polymer papers

A high-resolution X-ray photoelectron spectroscopy study of trifluoroacetic anhydride labelling of hydroxyl groups: demonstration of the β shift due to $-OC(O)CF_3$

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Derivatization with trifluoroacetic anhydride (TFAA) followed by X-ray photoelectron spectroscopy (X.p.s.) analysis is a useful method for estimating the surface concentration of hydroxyl groups in polymeric materials. High-resolution X.p.s. analysis of TFAA-derivatized poly(vinyl alcohol) and plasma-polymerized poly(allyl alcohol) reveals significant chemical shifts in the carbon atoms attached to the $-OC(O)CF_3$ group and carbon atoms in the β position relative to this group.

(Keywords: X-ray photoelectron spectroscopy; derivatization; poly(vinyl alcohol); plasma polymerized poly(allyl alcohol); β shift)

INTRODUCTION

In X-ray photoelectron spectroscopy (X.p.s.) there is only a small range of chemical shifts in the C 1s core level, and frequently carbons in different functional groups occur at the same, or very similar, binding energy. Carbon atoms in hydroxyl and ether environments are an example of this; both occur at 286.5 eV and cannot be separated spectroscopically even with the aid of peak-fitting routines. To overcome this problem, derivatizing agents have been identified and tested for many functional groups. The features of a good label are[1]:

(i) it contains a unique atom or functional group;
(ii) it is specific to the functional group of interest and reacts quantitatively (ideally to 100%); and
(iii) the labelling process itself should not perturb the surface.

The vapour-phase labelling of hydroxyl groups with trifluoroacetic anhydride (TFAA) has been shown to satisfy these three criteria. TFAA reacts with nearly 100% of the hydroxyl groups in poly(vinyl alcohol) (PVA), without appreciably labelling carbonyl or carboxyl polymers[2]†, and the CF_3 tag is easily detected by X.p.s. owing to its large chemical shift (compare to carbon–oxygen functionalities)‡.

In a recent study, the authors[3] have used TFAA to label hydroxyl groups in a plasma polymer (PP) of allyl alcohol, in order to investigate functional group retention with plasma power (W) and monomer flow rate (F). Determination of the hydroxyl concentration directly from the C 1s core level is complicated by the probable presence of ether environments. However, whilst TFAA was found to label hydroxyl groups successfully, a result in agreement with Gombotz and Hoffman[4], considerable difficulty was encountered in obtaining a chemically acceptable fit of the C 1s core level. In our attempted fits, we used peaks for hydrocarbon, C–O, C=O, O–C=O, $O=C-CF_3$ and CF_3 of constant full width at half-maximum (f.w.h.m.) at the known binding energies of these functionalities.

To obtain a better insight into this problem, the high-resolution capability of the Scienta ESCA300 spectrometer has been employed to compare labelled and unlabelled PP with labelled conventional PVA. During the course of this work, strong evidence has been obtained for a significant β shift due to the $-OC(O)CF_3$ group and an unusually large shift in the carbon attached to this moiety.

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[†] In a recent study by A. Chilkoti and B. D. Ratner (*Surf. Interface Anal.* 1991, **17**, 567), it is shown that TFAA is also very reactive towards epoxides and, therefore, when epoxides are present, TFAA labelling will lead to an overestimation of the hydroxyl concentration

[‡] Labelling with TFAA also introduces fluorine, and the F 1s signal could alternatively be used to determine hydroxyl concentrations

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EXPERIMENTAL

The PP was prepared from allyl alcohol (supplied by Aldrich Chemical Co). The plasma reactor used was based on the design reported by Munro and Till[5]. Polymerization was carried out at a pressure (p) of ca. 0.2 Torr, a flow rate of monomer of 3.1 cm^3(STP) min^{-1} and an r.f. power of 10 W, i.e. a W/F of 3.2. The PP was obtained as a thin film on silicon substrate; a polymerization time of 10 min was found to be sufficient to deposit a film thick enough to exclude all substrate signals in the X.p.s. analysis.

Derivatization of hydroxyls in the PP by TFAA (supplied by Aldrich) was achieved by exposing the PP to TFAA vapour for 3 h in a sealed vessel. The PP was then removed and dried overnight in a vacuum desiccator. This method when applied to PVA labelled ca. 100% of surface hydroxyls. The preparation and derivatization of the PP will be considered in further detail elsewhere[3].

PVA was cast as a thick film on aluminium foil by evaporation of a solution in water. Derivatization was achieved as above; complete derivatization was achieved in ca. 10 min.

All X.p.s. spectra were recorded on a Scienta ESCA300 spectrometer. This employs a high-power rotating anode and a monochromatized Al Kα X-ray source, high-transmission electron optics and a multichannel detector. The design and performance of the spectrometer have already been described[6,7]. The spectrometer was operated at 0.5 mm slit width and 150 eV pass energy, giving an instrument resolution of 0.35 eV. The X-ray source was run at a power of 3.15 kW, and spectral acquisition times were limited to minimize X-ray-induced sample damage. Charge compensation was achieved by the use of a low-energy electron flood gun (VSW EG2) and the electron take-off angle employed was 45°. The spectra were shifted to low binding energy as a result of a small net negative charge on the sample surface, arising from the charge compensation. Spectra are displayed as they were recorded and require referencing to a common point (this is usually unfunctionalized hydrocarbon at 285 eV).

RESULTS AND DISCUSSION

Figure 1 shows the labelled and unlabelled C 1s core-level curve fits for the PP; from a previous study[8], we believe curve fits to be accurate to ±0.05. Curve fit parameters are shown in *Table 1*. The area ratios of the carbonyl:hydrocarbon and carboxylate:hydrocarbon peaks obtained from fitting the unlabelled spectrum were used in the subsequent fit of the labelled PP. These ratios ought not to have been perturbed by labelling. To obtain a good fit for the labelled PP (*Figure 1a*) it was necessary to use larger f.w.h.m.s for the hydrocarbon and C–O peaks (1.35 and 1.47 eV respectively) than used for the other peaks in the spectrum (1.01–1.15 eV). Whilst the use of these larger f.w.h.m.s gives a good mathematical fit, chemically there is no justification for broadening the hydrocarbon and C–O peaks. Hence, it must be that the derivatization has introduced additional components into the C 1s core level, which occur close to these peaks.

Displayed in *Figure 2* is the C 1s core-level fit for labelled PVA; the uncorrected binding energies of the component peaks are included in *Table 1*. Charge referencing the centres of the hydrocarbon peaks for the labelled PP and PVA to 285 eV results in a peak position for the CF_3 group of 293.43 eV in the PP, but only 292.65 eV in the PVA, a difference of 0.76 eV. Since the CF_3 environments in the two polymers are expected to be virtually identical, it seems unlikely that referencing both spectra to 285 eV is correct. From the structure of the labelled PVA (*Figure 3a*) it can be seen that the hydrocarbon environments are separated from the $-OC(O)CF_3$ labels by only one carbon. These environments are therefore perhaps susceptible to the electron-withdrawing influence of the labels, and hence chemically β shifted. In the PP there is expected to be a considerable quantity of hydrocarbon not influenced by labelling, and therefore this peak would be expected to be closer to 285 eV. This hypothesis is supported by looking at the binding energy of the F 1s core-level signal. For the PP and PVA this peak shows a constant separation from the CF_3 group but a variable position relative to the 'hydrocarbon'. Assuming the hydrocarbon of the PP to be correctly referenced to 285 eV, referencing the labelled PVA spectrum to the CF_3 group at 293.43 eV (as in the PP) gives peak positions for the hydrocarbon of 285.76 eV and the C–O of 287.47 eV. The binding energy of the C–O peak is shifted by 0.97 eV to higher binding compared to the normal position of the C–O group at 286.5 eV.

Table 1 Uncorrected C 1s binding energies obtained from peak fits in *Figures 1a, 1b* and *2*

Sample	Environment	Position (eV)	F.w.h.m. (eV)	Area (%)
PP+TFAA	$\underline{C}$–H	282.44	1.35	52.9
	$\underline{C}$–O	284.43	1.47	18.9
	$\underline{C}$=O	285.17	1.15	3.7
	O=$\underline{C}$–OH	286.48	1.04	0.5
	O=$\underline{C}$–CF_3	287.67	1.05	11.7
	$\underline{C}F_3$	290.85	1.01	12.2
PP	$\underline{C}$–H (*1*)[a]	281.52	1.13	69.4
	$\underline{C}$–O (*3*)	283.02	1.11	25.6
	$\underline{C}$=O (*5*)	284.42	1.14	4.5
	O=$\underline{C}$–OH (*6*)	285.85	1.14	0.7
PVA+TFAA	$\underline{C}$–H (2)	283.97	1.30	29.1
	$\underline{C}$–O (*4*)	285.68	1.21	26.0
	O=$\underline{C}$–CF_3 (*7*)	288.50	1.12	21.8
	$\underline{C}F_3$ (*8*)	291.62	1.16	23.2

[a] The binding energies of peaks in *Figures 1b* and *2* have been corrected for charging in *Table 2*. Numbers in (*italics*) correspond to assignments used in *Table 2* for these peaks

In order to obtain a chemically reasonable fit for the labelled PP it has to be considered that there are both labelled and unlabelled C–O environments, producing two distinct chemical shifts with labelled C–O and adjacent hydrocarbon environments being shifted to higher binding energy. *Figure 3b* shows the TFAA labelling of a primary alcohol. From the monomer structure, and high retention of hydroxyl measured in the PP[3], we believe that the majority of alcohol environments in the PP exist as primary alcohols, and any contribution from secondary or tertiary alcohols is most probably too small to affect the peak fit.

The fit in *Figure 4* of the C 1s core-level spectrum of labelled PP has been made assuming splitting in the hydrocarbon and C–O peaks on labelling. The new peaks are fitted with the same intensity as the CF_3 peak, and a similar f.w.h.m. has been used throughout the spectrum (1.15 eV). In *Figure 4*, the separation between hydrocarbon unaffected by labelling and C–O–C environments is 1.59 eV, within 0.1 eV of that used in the

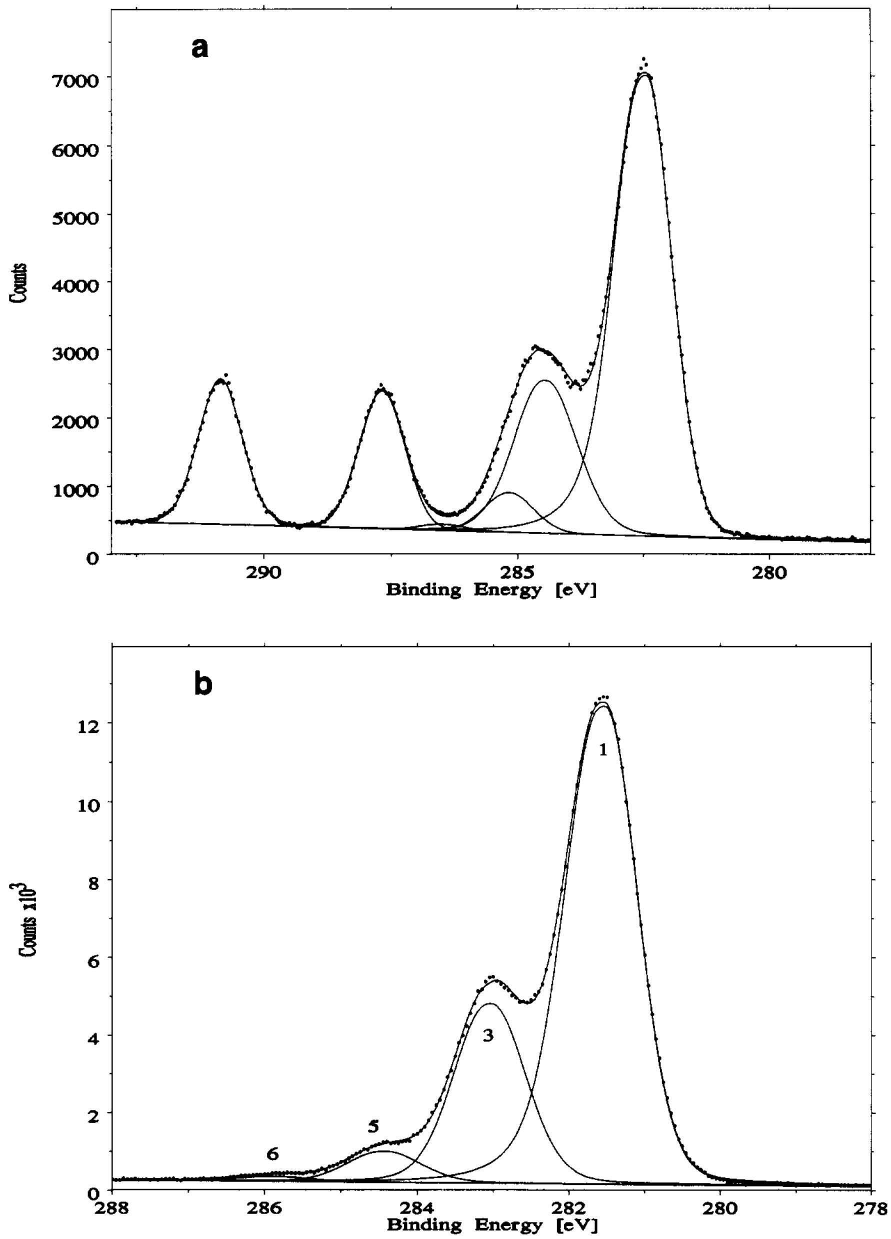

Figure 1 Labelled and unlabelled PP C 1s core-level fits using peaks for hydrocarbon, C–O, C=O, O–C=O, O=C–CF_3 and CF_3. Uncorrected binding energies of peaks given in *Table 1*. Peak numbers correspond to those assigned in *Table 2*

Table 2 Corrected C 1s binding energies obtained from PVA and PP

	C 1s core level								F 1s
	(*1*) $\underline{C}H$	(*2*) $\underline{C}H(CX)_n$[a]	(*3*) $\underline{C}OR$[b]	(*4*) $\underline{C}OX$	(*5*) $\underline{C}=O$	(*6*) $\underline{C}O_2R$	(*7*) $O\underline{C}(O)CF_3$	(*8*) $\underline{C}F_3$	(*9*) $C\underline{F}_3$
PVA	285.00		286.47						
PVA + TFAA		285.87 ($n=2$)		287.58			290.40	293.52	689.03
PP	285.00		286.50		287.90	289.33			
PP + TFAA	285.00	285.59 ($n=1$)	286.59	287.35	287.90	289.30	290.33	293.52	688.97

[a] X = –$OC(O)CF_3$
[b] R = H or C

fit of the unlabelled PP. In the previous fit of the labelled PP (*Figure 1a*) the position of the CF_3 peak was 293.41 eV, with hydrocarbon referenced to 285 eV. In this fit, the CF_3 peak appears at 293.52 eV. This discrepancy (0.11 eV) implies that the referencing of the hydrocarbon peak in *Figure 1a* to 285 eV was not strictly accurate. In order to demonstrate the presence of the β shift in the labelled PVA, the CF_3 peak was corrected to 293.41 eV. This gave a β shift of 0.76 eV. However, using the more chemically correct fit of *Figure 4*, referencing the CF_3 in labelled

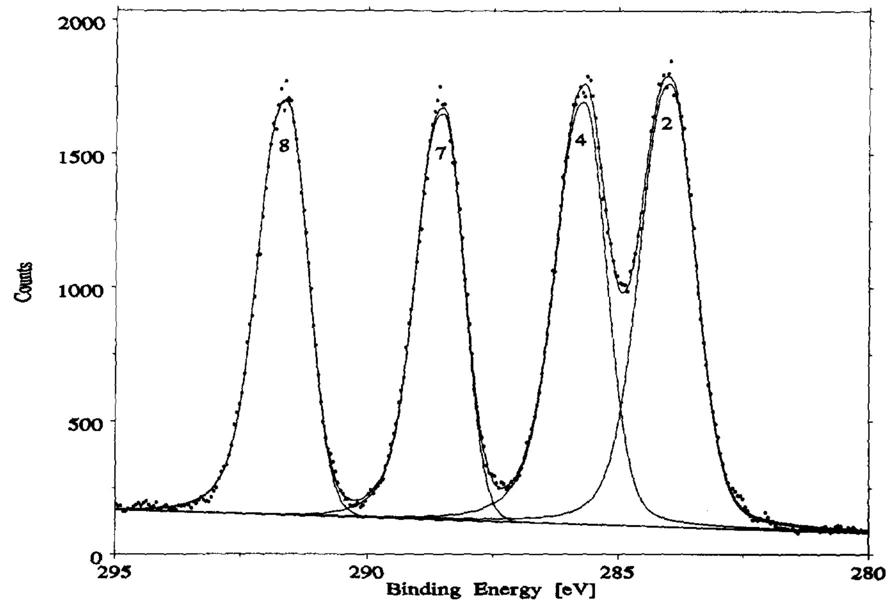

Figure 2 Labelled PVA C 1s core-level fits. Uncorrected binding energies of peaks given in *Table 1*. Peak numbers correspond to those assigned in *Table 2*

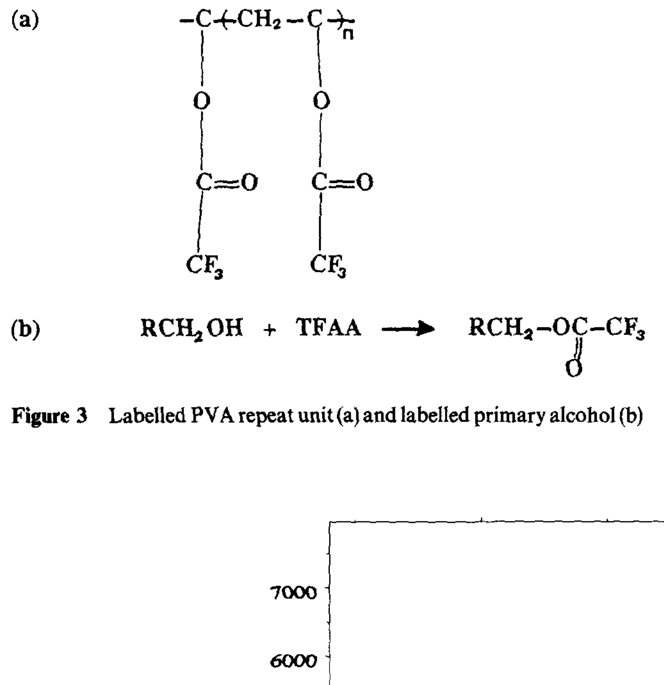

Figure 3 Labelled PVA repeat unit (a) and labelled primary alcohol (b)

PVA to 293.52 eV, the β-shifted carbon appears at 285.87 eV, i.e. a β shift of 0.87 eV. Similarly, the position of the C–O peak in labelled PVA is now at 287.58 eV, a chemical shift of 2.58 eV, which is 1.08 eV larger than the normal shift for C–O.

The best fit for the PP was obtained using a chemical shift of 2.35 eV for labelled hydroxyls, which is close to that deduced from the labelled PVA (2.58 eV). The shift of the β-CH_2 group found to give the best fit was 0.59 eV, slightly less than that deduced from the labelled PVA (0.87 eV). This is probably because in the PVA the β-CH_2 group is influenced by two TFAA tags (*Figure 3a*). In the PP there will only be a very low occurrence of hydrocarbon environments β to two hydroxyls.

Table 2 summarizes the binding energies for the

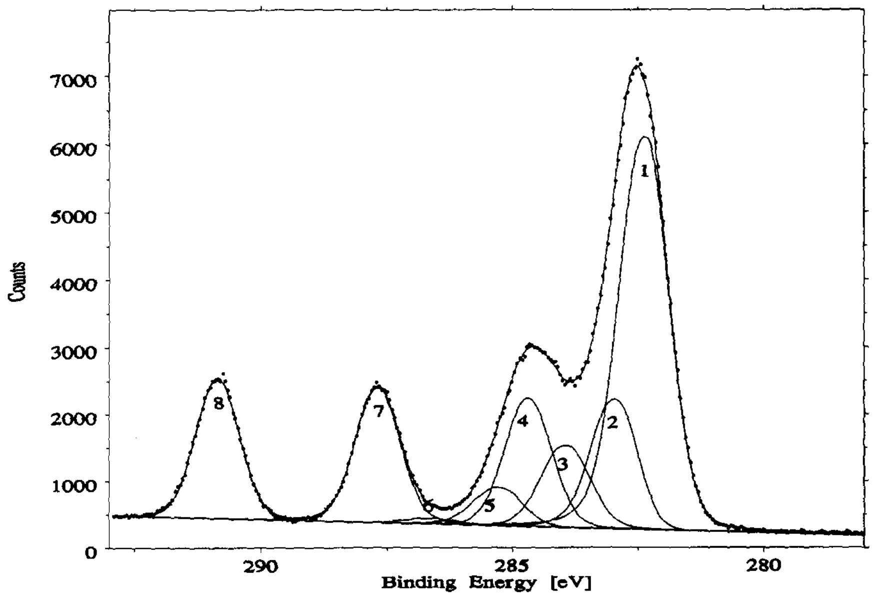

Figure 4 Labelled PP C 1s core-level fit using additional peaks for β-shifted CH_2 and labelled C–O. Corrected binding energies for peaks *1–8* given in *Table 2*

functional groups in the labelled and unlabelled PP and the labelled PVA after appropriate charge referencing.

CONCLUSIONS

β shift effects in polymers have been widely reported, particulary in fluorine-containing systems, owing to the strong electron-withdrawing capacity of this atom[9]. In the TFAA-labelled PP and PVA, β shifts of ca. 0.6 eV and ca. 0.9 eV, respectively, were detected due to $-OC(O)CF_3$.

The β shift due to $-CO_2R$ was predicted theoretically by Meier and Pijpers[10] and has been demonstrated experimentally in several high-energy-resolution X.p.s. studies[8,11]. In unmonochromated X.p.s., β shifts are usually small compared with the C 1s component linewidths and are not necessarily required in peak-fitting work. However, in monochromated X.p.s., it is essential to consider β shift effects in order to obtain chemically reasonable curve-fitting results, and to obtain binding energy consistency in related materials.

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