

# Polymerization of Chlorofluorocarbon-22 and Acetonitrile

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**ABSTRACT:** Chlorofluorocarbon-22 (HCClF<sub>2</sub>) gas can react with acetonitrile to form a halogen-free carbon-based polymer when solid potassium hydroxide particles are present. The reaction can be carried out under normal pressure and at room temperature. The polymer is powdery and amorphous. The structure of the polymer has been studied by elemental analysis, Fourier transform IR, Raman, and mass spectroscopies. The results demonstrate that the polymer has a carbonic backbone. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 116–120, 2001

**Key words:** polymerization; chlorofluorocarbon; acetonitrile; potassium hydroxide

## INTRODUCTION

Destruction of chlorofluorocarbons (CFCs) is important in view of environmental protection, because these compounds can release chlorine atoms under high-energy UV photolysis and lead to the depletion of the ozone layer.<sup>1</sup> However, CFCs are among the most inert compounds known, mainly because of the great strength of the carbon–fluorine bond and the high electronegativity of fluorine.<sup>2</sup> Very few reactions of fluorocarbons have been discovered; most involve the more reactive fluoroarenes.<sup>3</sup> However, none of these reactions are applicable to the destruction of CFCs under moderate conditions.

This report describes the novel condensation polymerization reaction of CFC-22 and acetonitrile (AN) at room temperature and normal pressure. The reaction is carried out in the presence of

solid particles of potassium hydroxide (KOH). The product is a halogen-free amorphous carbon-based polymer. This finding develops a new aspect of CFC chemistry and may provide a new technique for disposing of CFCs.

## EXPERIMENTAL

### Materials

Analytical grade AN and solid potassium hydroxide (>85% by weight) were purchased from Nanjing Chemical Factory. The AN was used after distillation. The KOH was dried at 100°C under a vacuum for 24 h and then ground into particles with diameters smaller than ~1 mm. The CFC-22 (Freon-22) was a product of Mitsubishi Company. It was sealed in a steel can and used without further treatment.

### Polymerization

The polymerization was performed by introducing CFC-22 gas into a packed column (1-cm diameter

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and 10-cm length) of solid KOH particles (10 g) mixed with 0.5 g of AN. During the reaction process, one end of the column was connected to the freon can and the another end was sealed for to avoid the escape of AN. A light overpressure of CFC-22 was maintained in the system by controlling the flowing rate of the freon gas. The reaction temperature was controlled at 25–30°C by cycling water surrounding the column and the system was stirred by vibration. Every 3 h the column was weighed to measure the amount of reacted CFC-22. The reaction was stopped when no apparent weight increment was found. The total time of reaction was about 18 h. The freon reacted immediately with the AN in the presence of solid KOH. The surface of the base became brown initially and then gradually changed into dark brown. After the reaction, the solid reaction mixture was put into a large amount of water to dissolve the excess base and the salts formed during the reaction process. The product dispersed well in the strong alkaline medium and only part of the product was deposited in several days. Therefore, the solution was neutralized with 6 mol/L aqueous HCl to accelerate the deposition. The rough product as black particles was filtrated and washed with distilled water. The clean product was dried at 200°C under a vacuum for 24 h.

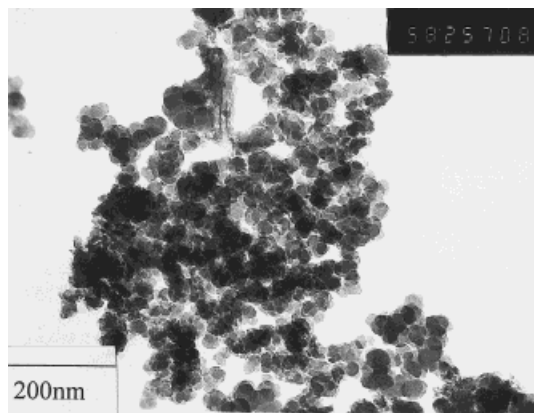
At the end of the reaction the total amount of reacted CFC-22 was measured to be 1.01–1.03 g. Thus, the molar ratio of reacted CFC-22 and AN was calculated to be 0.96–0.98. This value was very close to 1.0, indicating that the CFC-22 reacted with equal moles of AN to form the final product. The conversion of the reaction ( $f$ ) calculated from the weight of the product was 85–91% according to eq. (1):

$$f = [w_P r_1 / (w_F r_2 + w_A r_3)] 100\% \quad (1)$$

where  $w_P$ ,  $w_F$ , and  $w_A$  are the weights of the product, reacted CFC-22, and AN, respectively; and  $r_1$ ,  $r_2$ , and  $r_3$  are their corresponding carbon contents.

### Characterizations

The IR and Raman spectra were recorded on an IFS-66V Fourier transform IR (FTIR) spectrometer with a KBr pellet and a RM1000 Raman spectrometer (Renishaw PLC), respectively. The Raman spectrum was obtained by using a 633-nm laser excited at 0.5 mW and was accumulated for 30 s. Elemental analysis was performed by a Per-



**Figure 1** The transmission electron micrograph of the product.

kin–Elmer 240 C elemental analyzer and a VG Mark-II XPS spectrometer. Scanning electron microscopy pictures were taken using an X-560 electron micrographer. The X-ray diffraction examination was carried out by using a wide-angle X-ray diffractometer (XD-3A, Shimadzu) with a Cu target. The time of flight second ion mass spectrum was recorded on an Esquire LC mass spectrometer. The powdery solid product was used directly as the sample.

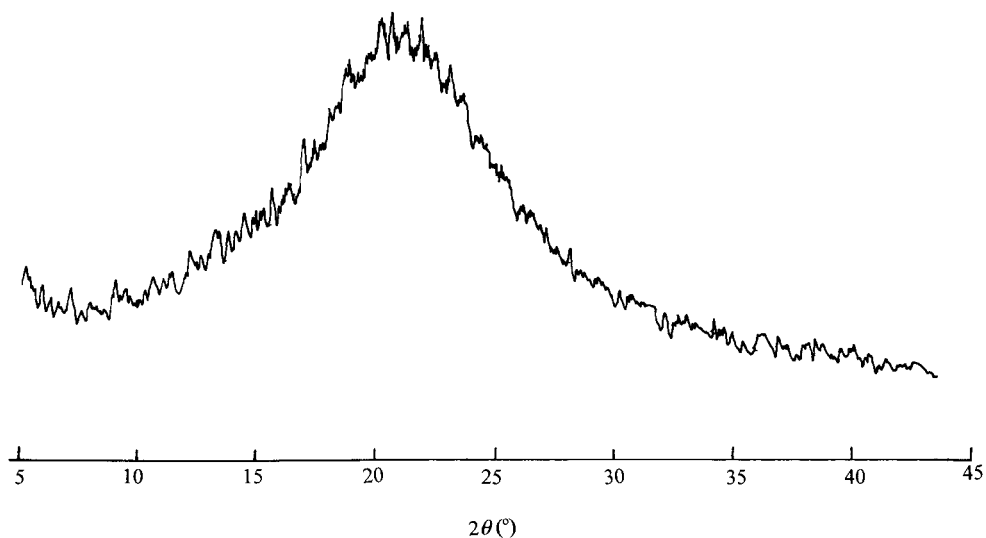
## RESULTS AND DISCUSSION

### Physical Properties of Product

The black solid product was powdery and insoluble in water or the usual organic solvents such as methanol, acetone, and benzene at room temperature. Transmission electron microscopic examination showed the particles had diameters in the range of 20–30 nm and were aggregated to form relatively larger bodies (Fig. 1). X-ray diffraction showed only a broad band centered at  $2\theta = 21^\circ$ , indicating the product to be amorphous (Fig. 2).

### Structure of Product

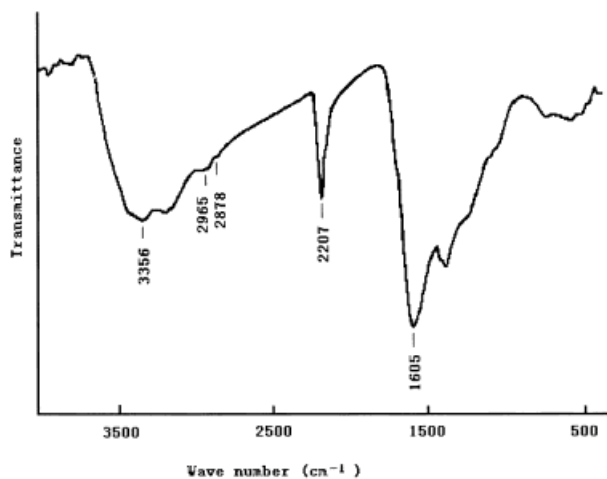
The elemental analysis indicated that the product contained 62.02% carbon, 3.49% hydrogen, 24.15% nitrogen, 4.25% chlorine, 1.61% fluorine, and 4.48% oxygen (by weight). Thus, it had a composition formula of  $C_{3.00}H_{1.44}N_{1.00}O_{0.16}Cl_{0.07}F_{0.05}$ . This result demonstrated that AN was one of the reactants of the reaction and the halogen atoms of CFC-22 were extensively eliminated. The C/N atomic ratio of the product was found to be accurate at 3.0.



**Figure 2** The wide-angle X-ray diffraction pattern of the product.

This also confirmed that the product was formed from equal moles of CFC-22 and AN.

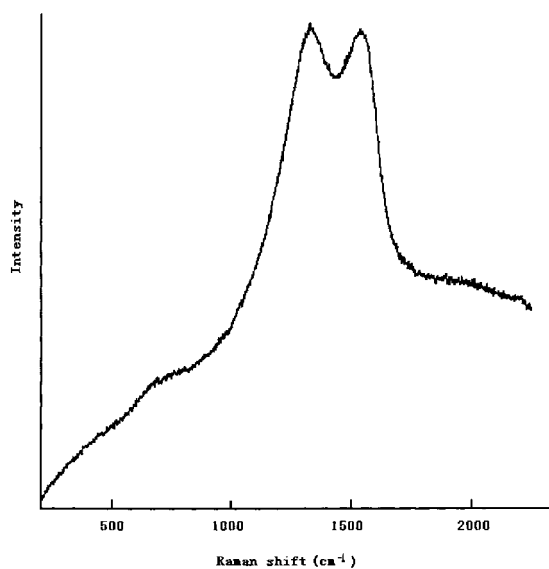
The FTIR spectrum of the product is illustrated in Figure 3. This figure shows weak absorption of C—Cl bonds in the region of  $500\text{--}700\text{ cm}^{-1}$  and C—F bonds in the region of  $1000\text{--}1400\text{ cm}^{-1}$ , also indicating extensive dehalogenation. A strong band centered at about  $1610\text{ cm}^{-1}$  was assigned to a C=C stretching vibration.<sup>4</sup> The band at  $2210\text{ cm}^{-1}$  was attributed to the nitrile group (—CN). The weak bands typical of valence vibrations of  $\text{CH}_2$  or CH were found in the region of  $2800\text{--}2990\text{ cm}^{-1}$ . The broad bands at the frequencies over  $3000\text{ cm}^{-1}$  can be assigned to adsorbed water and amide groups formed by the side reaction of —CN groups.



**Figure 3** The FTIR spectrum of the product.

In the Raman spectrum (Fig. 4) there are two strong and broad bands at around  $1600$  and  $1400\text{ cm}^{-1}$ , which are common for all forms of polycrystalline graphite or “amorphous carbons” with broad distributions of  $\text{sp}^2$  and  $\text{sp}^3$  bonded carbon atoms.<sup>5</sup> These results indicated that the product had a carbon-like backbone. The —CN band close to  $2200\text{ cm}^{-1}$  is very weak because of low Raman sensitivity.

On the basis of the elemental analysis and spectral examinations described above, the reaction and the structure of the product can be simply postulated as follows:



**Figure 4** The Raman spectrum of the product.

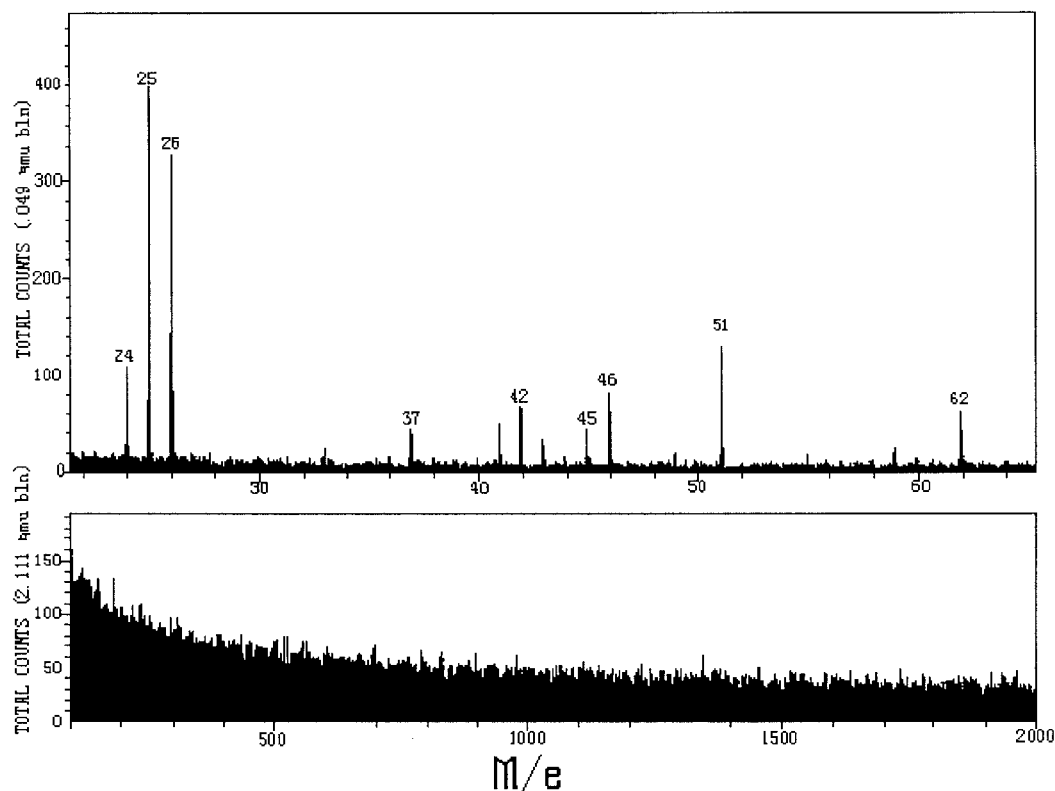
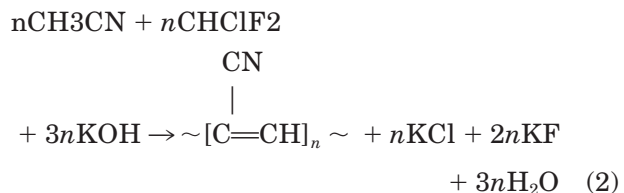


Figure 5 The time of flight second ion mass spectrum of the product.



It should be noted here that a small part of the —CN groups (~10%, according to the hydrogen and oxygen contents of the polymer) in the chain should instead be by —CONH<sub>2</sub> or —COOH.

The mass spectrum shown in Figure 5 also confirms the structure of the product expressed in eq. (2). The assignments of the main lines of the spectrum are listed in Table I. According to this

table, the molecules of the product can be broken into short carbon segments such as CN, C<sub>2</sub>, C<sub>2</sub>H, C<sub>3</sub>H, C<sub>4</sub>H, C<sub>3</sub>HN, C<sub>5</sub>H<sub>2</sub>, or C<sub>4</sub>N. The line at  $m/e = 51$  was attributed to the particles of polymer repeat units. The amide and carboxyl groups were also monitored as shown in Table I. There were almost continuous particle lines observed, even in the region of  $m/e > 500$ . This showed that the product was a polymer. The low resolution of the mass spectrum in the region of the large particles was mainly due to the sample being solid.

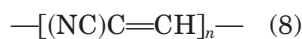
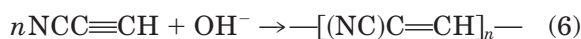
#### Mechanism Considerations

The mechanism of the reaction was not very clear here. However, the most possible route may have

Table I Assignments of Main Lines in Mass Spectrum of Product

<i>m/e</i>	24	25	26	37	42	43
Assignment	C <sub>2</sub>	C <sub>2</sub> H	CN, C <sub>2</sub> H <sub>2</sub>	C <sub>3</sub> H	N=C=O	HN=C=O
<i>m/e</i>	44	45	46	49	51	62
Assignment	H <sub>2</sub> NC=O	COOH	HCOOH	C <sub>4</sub> H	NC—C≡CH	C <sub>5</sub> H <sub>2</sub> , C <sub>4</sub> N

involved anionic polymerization. In the system without AN, CFC-22 was stable to solid KOH particles and no reaction was detected. This result indicated that CFC-22 was chemically much more stable than chloroform and other halogenated hydrocarbons.<sup>6-8</sup> Therefore, the CFC was activated by AN. The AN can form carbonic anions in an alkaline medium,<sup>9</sup> and the anions can attack the halide molecules as follows:



Reaction (4) is a reasonable substitution reaction between alkyl nitrides and halides.<sup>10</sup> Reaction (5) is an elimination reaction and can easily happen in an alkaline medium.<sup>11</sup> Furthermore, this reaction produces active monomers and can be polymerized into the final product through reactions (6)–(8).

## CONCLUSIONS

In conclusion, CFC-22 is chemically active and can react with AN when in the presence of solid potassium hydroxide particles. The reaction can produce a carbon-based polymer even under normal pressure and at room temperature. The mechanism of the reaction and the application of the product are not clear now and need further investigations. Nevertheless, this is the first example of polymerization of CFCs and AN in solid alkaline media.

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