

XPS Study of Fluoro-poly(aryl ether)s

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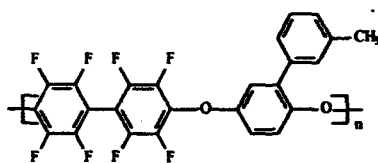
Introduction

Fluorine has a set of unique properties, such as small size, formation of very strong bonds, and strong electronic effects, which make it an extremely valuable substituent in the molecular design of effect-chemicals.¹ In recent years, fluorine-containing polymers were widely studied for applications as films, coatings for optical and microelectronic devices, gas separation membranes, and as matrix resins in composites.² X-ray photoelectron spectroscopy (XPS) has been utilized extensively as an analytical tool to study the chemical structure of polymers. The study of fluorinated systems is a particularly fertile area of research by XPS technique, because the highly electronegative fluorine substituent induces large shifts in the binding energies of carbon 1s levels³.

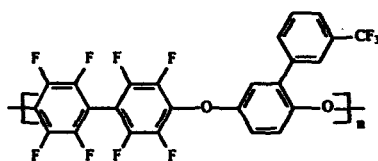
A series of fluorinated poly (aryl ethers) have been synthesized by us recently.⁴ They have high thermal stability, low dielectric constants, low moisture absorption and good solubility. In this paper, we have characterized the fluorine-containing poly (aryl ethers) using XPS.

Experimental

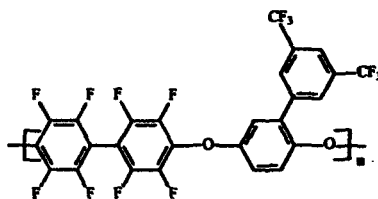
Samples. The fluorinated poly (aryl ethers) was synthesized by us. The results of IR, ¹H NMR and ¹⁹F NMR were agreed with the supposed structure. Their structure was as follows:



8F-PAE



11F-PAE



14F-PAE

Data Collection and Analysis. The XPS spectra were collected on a VG ESCALAB MK II spectrometer with Mg K α X-ray source (1253.6eV photons). The X-ray source was operated at 13 kV and 20 mA. The polymer powder samples were mounted onto standard VG sample studs with double sided adhesive tapes and pumped into the preparation chamber to 10⁻⁸ mbar before being introduced into the XPS chamber. The pressure in the XPS analysis

chamber was maintained at 10^{-9} mbar or lower during collection. In the data analysis, the binding energy (BE) of the core level C1s peak was set at 284.8eV to compensate for surface-charging effects.³ The experimental spectra were fitted into components of Gaussian line shape. All of the individual spectra were smoothed with a seven-pointed averaging routine.

Results and Discussion

Figure 1 (a),(b),(c) represented the carbon 1s XPS core level spectra of 8F-PAE, 11F-PAE and 14F-PAE, respectively. The C1s, O1s and F1s binding energies for polymers were listed in Table 1 (a),(b),(c).

The C1s spectrum of 8F-PAE was fitted smoothly into four component peaks. The peak at 288.6eV was associated with the \underline{C} -F carbons of benzyl rings. The peak at 286.8eV was proposed to correlate with \underline{C} -O carbons. The peak at 285.5eV was associated with the \underline{C} -H and \underline{C} -C carbons of benzyl ring and side groups. The deconvoluted spectrum showed a small peak at 284.8eV binding energy due to hydrocarbon contamination which was used for calibration purpose.

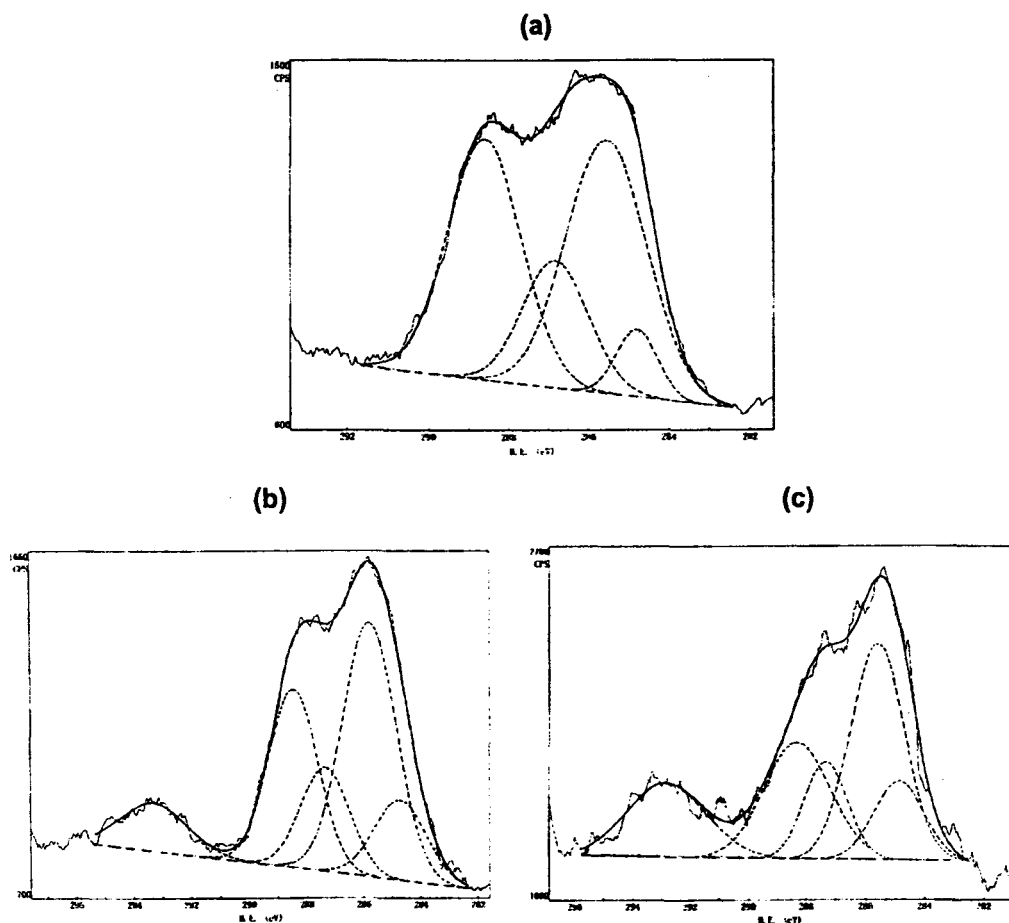


Figure 1. Carbon 1s Spectrum for F-PAEs: 8F-PAE(a), 11F-PAE(b), 14F-PAE(c).

In comparison to the 8F-PAE, the C1s spectrum of 11F-PAE (Figure 1 b) showed a new component at 293.3eV, which was attributed to the $-\text{CF}_3$ function. When two $-\text{CF}_3$ functions were introduced onto polymer, an even higher peak at 292.8eV was showed (Figure 1 c).

The results of O1s and F1s were used to further confirm the structure of polymers. The O1s peak of 8F-PAE was divided into two peaks, small one from surface absorbent H_2O (BE=532.3eV), another from polymer mainly (BE=534.3eV). The O1s spectra of 11F-PAE and

14F-PAE had the similar results. The F1s spectra had unique features. Only one peak was showed for each of polymers, which was associated with the E-C fluorines of benzyl rings and side groups.

Table 1. XPS Peaks for F-PAEs: 8F-PAE(a), 11F-PAE(b), 14F-PAE(c).

(a)			
C _{1s}	BE	=284.8eV	(Contaminated carbon)
		=285.5eV	(C-H, C-C)
		=286.8eV	(C-O)
		=288.6eV	(C-F)
O _{1s}	BE	=532.3eV	(Surface absorbent oxygen)
		=534.3eV	(Q-C)
F _{1s}	BE	=688.1eV	(C-F)
(b)			
C _{1s}	BE	=284.8eV	(Contaminated carbon)
		=285.8eV	(C-H, C-C)
		=287.3eV	(C-O)
		=288.4eV	(C-F)
		=293.3eV	(CF ₃)
O _{1s}	BE	=532.4eV	(Surface absorbent oxygen)
		=534.4eV	(Q-C)
F _{1s}	BE	=688.1eV	(C-F, CF ₃)
(c)			
C _{1s}	BE	=284.8eV	(Contaminated carbon)
		=285.6eV	(C-H, C-C)
		=287.3eV	(C-O)
		=288.3eV	(C-F)
		=292.8eV	(CF ₃)
O _{1s}	BE	=531.1eV	(Surface absorbent oxygen)
		=533.9eV	(Q-C)
F _{1s}	BE	=687.8eV	(C-F, CF ₃)

Conclusions

X-ray photoelectron spectroscopy (XPS) was used to characterize the structure of the fluorine-containing poly(aryl ethers). In comparison to the 8F-PAE, the C1s spectrum of 11F-PAE showed a new component due to introduction of -CF₃ function. An even higher peak was showed after introduction of another -CF₃ function. The O1s and F1s spectra were used to further confirm the structure of polymers.

References

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