

# Transparent carbon–fluorine compounds prepared by the heat treatment of pitch fluoride under a fluorine atmosphere

Hiroyuki Fujimoto, Masaaki Yoshikawa, Akihiro Mabuchi and Toshiyuki Maeda

Research & Development Center, Osaka Gas Co., Ltd., 6-19-9, Torishima Konohana-ku Osaka 554 (Japan)

## Abstract

Pitch fluoride prepared from mesophase pitch at 70 °C was heat treated in a fluorine atmosphere over the temperature range from 200 to 400 °C. The compounds obtained were a colorless transparent solid with a composition between  $\text{CF}_{1.38}$  and  $\text{CF}_{1.50}$ , and a liquid fluorocarbon which was colorless and transparent. The yields of both compounds depended on the heat-treatment temperature. From 200 to 280 °C, the solid compound was obtained as the main product, together with the liquid fluorocarbon as a by-product. Above 280 °C, the liquid compound was the main product and the solid the by-product. The liquid compound was selectively obtained at 400 °C. These compounds are composed of chair-type condensed cyclohexane rings with  $\text{CF}_2$ ,  $\text{CF}_3\text{CF}_2^-$  and  $\text{CF}_3\text{CF}^-$  groups in the periphery of the rings. The difference between these compounds is mainly in their molecular weights.

## Introduction

Recently, we have reported that mesophase pitch reacts smoothly with elemental fluorine between 50 and 130 °C to give pitch fluoride with a composition between  $\text{CF}_{1.30}$  and  $\text{CF}_{1.59}$  [1, 2]. This compound has a similar structure to graphite fluoride,  $(\text{CF})_n$ , as shown in Fig. 1. The fluorine atoms bond to each carbon from above and below the carbon network to form chair-type condensed cyclohexane rings and these rings are cross-linked by perfluorocarbon bridges. This fluorination reaction is basically caused by the addition of fluorine to carbon double bonds and the displacement of hydrogen by fluorine according to the equation:



However, the addition and displacement of fluorine is such an exothermic reaction that it is accompanied by a ring-opening reaction and cleavage of the methylene bridges, the relative amounts of which are affected by the fluorination temperature. Therefore, in order to restrict the ring-opening reaction, fluorination must be carried out at relatively low temperatures, for instance, 50 to 70 °C.

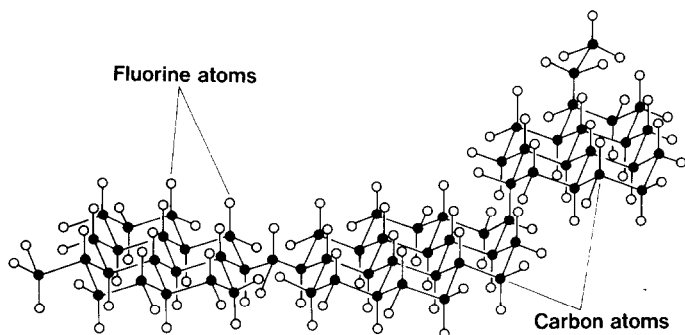


Fig. 1. Average structure of pitch fluoride.

On the other hand, it should be noted that pitch fluoride is not formed fully perfluorinated at temperatures lower than 70 °C because of the insufficient diffusion energy of the fluorine atoms. As a result, unreacted carbon atoms remain in the bulk in the form of double-bonded carbon. Therefore, the color of the pitch fluoride is not white like graphite fluoride,  $(CF)_n$ , but yellowish white.

In this study, pitch fluoride prepared at relatively low temperatures was heat treated at 200 to 400 °C in a fluorine atmosphere in order to attempt to prepare the perfluorinated compound.

## Experimental

### *Preparation of mesophase pitch*

The preparation of mesophase pitch was carried out by the conventional procedure, as described elsewhere [1].

### *Preparation of pitch fluoride and its heat treatment in a fluorine atmosphere*

First, it is necessary to prepare the pitch fluoride which is to be heat treated under a fluorine atmosphere. However, in this study, the heat treatment was carried out immediately after the preparation of the pitch fluoride, according to the following method.

Mesophase pitch with a composition as shown in Table 1 was placed in a nickel boat, which was then hung in the middle of a vertical nickel reaction vessel. The inside of the reaction vessel was evacuated and filled with argon until the internal pressure reached atmospheric pressure. Thereafter, fluorine gas was passed into the reaction vessel for 10 h at a flow rate of 6 ml/min, while the temperature in the reaction vessel was maintained at 70 °C (first step). Secondly, the sample inside the vessel was heated up to a selected temperature between 200 and 400 °C at a rate of 1 °C/min, and this temperature was then maintained for 12 h (second step). A transparent solid fluorocarbon (S-type) and a liquid fluorocarbon (L-type) were thus obtained. Both the obtained compounds were subjected

TABLE 1

Physical and chemical properties of mesophase pitch used as a starting material

C content (wt%)	H content (wt%)	N content (wt%)	H/C	BI <sup>a</sup> (wt%)	QI <sup>b</sup> (wt%)	ST <sup>c</sup> °C
95.08	3.88	0.75	0.49	93.87	17.94	303

<sup>a</sup>Amount of benzene-insoluble material in pitch.<sup>b</sup>Amount of quinoline-insoluble material in pitch.<sup>c</sup>Softening point.

TABLE 2

Heat treatment conditions for pitch fluoride under an F<sub>2</sub> atmosphere

Heat-treatment temperature (°C)	Yields <sup>a</sup>		F/C atomic ratio	
	S-type (%)	L-type (%)	S-type	L-type
210	214.8	19.1	1.38	1.62
250	98.6	59.2	1.39	1.56
300	56.0	102.8	1.45	1.67
350	25.0	147.8	1.51	1.85
400	0.0	163.9	---	1.79

$$^a\text{Yield} = \frac{\text{Weight of product}}{\text{Weight of pristine pitch}}$$

to various analyses. The results of the heat treatment of pitch fluoride are summarized in Table 2.

### *Analyses of the fluorinated products*

Elemental analyses were carried out by the traditional oxygen flask method. X-ray diffraction measurements were carried out with a JEOL diffractometer (DX-GO-S). Differential thermal analyses and thermal gravimetry (TG) were carried out with a Shimadzu DT-40 in an argon atmosphere. <sup>19</sup>F NMR spectra were measured by a JNM-GX270 (JEOL, Japan) at 254.3 MHz using hexafluorobenzene as solvent, and the CF<sub>3</sub> group of benzotrifluoride was taken as a standard sample for chemical shifts (0 ppm).

## Results

### *Effects of the heat treatment of pitch fluoride on the yields of S-type and L-type fluorocarbons*

Heat treatment of pitch fluoride yielded two kinds of fluorocarbons, an S-type and an L-type. The former was a solid colorless and transparent

fluorocarbon, and the latter was a liquid fluorocarbon, also colorless and transparent. The L-type was a viscous fluid containing some volatile materials. Therefore, the viscosity gradually became higher when it was kept for a few weeks in an air atmosphere, even at ambient temperature. The S-type compound was obtained in the nickel boat hung in the heating zone, while the liquid fluorocarbon was obtained at the bottom of the vertical reaction vessel which was cooled down by water. Therefore, it is likely that the liquid fluorocarbon is formed by vaporization of some component contained in pitch fluoride, or by a decomposition reaction during the heat treatment of pitch fluoride.

The yields of these compounds depend on the heat-treatment temperature. In Fig. 2, the yields of the S-type and L-type fluorocarbons are plotted as a function of the heat-treatment temperature of pitch fluoride. The yield of the S-type fluorocarbon decreases with an increase in the heat-treatment temperature and, finally, at 400 °C it is not obtained at all. On the other hand, the yield of the L-type increases with an increase in temperature and it is selectively obtained at 400 °C.

The heating rate of the furnace for the heat treatment was programmed within  $\pm 0.5$  °C up to the heat-treatment temperature. However, the observed heating pattern indicated a small exothermic peak at around 130 °C. It is thought that the pitch fluoride formed in the first-step process decomposed exothermically or was attacked by fluorine ions.

#### *X-ray diffraction measurements*

Figure 3 shows the X-ray diffraction pattern of the S-type compound, together with the original pitch fluoride prepared at 70 °C. There was no remarkable change in the pattern before and after heat treatment, except

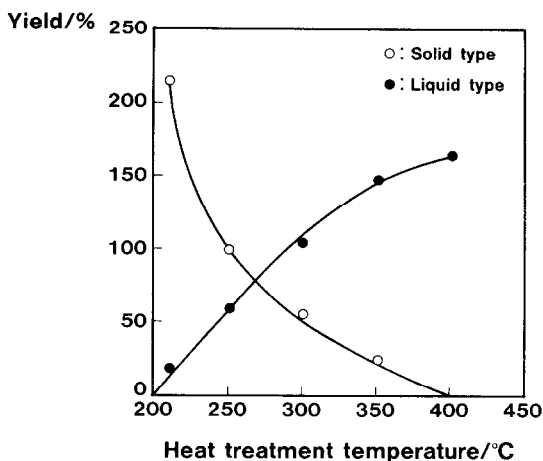


Fig. 2. Yields of the S-type and L-type fluorocarbons as a function of the heat-treatment temperature.

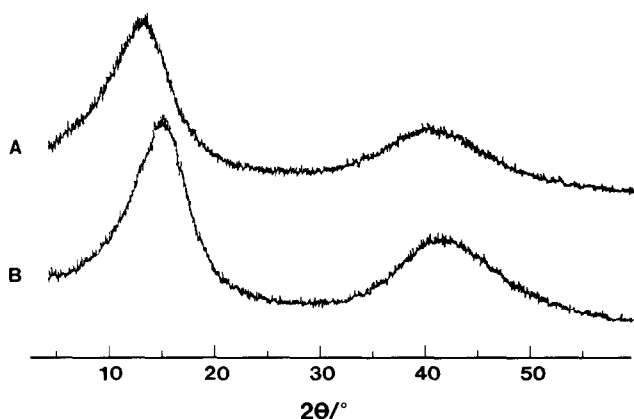


Fig 3 X-ray diffraction patterns (A) original pitch fluoride, (B) S-type fluorocarbon

that the main peak at around  $13^\circ$  shifted slightly to a higher angle and the peaks became sharper. It is concluded that the basic structure of the S-type compound is similar to that of the original pitch fluoride.

#### *$^{19}\text{F}$ NMR spectra of S-type and L-type compounds*

Figure 4 shows the  $^{19}\text{F}$  NMR spectra of S-type and L-type compounds prepared by heat treatment at  $210^\circ\text{C}$ , together with the original pitch fluoride. Figures 4A and 4B show the spectra of the L-type and S-type, respectively. Both the solid and liquid compounds have basically the same

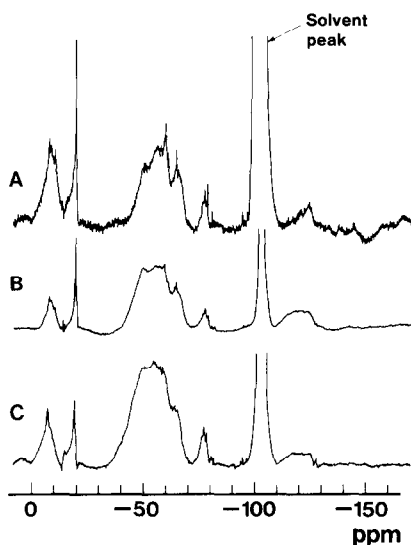


Fig 4  $^{19}\text{F}$  NMR spectra (A) L-type compound; (B) S-type compound, (C) original pitch fluoride.

peaks as the pitch fluoride prepared at 70 °C. Consequently, the fundamental structures are almost the same as that of the original pitch fluoride. The most noticeable point is that the peak centered at -18 ppm (which is assigned to a  $\text{CF}_3\text{CF}_2-$  group) of the S-type and L-type compounds is more intense than in the original pitch fluoride. This functional group can only be formed by ring-opening of the cyclohexane ring in pitch fluoride. Accordingly, the formation of S- and L-type compounds is considered to be caused by the ring-opening reaction and the cleavage of C-C bonds. Almost the same results were obtained for samples prepared at temperatures higher than 210 °C.

#### *Chemical compositions and molecular weights of the S-type and L-type compounds*

As the relative amount of the  $\text{CF}_3\text{CF}_2-$  group is increased by the ring-opening reaction during heat treatment, it is expected that the F/C atomic ratio of both S and L compounds would be higher than that of the original pitch fluoride. Table 2 shows the results of the elemental analyses of the resulting compounds. The F/C atomic ratio of the solid S increases up to 1.50 with increasing heat-treatment temperature. This is consistent with an increase in the number of  $\text{CF}_3\text{CF}_2-$  groups during perfluorination of the pitch fluoride. On the other hand, for the L-type, such a relationship between F/C and temperature was not observed. This is presumably due to the vaporization of volatile materials contained in the L-type compound. Therefore, the atomic ratios measured were for the residual non-volatile L-type compound. Molecular weights were measured for the S-type compound heat treated at 210 °C and the L-type compound heat treated at 400 °C and were found to be 2070 and 850, respectively. Considering that the molecular weight of the original pitch fluoride is about 2700 [3], it is obvious that the pitch fluoride was excessively fluorinated and decomposed by the heat treatment accompanying the ring-opening reaction, the cleavage of the C-C bonds and the addition of fluorine atoms to double bonds which remain in the bulk of pitch fluoride.

#### *Thermal behavior of the S-type compound*

Heat treatment of pitch fluoride improved the thermal stability of the S-type compound. Figure 5 shows the TG curves of the S-type compound heat treated at 300 °C (A) and the original pitch fluoride prepared at 70 °C (B). The pitch fluoride began to decompose exothermically at around 180 °C, while the S-type compound was stable up to almost 300 °C.

## **Discussion**

Based on the results of elemental analyses, molecular weights and the structure of the original pitch fluoride, the average structure of the liquid fluorocarbon is concluded to be as shown in Fig. 6. The fluorine

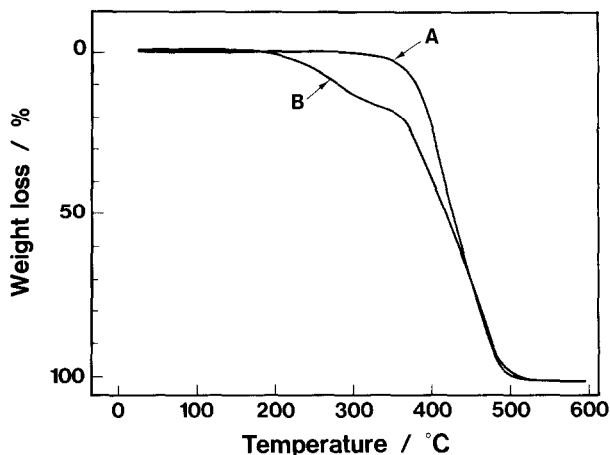


Fig 5 TG curves: (A) S-type compound heat treated at 300 °C, (B) original pitch fluoride.

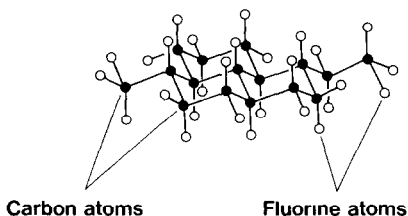


Fig 6 Average structure of the liquid fluorocarbon

atoms bond to the carbon atoms from above to below the carbon ring network to form two or three condensed cyclohexane rings, and the periphery of the network consists of  $\text{CF}_2$ ,  $\text{CF}_3\text{CF}_2^-$ ,  $\text{CF}_3\text{CF}^-$  groups, etc. The S-type structure is similar, and the difference between the compounds is mainly due to their molecular weights. Accordingly, the S-type compound either has a structure such that the condensed cyclohexane rings are cross-linked by perfluorocarbon bridges, or it has more cyclohexane rings than the L-type compound. Considering the structural similarity of these compounds to the original pitch fluoride, the condensed rings would be chair-type.

## References

- 1 H. Fujimoto, A Mabuchi, T Maeda, Y Matsumura, H Touhara and N Watanabe, *Carbon*, submitted for publication
- 2 T Maeda, H Fujimoto, M Yoshikawa, N Watanabe and H Touhara, *J Fluorine Chem*, 54 (1991) 40
- 3 H Fujimoto, T Maeda, M. Yoshikawa and N Watanabe, *J. Fluorine Chem*, in press