

XPS Study of Dimethylolurea Polymers and Hollow Fibers Modified by These Polymers. II. XPS Study of Hollow Fibers Modified by Dimethylolurea Polymers

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SYNOPSIS

Polysulfone ultrafiltration hollow fibres are modified on the surface with polymers obtained by polycondensation of dimethylolurea (DMU). Depending upon the reaction conditions, polymers on the surface present a gel or a film form. In the first case the membranes are called "gel-supported" and in the second case "coated." Modified and unmodified polysulfone membranes were analysed by XPS spectroscopy. The modifications observed on a modified membrane were studied by reference to the previous article dealing with XPS analysis of gel and film DMU polymers. The study showed that gel-supported membranes are modified by a polymer of a gel-type chemical structure whereas coated membranes are modified by a polymer of film-type chemical structure. The nature of the support, polysulfone, does not affect the final form of the polymer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The most serious operational constraint in the use of biological solution ultrafiltration with polysulfone membranes is that of fouling. This behaviour is often assigned to the hydrophobic character¹⁻³ of the polysulfone that involves nonselective adsorption of proteins onto the membranes. Therefore, to limit this problem a lot of work have been done to increase surface hydrophilicity by chemical reaction, for example sulfonation of polysulfone,⁴⁻⁶ or by coating with hydrophilic components⁷⁻⁹ or surfactant.^{10,11}

Among the possible hydrophilic components, polymers obtained by polycondensation of dimethylolurea (DMU) coated onto polysulfone membranes should give good hydrophilicity because DMU has carbonyl and hydroxy functional groups. Therefore, we modified polysulfone membranes with this kind of polymer.

Depending upon the reaction conditions, polycondensation gives a gel or a film form of the polymer. So two kinds of modified membranes are obtained: when they are obtained using gel reaction conditions they are called gel-supported, whereas they are called coated after being prepared by film reaction conditions. The first has been patented.¹²

In part I of this article,¹³ we showed by XPS that the gel form is mainly composed of dimethylene ether groups whereas in the film there are essentially diaminomethylene groups. Here, we will describe the synthesis of modified membranes and their studies by XPS. The aim of this work is to determine if polycondensation on the membrane modifies the final form of the polymer. Previously we analysed the unmodified polysulfone by XPS.

EXPERIMENTAL

Materials

The membranes were microfiltration polysulfone hollow fibres produced by the Lyonnaise des eaux-

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Dumez company. They had a mean pore diameter of 150 nm, an internal diameter of 0.86 mm, and an external diameter of 1.35 mm. The hydraulic permeability coefficient was 31.10^{-10} m/s·Pa (which corresponds to a flux of 1.12 m³/h·m³ bar). They were spun using a wet-dry technique.¹⁴

Before utilisation, the fibres were washed several times with ultrafiltered water and dried overnight at 40°C.

Sample Preparation

Sample membranes, about 5-cm long were washed and dried. After that, they were modified using an aqueous solution containing 0.5% ammonium chloride (Prolabo) with 3% DMU (Prolabo). This solution exhibits a very low acidity (pH 6.8).

Gel-supported membranes were obtained by immersion of the polysulfone membranes into the modification solution that was maintained at room temperature (20–25°C) with slow stirring (60 rpm) for 2 days. In such a way, polycondensation occurs slowly in the presence of an excess of water and gel should be obtained.

Coated membranes were obtained by immersion of the polysulfone membranes into the modification solution that was maintained at room temperature

(20–25°C) with slow stirring (60 rpm). Imbibing time was fixed at 5 hours to insure that the DMU and NH₄Cl diffused into the whole support membrane. Excess solution was then drained off and the DMU-containing membranes transferred to an oven. The oven was heated to 80°C for 30 min. The oven was then cooled and the fibres removed.

After that, in both cases, modified membranes were washed several times with a mixture of water/ethanol (30/70, v/v), and flattened with a slow crushing, washed again and dried overnight at 40°C.

The chemicals were of p.a. grade and the water was ultrafiltered and passed over an ion exchanger.

XPS Analysis

The XPS studies were performed with an XPS lab Mk II apparatus (V.G.) spectrometer, using non-monochromatized aluminum radiation from an AlK α X-ray source (1486.6 eV photons) and a three-channel electron detector. In order to avoid any degradation under radiation, the X-ray power source was limited to 100 W (10 mA, 10 kV) and the analyser pass energy fixed at 50 eV (survey scan) and at 20 eV (region scans). Typical operating pressures were 10^{-9} mbar. Calibration was made by reference to aliphatic carbon C_{1S} (E_b = 285 eV).

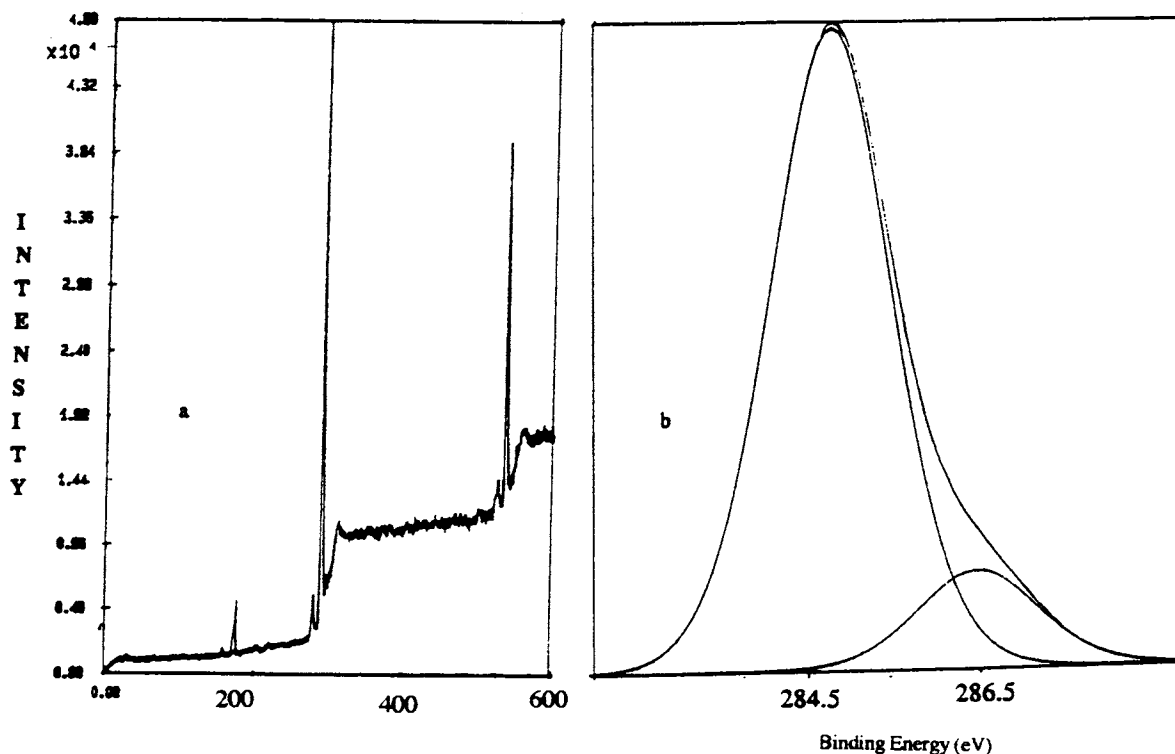
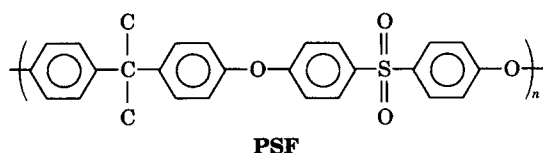


Figure 1 The (a) survey and the (b) C_{1S} core-level XPS spectra for polysulfone.

RESULTS AND DISCUSSION

XPS Study of Polysulfone Membranes

The survey XPS spectrum is represented in Figure 1. The C_{1s} , O_{1s} , and S_{1s} spectral regions yielded 81.3, 15.7, and 3% of these elements, respectively. These values are close to those calculated theoretically that are for C, 84.4, for O, 12.5, and for S, 3.1%. The chemical structure of polysulfone represented below shows the presence of three kinds of carbons. They should have different binding energies.



As a matter of fact polysulfone contains C—C or C=C carbons, C—S carbons, and C—O carbons. However, the electronegativity of S is close to that of C. The shift of C due to N should be very low, and the contribution of the C—N atoms can be added to the C—C atoms. Then the carbon peak was decomposed using two peaks C_1 and C_2 . This is in good agreement with the shape of the peak (Fig. 1). The result of this decomposition is reported in Table I. The peaks obtained at 284.8 and 286.8 eV were ascribed to C—C or C—S and C—O, respectively.

These results should be compared to the XPS analysis of PSF carried out by Clark and al.¹⁵ They decomposed the carbon signal into three peaks. The binding energy and the amount of each component are reported in Table I. The carbon peak obtained at 285 eV is ascribed to C—C, the carbon at 285.6 eV to C—S, and the last one at 286.6 eV to C—O. We noted that the binding energy of C—S is effectively close to the binding energy of C—C (the difference is only 0.6 eV). The approximation we made in adding up the two peaks corresponding to C—C and C—S appears reasonable. We also noted that the intensity of the two peaks corresponding to C—C and C—S determined by Clark and al.,¹⁵

equal to 89%, is close to the value we obtained for these two carbons (87%).

XPS Study of Gel-Supported and Coated Membranes

The survey XPS spectra of these two kinds of membranes are represented in Figure 2. They show the presence of C at 286.2 eV, N at 400.2–400.1 eV, O at 532.4 eV, and S at 168.2–167.9 eV. These binding energies are reported in Table II, as well as the results of quantitative XPS analysis of PSF and gel and film-DMU polymers.

The S atom is only present in PSF and N is only present in DMU. The fact that these two elements (S and N) appear in XPS spectra of modified membranes means that both PSF and DMU are analysed. Modified membranes can be considered like a mixture of PSF and DMU. From the C_{1s} , O_{1s} , N_{1s} , and S_{1s} spectral regions, the amount of these elements, and thus the N, O, and S to C ratio can be reached. They are reported in Table II.

Due to the fact that PSF does not contain N, the fraction f of PSF and $(1 - f)$ of DMU analysed on modified membranes can be calculated from the N/C atomic ratios determined on modified membranes and on DMU polymer, using the following relation:

$$(N/C)_{\text{mod mb}} = (N/C)_{\text{DMU}} \cdot (1 - f)$$

where mod mb is the modified membrane and DMU is the DMU polymer (gel or film). Therefore, in the gel-supported sample the fraction f_1 of PSF is equal to 0.5 and the fraction $(1 - f_1)$ of DMU is also equal to 0.5. In the sample of coated membrane the fraction f_2 of PSF is equal to 0.8 and the fraction $(1 - f_2)$ of DMU is equal to 0.2.

More DMU was present when DMU-polymer was obtained with the gel reaction conditions. This is in a good agreement with the sample preparation.

In both cases, the C_{1s} peak appears to include three components (Fig. 3). Consequently, the decomposition was performed using three peaks C_1 , C_2 , and C_3 . The binding energy of each peak component is reported in Table III. They are close in

Table I Comparison of Binding Energies and Amounts of Carbon Present on Surface of PSF Membrane

| | Binding Energies (eV) | | | Proportions (%) | | |
|-------------------------------------|-----------------------|-------|-------|-----------------|-----|-------|
| | C_1 | C—S | C_2 | C_1 | C—S | C_2 |
| PSF membrane | 284.8 | | 286.8 | 87 | | 13 |
| PSF from Clark et al. ¹⁵ | 285 | 285.6 | 286.6 | 82 | 7 | 11 |

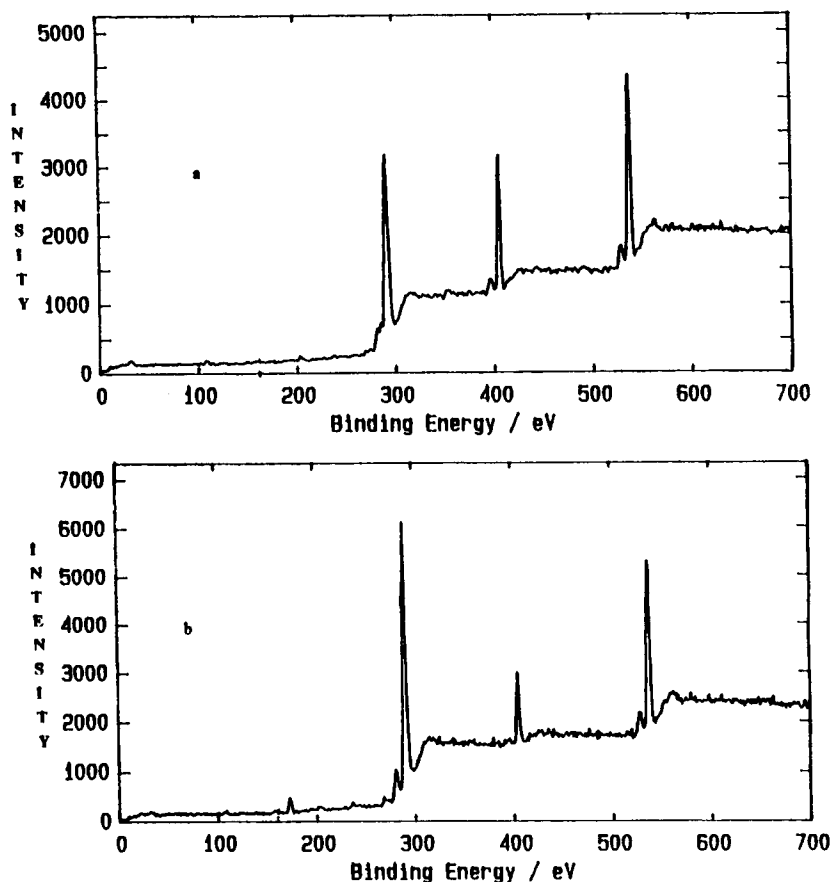


Figure 2 The survey XPS spectra of (a) gel-supported and (b) coated membranes.

both samples (gel-supported and coated membranes). Their positions are also rather close to those obtained by gel and film XPS analysis (Table III).

We showed that the carbon peak of PSF can be decomposed using two peaks C_1 and C_2 (Tables I, III). We found that their binding energy is close to the position of carbons C_1 and C_2 obtained with modified membranes and of course, with gel and film DMU. Therefore, in the XPS spectra of modified

membranes, the intensities of carbons C_1 and C_2 are due to the contribution of both PSF and DMU. The intensities of C_3 only arises from DMU.

From the fractions of PSF (f) and of DMU ($1 - f$) determined in modified membranes and from the amount of carbons in pure PSF ($C_{1\text{PSF}}$, $C_{2\text{PSF}}$) and in pure DMU ($C_{1\text{DMU}}$, $C_{2\text{DMU}}$, $C_{3\text{DMU}}$), it is possible to calculate the theoretical contributions $C_{1\text{Th}}$, $C_{2\text{Th}}$, $C_{3\text{Th}}$ of DMU in the mixture with the relations below:

Table II Binding Energies and Ratio to C of Atoms Present on Various Surfaces

| | Binding Energies (eV) | | | | | | |
|---------------|-----------------------|-------|-------|-------|------|------|-------|
| | C | N | O | S | N/C | O/C | S/C |
| Gel-supported | 286.2 | 400.2 | 532.4 | 168.2 | 0.27 | 0.30 | 0.008 |
| Coated | 286.2 | 401.1 | 532.4 | 167.9 | 0.11 | 0.23 | 0.02 |
| PSF | 285 | 0 | 531.8 | 168.1 | 0 | 0.19 | 0.03 |
| Gel-DMU | 287.2 | 400 | 531.9 | | 0.53 | 0.35 | |
| Film-DMU | 287 | 400.3 | 532.5 | | 0.54 | 0.37 | |

$$C_{1Th} = (f \cdot C_{1PSF} + (1 - f) \cdot C_{1DMU}) \cdot 100$$

$$C_{2Th} = (f \cdot C_{2PSF} + (1 - f) \cdot C_{2DMU}) \cdot 100$$

$$C_{3Th} = (1 - f) \cdot C_{3DMU} \cdot 100.$$

In the case of gel-supported membranes, the theoretical ratios of each C type are, respectively: $C_{1Th} = 54\%$, $C_{2Th} = 31\%$, and $C_{3Th} = 15\%$. These values are close to the experimental ones: $C_1 = 55\%$, $C_2 = 32\%$, and $C_3 = 13\%$. It can be deduced that the DMU-polymer on the surface of the gel-supported membrane has a gel structure.

In the case of the coated membranes the theoretical ratios of each C type are, respectively: $C_{1Th} = 77.1\%$, $C_{2Th} = 16.3\%$, and $C_{3Th} = 6.6\%$.

These values are rather close to the experimental ones, which are $C_1 = 75\%$, $C_2 = 16\%$, and $C_3 = 9\%$. It seems that the structure of the DMU-polymer on the surface of the coated membrane has a film structure. In this last case, the agreement between the theoretical and experimental values is not as good as in the first case. This could be due to the limited modification of the coated membrane. The fraction of modification $(1 - f)$ was equal to only 0.2.

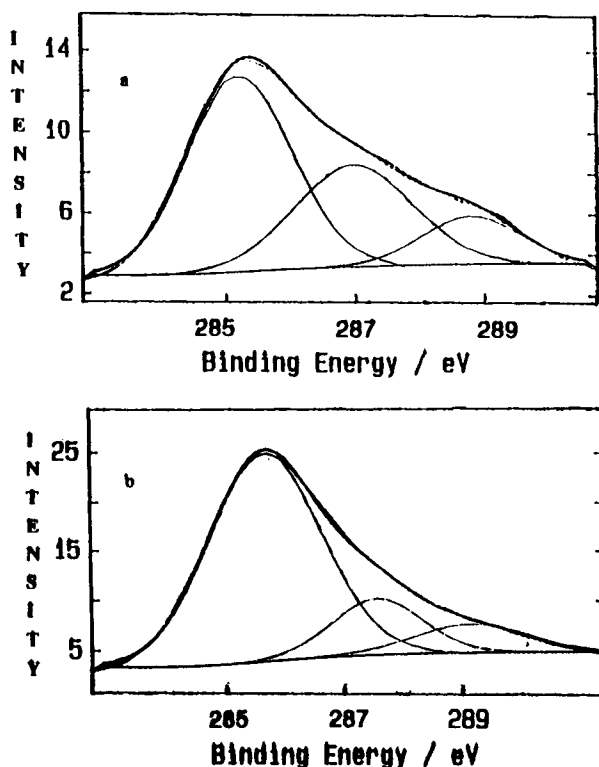


Figure 3 The C_{1s} core-level spectra of (a) gel-supported and (b) coated membranes.

Table III Binding Energies and Amounts of Carbon Present at Various Surfaces

| | Binding Energies (eV) | | | Proportions (%) | | |
|---------------|-----------------------|-------|-------|-----------------|-------|-------|
| | C_1 | C_2 | C_3 | C_1 | C_2 | C_3 |
| Gel-supported | 285.1 | 287.1 | 289.1 | 55 | 32 | 13 |
| Coated | 285.6 | 287.4 | 288.9 | 76 | 16 | 8 |
| PSF | 284.8 | 286.8 | 0 | 87 | 13 | 0 |
| Gel-DMU | 285 | 287.2 | 289.2 | 23 | 49 | 28 |
| Film-DMU | 285.4 | 287.4 | 289.1 | 42 | 28 | 30 |

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