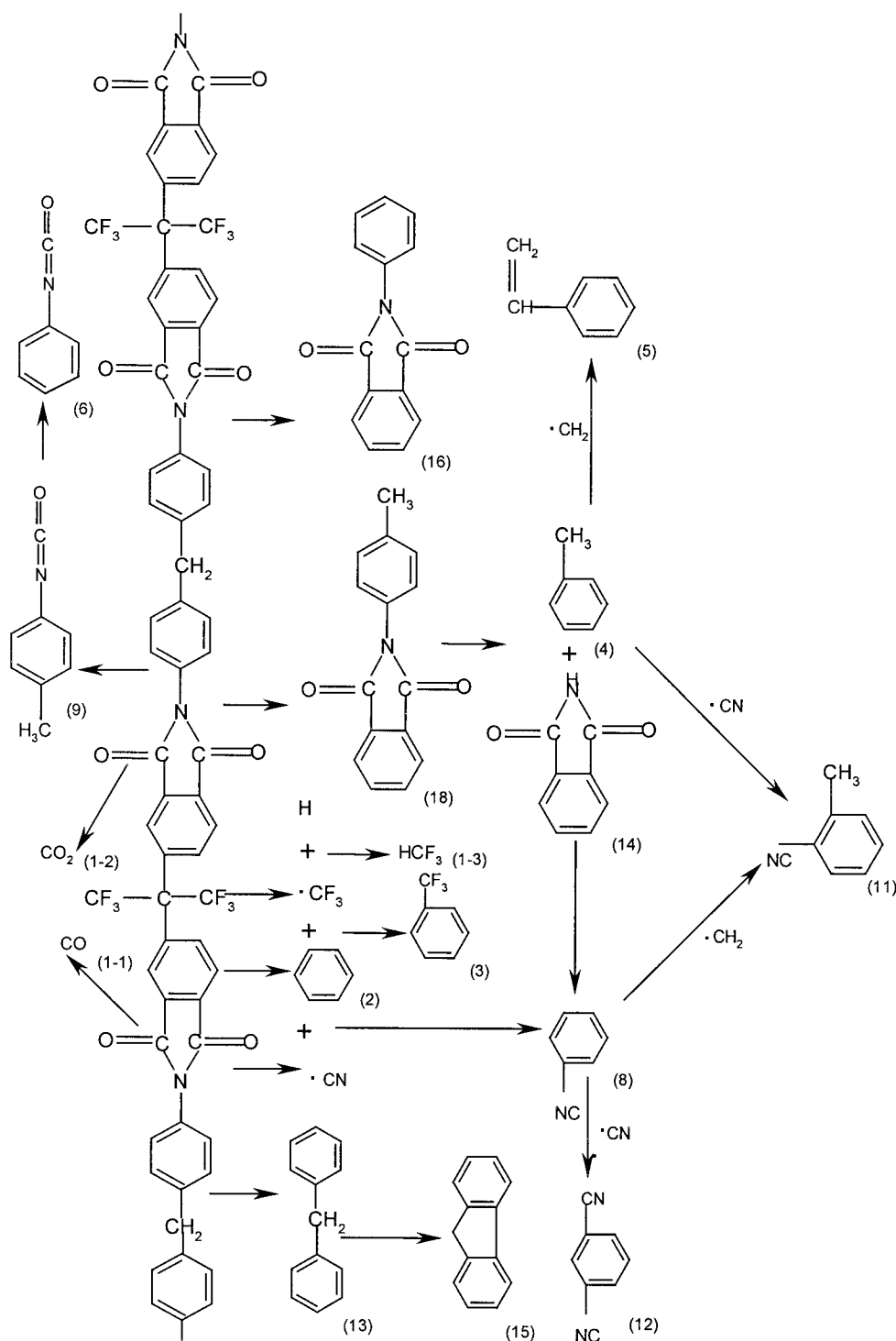


Figure 9 Degradation mechanism.

weaker bond energy of the C—C bond in $\text{CF}_3\text{—C—CF}_3$. The strong electron affinity of fluorine might result in a weaker C—C bond in $\text{CF}_3\text{—C—CF}_3$. The pyrolyzates of PIF2 depend on pyrolysis temperature.

The overall activation energy and preexponential factor were obtained by using dynamic TGA with Ozawa's method. A thermal degradation mechanism of PIF2 was proposed.

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