

XPS Study of Radiation Crosslinked Copolymer of Tetrafluoroethylene with Hexafluoropropylene

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SYNOPSIS

In this work the radiation-induced structural changes in F-46 were studied by XPS. In carbon-1s spectra of a highly crosslinked F-46 sheet, the slight increase observed in relative area under the peak due to CF₃ was explained by the radiation-induced scission of polymer chains. The peak at 287.6 eV appearing in the spectra caused by ionizing radiation was attributed to carbon structures without primary fluorine substituents, in both branching and unsaturated structures, while that at 289.3 eV was assigned to =CF groups in mid-chain double bonds.

INTRODUCTION

Since radiation was first used to modify the mechanical properties of polymers the confirmation and location of crosslinking and branching structures have been attractive but difficult problems for chemists who engaged in radiation polymer chemistry. The main reason for this is the nonmelting and nondissolving properties of crosslinked polymer, which limits the application of commonly employed analytical methods to study their crosslinking structures.

In this work, by means of X-ray photoelectron spectroscopy (XPS) the radiation-induced structural changes in the copolymer of tetrafluoroethylene with hexafluoropropylene (F-46) was studied. Because of the special sensitivity of the XPS method to the structural changes in fluoropolymers, the radiation-induced branching structures in F-46 were confirmed, for the first time, from its carbon-1s spectra.

EXPERIMENTAL

The F-46 samples used in this work were commercially produced particles which contain 14 mol %

hexafluoropropylene unit pressed under 270°C into sheets of 0.2 mm thickness. Sample sheets then were sealed under the 1×10^{-2} Pa into glass tubes.

Irradiation was carried out with a 70,000 Ci Co-60 source at 150°C and 220°C. The irradiation dose was controlled within 0–1100 kGy.

The XPS experiment was carried out using an ESCA-650B spectrometer with an ESCA PAC-660 computer and curve resolver which resolves the carbon-1s spectra on the basis of the curve-fitting method. The binding energy of the Au 4f_{7/2} level of a gold plated sample, 83.3 eV, was used to calibrate the binding energy.

In order to eliminate surface contamination, the surfaces of the sample were scraped away with a blade and then washed with alcohol and acetone before measurement.

The infrared measurement was made using a DIGILAB infrared spectrometer. The thickness of samples for this test was about 0.05 mm.

RESULTS AND DISCUSSION

Preliminary Observation of Carbon-1s Spectra of F-46

XPS is a surface analytical method based on the measurement of binding energies of core level electrons in the atomic or molecular orbits of substances

to be measured. When bonded with other atoms, owing to the effects of changes in chemical environment for a given atom on binding energies of core electrons, shifts in binding energies for a given level together with the changes in the relative intensities of the different peaks in XPS spectra may be used to acquire detailed structural information. Because of fluorine's high electronegativity, fluorine substituents in polymer chains are expected to induce large shifts in the binding energy of the carbon-1s levels. Thus radiation-induced structural changes in fluoropolymers can be reflected in their XPS spectra.

Curve (a) in Figure 1 shows the carbon-1s spectrum of F-46 before radiation crosslinking. Because of the relatively low content of hexafluoropropylene units in the F-46 used in this work, the observed carbon-1s spectra appears to contain a single peak. However, the peak is a broad one, especially in the part near its baseline, and resolution shows that the spectrum consists of three partially resolved peaks at 294.0, 292.1, and 290.1 eV respectively, and a isolated peak at 285.0 eV.

Regarding relation between the number and position of fluorine substituents in fluoropolymers and the binding energies of carbon-1s levels, a detailed investigation has been carried out by Clark^{1,2} and an experimental method for calculating binding energies was proposed. Generally speaking, a fluo-

rine substituent at an α position involves a shift of about 2.9 eV, a substituent at a β position gives about a 0.7 eV shift, and a CF_3 substituent will raise the binding energy of carbon-1s electrons 0.59 eV.³ Thus the observed three partially overlapped peaks in Figure 1(a) can then be assigned to CF_3 , CF_2 , and CF groups respectively, while the peak at 285.0 eV belongs to hydrocarbons arising from surface contamination of the samples.

Radiation-Induced Changes in Carbon-1s Spectra of F-46

It was reported that the radiation chemistry behavior of F-46 was dependent on irradiation temperature.^{4,5} When irradiation is carried out at a temperature below its glass transition point (about 80–90°C), it is a radiation degradable polymer, while irradiation *in vacuo* above its glass transition temperature will cause the formation of crosslinking structures. In this work, in order to obtain a highly crosslinked polymer, F-46 sheets were irradiated at 150°C to 1100 kGy and 220°C to 500 kGy respectively. The carbon-1s spectra of the resulting crosslinked F-46 are shown in Figure 1(b). Compared to the spectrum of unirradiated F-46, the following changes were be observed:

1. A slight increase in intensity of peak at 294.0 eV was found after irradiation, which indicates an increase in the relative content of CF_3 units in F-46.
2. Two new peaks can be clearly seen in the carbon-1s spectrum of irradiated F-46. The computer resolution shows that the position of these two new peaks are 287.6 eV (peak 1) and 289.3 eV (peak 2), values which indicate the formation of new radiation-induced structures in F-46.
3. Both the size and relative area under peaks 1 and 2 are different, and general observation shows that the relative area of peak 1 is twice as large as that of peak 2, corresponding to a difference in their relative content in F-46.

From the binding energies, it is clear that the peak 1 should correspond to a carbon structure which is bonded indirectly with several fluorine atoms. Much earlier work on radiation-induced active species in F-46⁵ has shown that when subjected to ionizing radiation *in vacuo*, three main kinds of radicals are formed:

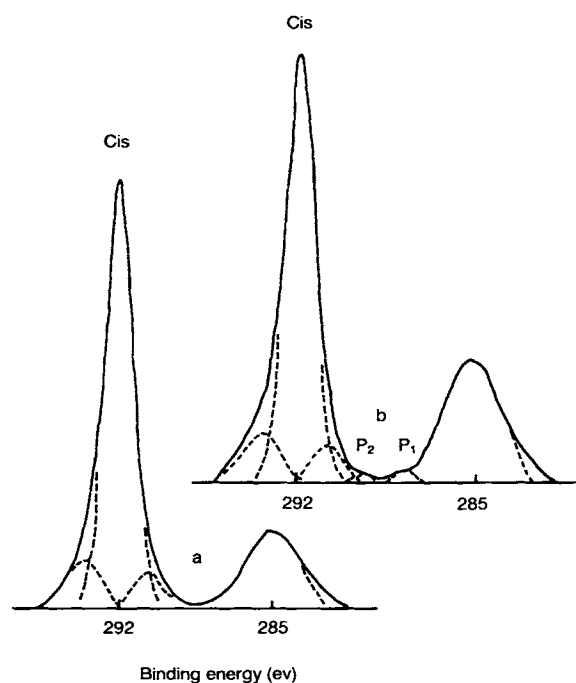
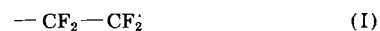
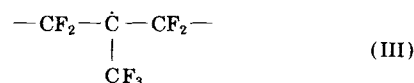
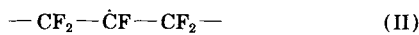
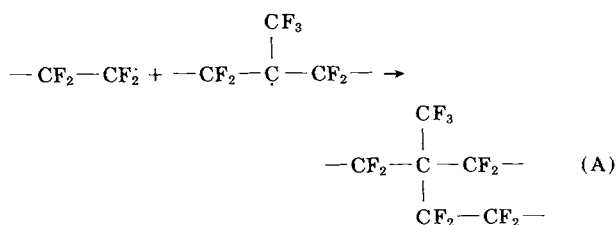


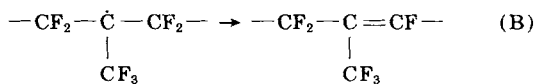
Figure 1 Carbon-1s spectra for F-46 (a) unirradiated (b) irradiated at 150°C to 1100 kGy.



Among them, only radical (III) is apparently derived from the hexafluoropropylene unit in F-46 and it seemed to be the predominant component.⁵ Thus the radiation-induced structural changes in F-46 are expected to result from certain reactions of these radicals. From the structure of these radicals, it seems that the carbon structure without primary fluorine substituents might arise from two sources. In the first place, the combination of radicals to form crosslinking or branching structures is expected to be a way of forming quaternary carbon. A consideration of steric inhibition caused by fluorine atoms and of the structure of radiation-induced radicals in F-46, however, shows that some combinations of radicals such as (II) + (II), (II) + (III) and (III) + (III) are forbidden.⁴ For this reason, the combination of radical (I) and (III) is one of the most probable radiation-induced branching structure in F-46.



A rough calculation using Clark's method gives the binding energy of the center carbon in structure (A) as 287.69 eV, which is obviously very close to that of peak 1. Secondly, the defluorination of radicals (II) and (III)



can result in the formation of unsaturated structures in F-46, in which the center carbon in structure (B) is not directly bonded with any fluorine atoms. The binding energy of the center carbon in structure (B) cannot be precisely calculated using Clark's method because of the presence of the double bond, but comparing the binding energy of =CF groups in a series of perfluoromolecules⁶ shows that the binding energy of similar groups in them was found to be from 289.2–289.4 eV, with 289.4 eV being the average value. The existence of radiation-induced unsaturated structures in F-46 can also be clearly proved by the observed differences in the infrared spectra

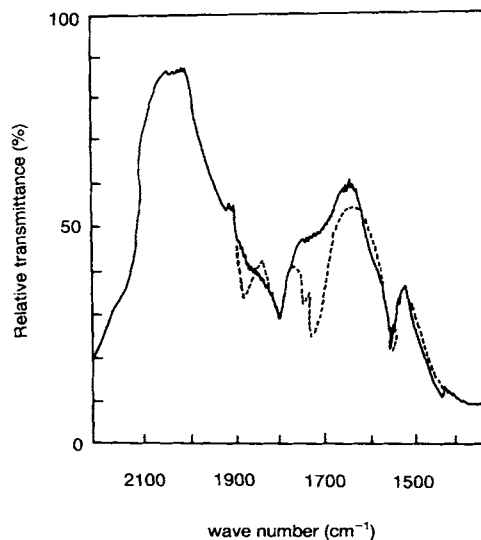
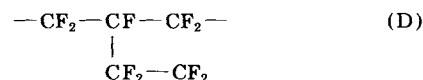


Figure 2 Infrared spectra for F-46 sheets (—) before and (----) after irradiation at 150°C to 1100 kGy.

of F-46 before and after irradiation (see Fig. 2). These IR spectra show that, after irradiation, the absorption band at 1733 cm^{-1} due to mid-chain double bonds and at 1880 cm^{-1} corresponding to $-\text{C}-\text{F}^{\text{O}}$ (resulting from the reaction between radicals and residual oxygen in the system) are increased markedly, while that at 1780 cm^{-1} due to end-chain double bonds remains almost unchanged. Moreover, the formation of structure (C) will also be expected to make a contribution to the absorption observed for mid-chain double bonds in Figure 2.

Thus from the point of view of binding energy, the peak 2 at 289.3 eV can be reasonably assigned as being due to =CF groups in both structures (B) and (C). On the other hand, it should be noted that the formation of structure (A) would result in a decrease in the relative content of CF groups in F-46; carbon spectra of crosslinked F-46 do not suggest this occurs to any large extent. This can be explained as follows, however, when subjecting polytetrafluoroethylene to ionizing radiation, although the most important effect is scission of polymer chains, crosslinking or branching reactions can also occur to a certain extent.⁸ Thus for F-46 in which some units are similar to that in polytetrafluoroethylene, an assumption that branching structure concerning with radical (I) and (II) is formed in it seems reasonable. Therefore we assert that it is formation of branching structure



which compensates for the loss in CF content caused by the formation of structure (A). Because of their very close binding energies (290.0 eV for CF group in structure (D) calculated using Clark's method, and 290.1 for CF already existing in F-46 and observed in its carbon-1s spectra.) which are a result of their similar chemical environment, peaks due to these two structures will be expected to overlap with each other so that they cannot be resolved.

CONCLUSION

It is clear from the foregoing that the main radiation-induced structural changes in F-46 include branching, double bond formation and scission of polymer chains. The main branching structures are structure (A) and structure (D), while the main unsaturated structures are mid-chain double bonds. This is quite different from the case in polytetrafluoroethylene where the main unsaturated structures caused by ionizing radiation are end-chain double bonds.¹⁰ On the other hand it was noted that though F-46 sheets were irradiated under the crosslinking conditions,

the radiation-induced degradation still occurs to a certain extent.

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