XPS Studies on Radiation-Induced Structural Changes in the Copolymer of Tetrafluoroethylene and Ethylene

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SYNOPSIS

In this work, the radiation-induced structural changes in the copolymer of tetrafluoroethylene and ethylene (F-40) were studied by X-ray photoelectron spectroscopy (XPS). During irradiation, some CF_2 groups in the polymer were found to have been converted into carbon structures that bonded indirectly with fluorine atoms. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The homopolymer of tetrafluoroethylene (PTFE) is a typical radiation degradative polymer, and a very small irradiation dose leads to a dramatic deterioration of its mechanical properties due to predominant scission of the molecular chains.[1] The copolymer of tetrafluoroethylene with ethylene, however, was reported to be able to form cross-linking structures by ionizing radiation.[2] Because of the unavailability of a suitable solvent for the polymer, little work on radiation-induced structural changes of the polymer has been reported. In this work, by X-ray photoelectron spectroscopy (XPS), the radiation-induced structural changes in F-40 were studied. The experimental results showed that some CF_2 and CH_2 groups in F-40 undergo structural changes during irradiation.

EXPERIMENTAL

The F-40 used in this work was from the Shanghai Institute of Organic Fluorochemistry. XPS analysis showed that it was a highly alternated copolymer of tetrafluoroethylene and ethylene. Powder samples were pressed under 240°C into 0.1 mm sheets and then sealed into glass tubes under 0.2 Pa.

Irradiation was carried out with a 70,000 Ci Co-60 Source. The dose rate was 1 Mrad/h.

The XPS measurement was made on an ESCA-650B-type X-ray photoelectron spectroscope. The surface of the samples was cleaned with acetone and alcohol before measurement. The binding energy of peaks was calibrated with that of 87.3 eV, the binding energy of the $4f_{7/2}$ electron of gold plated on samples.

RESULTS AND DISCUSSION

F-40 is a highly alternated copolymer of tetrafluoroethylene and ethylene and its typical structure can be described as

$$-CF_2-CF_2-CH_2-CH_2-$$

Because of the difference in their chemical environment, the core-level electrons of carbon atoms in $-CF_2-$ and $-CH_2-$ units will have different binding energies. Thus, in the C(1s) spectra of the copolymer, two resolved peaks with an equal area corresponding to above two units could be observed, as shown in Figure 1. On the other hand, the presence of a few unalternated units could also be observed in the spectra by the appearance of a peak between the two main peaks. The weak peak at 285.0 eV results from hydrocarbon contamination of the sample surface and can also be used for calibration of binding energies. With the available reference

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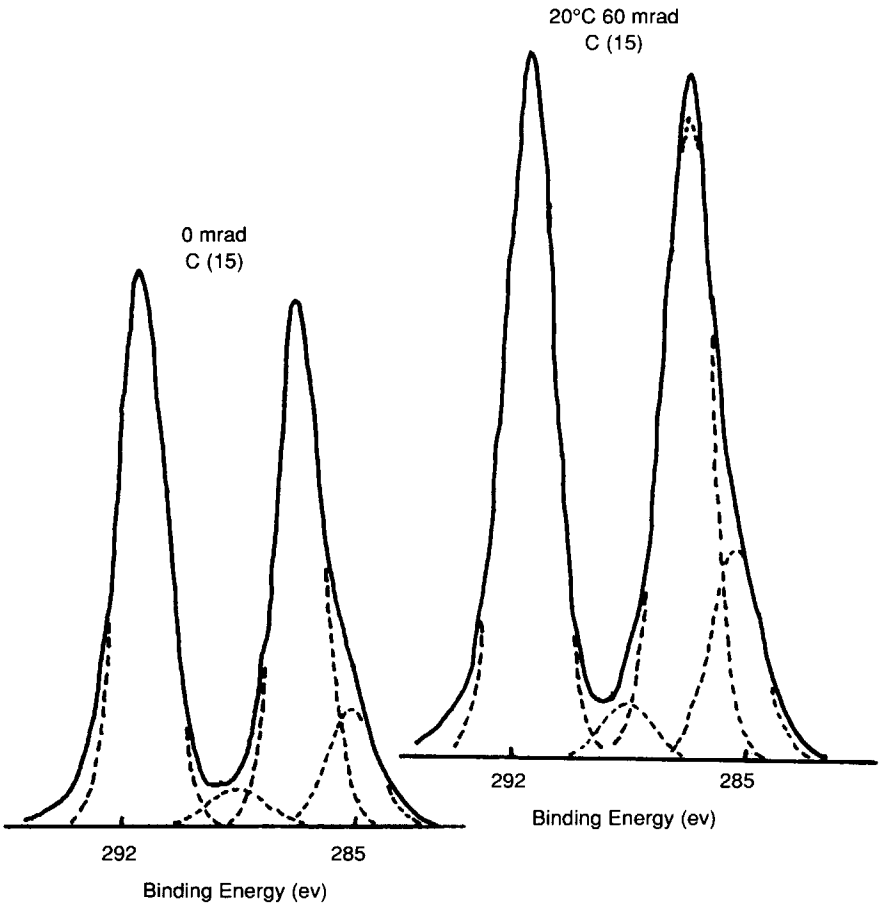

Figure 1 The C(1*s*) spectra of F-40 before and after irradiation.

data for fluorinated polymeric materials,[3] the following assignments of the chemical binding state are made:

Binding Energy (eV)	Chemical Binding State
285.0	—CH_2—$\underline{CH_2}$—CH_2—
286.3	—$\underline{CF_2}$—$\underline{CH_2}$—CH_2—
287.5	—CH_2—$\underline{CF_2}$—CF_2—CF_2—
	—$\underline{CF}$=CH—
291.4	—CH_2—$\underline{CF_2}$—CF_2—

After irradiation, a general observation was that two main peaks due to —CF_2— and —CH_2— showed broadening, and the strength of the peak at 287.3 eV originally due to unalternated units in the copolymer was observed to increase slightly. More detailed changes in the structure caused by irradiation could be seen from Figure 2, which shows changes in the relative content of components corresponding to peaks at 291.3, 287.3, and 286.3 eV, respectively, with increasing irradiation dose. It could be seen that from the loss of fluorine atoms caused by irradiation, as shown by the observation of a light yellow color of the irradiated sample, which illustrates the formation of unsaturated structures caused by dehydrofluorination of the polymer chain, and also by the observation of fluorine ions in the solution of KOH, whose absorbed radiation caused volatile products, the content of CF_2 reduces gradually in the dose range examined with increasing irradiation dose, whereas that of the peak at 286.3 eV corresponding to CH_2 units in the copolymer and/or carbon structure bonded indirectly with fluorine atoms increases in the low dose range (40 Mrad) and then decreases at high dose. In the dose range above 40 Mrad, the relative content of peak at 287.3 eV due to unalternated structure and/or CF= structure was observed to increase with increasing irradiation dose.

Many earlier references[4,5] have shown that when fluoropolymer is exposed to ionizing irradiation the

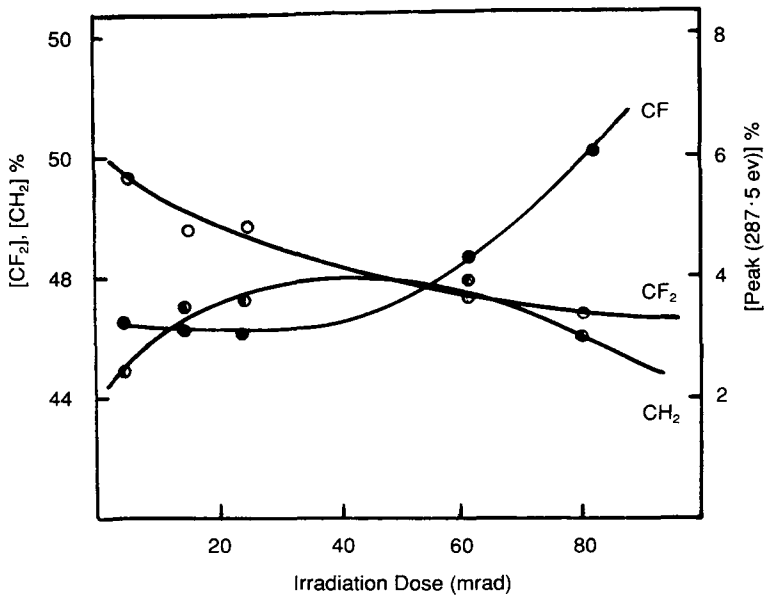

Figure 2 The changes in relative content of components in Figure 1 with irradiation: (○) CF_2; (◐) CH_2; (●) peak at 287.5 eV.

initial reactions involve a fragment of the C—F, C—H, and C—C bonds, leading to the formation of radicals. These radiation-induced macromolecular radicals may either react with an adjacent one under cross-linking or undergo elimination of hydrogen and fluorine atoms to form unsaturated structures. For F-40 examined, the possible radiation-induced macromolecular radicals, on the basis of ESR work on polyvinylidene fluoride,[4] include

$$-CF_2-\dot{C}F_2 \qquad -CH_2-\dot{C}H_2$$

$$-CF_2-\underset{\cdot}{C}F-CH_2-CH_2-$$

$$-CH_2-\underset{\cdot}{C}H-CF_2-CF_2-$$

Thus, the radiation-induced cross-linking structures in F-40 are expected to result from the different recombinations of these radicals. Our extracting experiment on cross-linked F-40 with high-temperature fluorochloro oil (oligomer of trifluorochloroethylene) showed that exposing F-40 to 20 Mrad leads to the formation of 55% gel in the polymer. In the dose range below 20 Mrad, as shown in Figure 2, it can be seen that the relative content of the peak at 287.3 is independent of increasing irradiation dose, whereas that of the peak at 291.3 eV decreases and those at 286.3 eV increase with increasing irradiation dose. On the basis of this observation, it is clear that during irradiation accompanied by the formation of cross-linking structure some CF_2 units are converted into a structure in which carbon atoms are bonded indirectly with fluorine atoms and, thus, the binding energy of its core-level electrons approaches to that of the CH_2 units in F-40. This conversion results in the observed increase in the strength of peak at 286.3 eV. Taking into account the molecular structure of F-40, it is evident that there are only two ways in which CF_2 units are changed into a carbon structures bonded indirectly with fluorine atoms:

$$-CF_2-CF_2- \rightarrow -\overset{|}{\underset{|}{C}}-CF_2- \quad (A)$$

$$-CH_2-CF_2- \rightarrow -CH_2-CF- \xrightarrow{-HF}$$

$$-CH=\underset{|}{C}- \quad (B)$$

The possibility of cross-linking reactions occurring twice at one point is unambiguously very small, and, thus, it is unlikely to form the cross-linking structure like (A) during irradiation. The high bond strength for HF, however, suggests that the reaction to form structure (B) might be an efficient process, though it is difficult to distinguish the type of cross-linking structures in the present work. In the high-dose range due to the limitation effect on movement of macromolecules and macromolecular radicals caused by the formation of cross-linking structures, macromolecular radicals are expected to undergo dis-

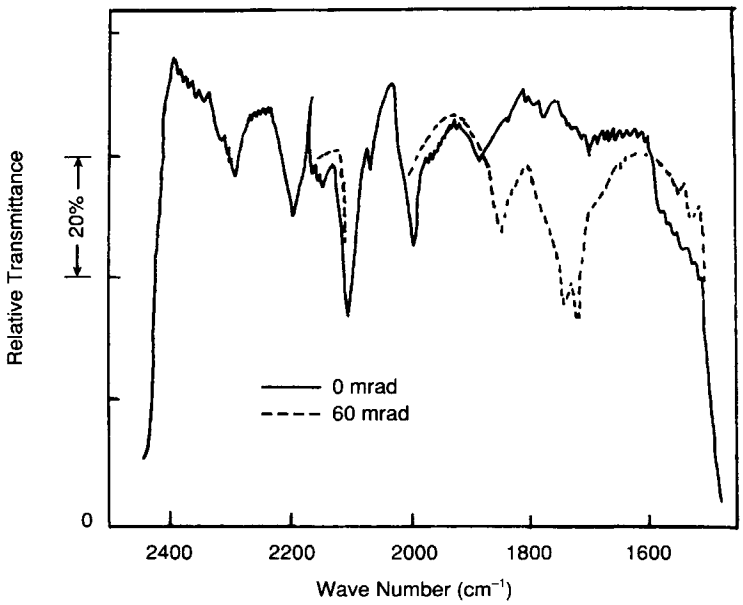

Figure 3 Infrared spectra of F-40 before and after irradiation.

proportionate recombination with fluorine or hydrogen atoms or some other reactions instead of forming a cross-linking structure. Some of these reactions, such as:

$$-CF_2-CF_2^{\cdot} \xrightarrow{H^{\cdot}} -CF=CF_2 + HF$$

$$-CF_2-CH_2^{\cdot} \xrightarrow{H^{\cdot}} -CF=CH_2 + HF$$

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are responsible for the observed increase in the relative content of peak at 287.3 eV. Figure 3 shows the changes in the infrared spectra of F-40 before and after irradiation. It can be seen that after exposure to 60 Mrad at ambient temperature the strength of absorption band between 1670 and 1720 cm due to C=CF (Ref. 6) increases considerably, which proves the formation of unsaturated structures in F-40 during irradiation. On the other hand, the formation of cross-linking structure (B) would affect the chemical environment of it adjacent CH_2 and CF_2 units, which, according to Clark's theory, will result in the lowering of the binding energy of core-level electrons in carbon atoms of these units. The observed broadening of main peaks of XPS spectra of F-40 after irradiation proves the reasonableness of the above suggestions.

In summary, the XPS study shows that the radiation-induced main structural changes are the conversion of CF_2 units into a carbon structure bonded indirectly with fluorine atoms and the formation of unsaturated structures. On the basis of the results of the extracting experiment and molecular structure of F-40, the conversion was attributed to result from the further dehydrofluorination of cross-linked and/or branched structures.

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