

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

I. XPS Study of Dimethylolurea Polymers

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SYNOPSIS

Polycondensation of dimethylolurea leads to the formation of a gel or a film according to the experimental conditions. Both forms of the polymer would be characterized by a specific chemical structure, i.e., dimethylene ether or diaminomethylene, respectively. We studied both forms of dimethylolurea polymer by XPS and have shown that it is possible to distinguish them using this technique. The study of the carbon peak shape attributed mainly a dimethylene ether structure to the gel and a diaminomethylene structure to the film.

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INTRODUCTION

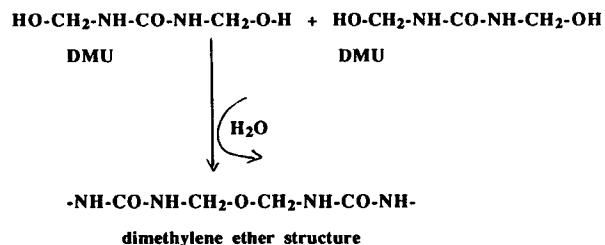
Electron spectroscopy for chemical analysis (or X-ray photoelectron spectroscopy [XPS]) is one of the most interesting methods for chemical characterization of sample surfaces. Introduced by Siegbahn and co-workers¹ in 1967, this technique has been used in several fields such as chemistry and, more recently, in biochemistry. XPS allows the determination of surface composition and the environment in which the atoms are sited to a depth of 30–40 Å. Therefore, the method has been widely used for the study of surface modifications by chemical reactions. For example, Zadorecki and Rönnhult² used the technique to analyze the surface of paper sheets that had been treated with trichloro-*s*-triazine in order to increase the hydrophobicity of the surface.

It has also been applied to choose among different isomeric structures, the real one that is formed by the reaction of 2-4-pentadion and H₂S, in the presence of concentrated HCl.³ Therefore, we used this method for the study of the polycondensation of di-

methylolurea (DMU). Depending upon the reaction conditions, polycondensation can lead two different forms of polymers:

1. When polycondensation is carried out at low temperatures, a gel form is obtained. It can absorb about 50% of its own weight of water.
2. When polycondensation is carried out at high temperatures, a film form is obtained. It can absorb about 5% of its own weight of water.

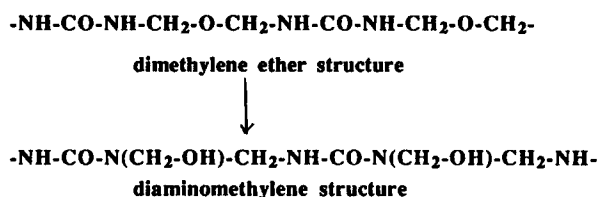
At low temperature, polycondensation might occur by successive etherification reactions followed by water elimination, leading to a dimethylene ether structure as shown in the mechanism⁴ below:



Films obtained at high temperatures, however, might essentially be composed of a majority of diamino-methylene structures due to the relative instability

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of the dimethylene ether groups,⁴ which can undergo transformation into diaminomethylene structures like that represented below:



De Jong and De Jonge⁵ studied the mechanism of formation of this kind of polymer, called urea-formaldehyde resins because they are obtained from urea and formaldehyde. In the particular case of DMU, 2 mol of formaldehyde react with 1 mol of urea.

To understand the structure of urea-formaldehyde resins, several analytical tools and techniques such as carbon-13 solution NMR,^{6,7} nitrogen-15 NMR,⁸ Raman spectroscopy,⁹ and infrared spectroscopy have been used. The structure, however, is still ambiguous. Furthermore, due to the difficulty of instrumental analysis, progress in the studies of gelation has been relatively slow. Gelation has been followed using X-ray, differential thermal analysis, infrared spectroscopy, thermal gravimetric analysis, and NMR.¹⁰⁻¹³

It appeared interesting to us to study this polymer using other techniques, such as XPS. It is well known that it is sensitive to the chemical structures of molecules. In this first article, we report the results of an XPS study of the surface of DMU polymers obtained by two different experimental polyconden-

sation conditions leading to either a gel (gel-DMU) or a film form (film-DMU). In the second article, we consider polysulfone ultrafiltration hollow fibers modified on the surface by DMU polymers and analyzed by XPS. They were obtained in the same experimental conditions as those described in the first article. The aim of these modifications is to enhance the hydrophilicity of the fibers in order to decrease fouling during ultrafiltration of macromolecular solutions, since fouling appears to be less important with hydrophilic membranes.¹⁴

In the present article, we first consider the synthesis of the two different polymers of DMU (gel and film) and their analyses by the usual methods like elemental analysis and infrared spectroscopy. Then, we examine the results of gel-DMU and film-DMU XPS analysis. We show that it is possible to distinguish between them using this method.

EXPERIMENTAL

Sample Preparation

The DMU polymers were obtained from an aqueous solution containing DMU and a catalyst: orthophosphoric acid, H₃PO₄ (Prolabo), or ammonium chloride, NH₄Cl (Prolabo). In the latter case, very low acidity of the solution (pH 6.8) decreased the polycondensation rate. More accurately, the polymers that were analyzed by XPS were obtained from a solution containing 3% DMU and 0.5% NH₄Cl and

Table I Elemental Analyses of DMU Polymers Obtained in Different Conditions

Solution Composition	Polycondensation Treatment			Polymer Form	
1. 3% DMU; 0.5% H ₃ PO ₄	4°C in solution			Gel	
2. 3% DMU; 0.5% H ₃ PO ₄	20-25°C in solution			Gel	
3. 3% DMU; 0.5% NH ₄ Cl	20-25°C in solution			Gel	
4. 3% DMU; 0.5% NH ₄ Cl	80°C until solvent evaporation			Film	
5. 3% DMU; 0.5% H ₃ PO ₄	80°C until solvent evaporation			Film	
DMU Polymer Experimental	C	H	N	O	C/N
1	21.7	45.1	18.5	14.5	1.1
2	20.4	44	17.1	18.4	1.2
3	22.8	46.7	17.7	13.3	1.3
4	22.1	46.8	17.4	13.9	1.2
5	21.6	44	18.4	16	1.1

1. when the solution was maintained at room temperature (20–25°C), with slow stirring (60 rpm) for at least 48 h, gel-DMU was obtained; and
2. when the solution was heated to 80°C until total solvent evaporation, DMU-film was obtained.

After that, all polymers were washed several times with a mixture water/ethanol (30/70; v/v), and dried overnight at 40°C. The chemicals were of p.a. grade and the water was ultrafiltered and passed over an ion exchanger.

Sample Analysis

The samples were analyzed by elemental analyses, infrared spectroscopy, and XPS. The elemental analyses (CHNO) were performed using a Carlo Erba 1106. The infrared absorbance spectra of semisolid polymers were taken as thin films between KBr discs. Absorbance spectra were obtained at 2 cm^{-1} resolution between 4000 and 500 cm^{-1} on a Perkin-Elmer spectrometer. The XPS studies were performed by using an ESCALab Mk II apparatus (V.G) spectrometer, using nonmonochromatized aluminum radiation from an $\text{AlK}\alpha$ X-ray source (1486.6 eV photons) and a three-channeltrons de-

tector. To avoid any degradation under radiation, X-ray source power was limited to 100 W (10 mA, 10 kV) and the analyzer pass energy fixed at 50 eV (survey scan) and at 20 eV (regions scans). Typical operating pressures were 10^{-9} mbar. Calibration was made by referencing to aliphatic carbon $\text{C}_{1\text{S}}$ ($E_b = 285$ eV).

RESULTS AND DISCUSSION

Five different samples of polymers were prepared using similar methods to those described in the Experimental section. They were studied by elemental analysis (Table I). The results show that their chemical composition does not depend on the experimental conditions or physical form.

The infrared spectra of gel and film polymers are similar (Fig. 1). They show two characteristic bands of urea derivatives¹⁵ at 1651 and 1548 cm^{-1} ascribed to C=O and CN, respectively. Therefore, gel and film cannot be distinguished by these two methods. Consequently, we have tried to identify them by XPS.

The survey XPS spectra of gel and film are represented in Figure 2. They are close. The $\text{C}_{1\text{S}}$, $\text{O}_{1\text{S}}$, and $\text{N}_{1\text{S}}$ spectral regions gave the amount of these elements, which are reported in Table II as well as

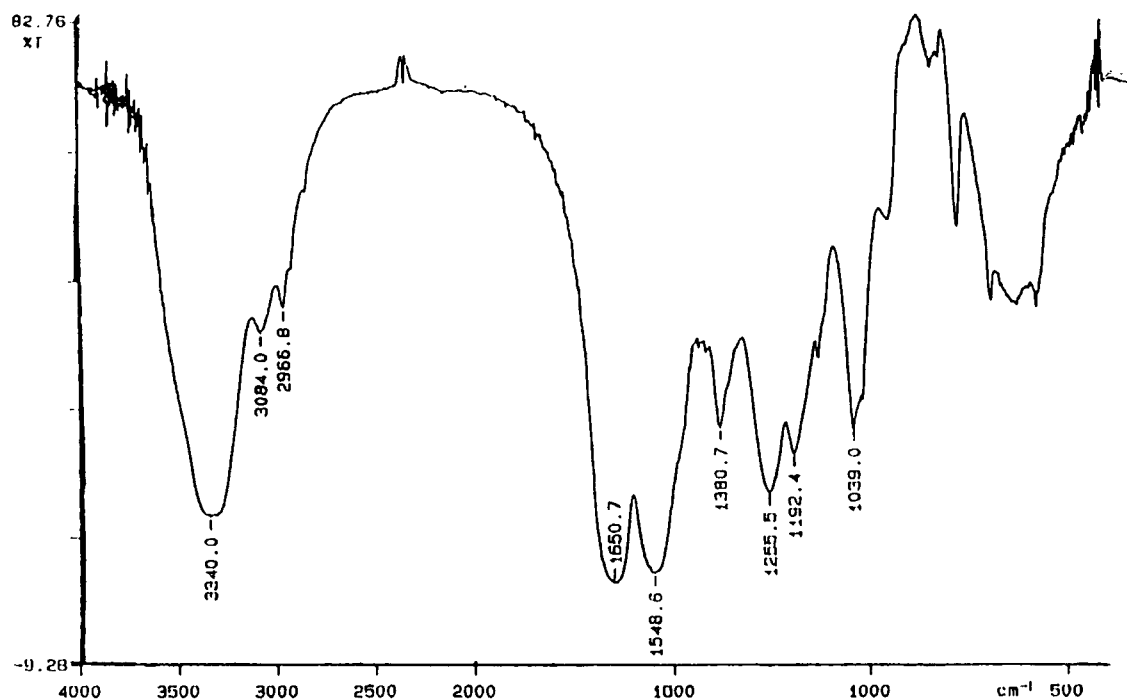


Figure 1 Infrared spectrum of gel and film polymers.

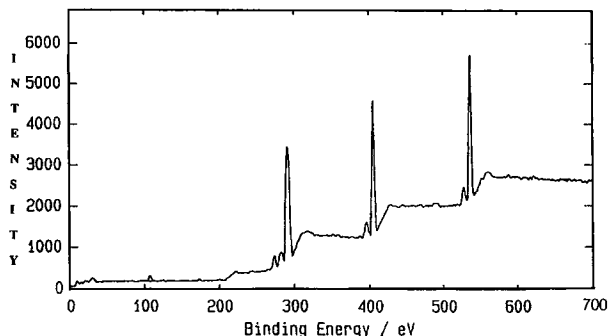


Figure 2 The general ESCA spectra of gel and film.

the carbon-to-nitrogen ratio. The values are similar for the two forms, but the shapes of the C_{1s} peak seem different (Fig. 3).

In both cases, the peak appears to be constituted by three components. Consequently, the decomposition was performed using the three peaks C₁, C₂, and C₃. The binding energy and the amount of each peak component are reported in Table III. As can be seen, the relative amounts of each depend strongly on the form, whereas the binding energy of the peaks are rather close in both polymer forms: 285–285.4 eV for C₁, 287.2–287.4 eV for C₂, and 289.2–289.1 eV for C₃. C₁ represents atoms linked only to carbon or hydrogen, and C₂ and C₃, carbon atoms bonded to electronegative atoms like nitrogen or oxygen, which are elements present in the dimethylolurea structure.

We can assign the peaks by considering the polycondensation mechanisms proposed in the Introduction. They were assigned (a) a majority dimethylene ether structure for the gel form and (b) a majority diaminomethylene structure for the film, as represented below:

- (a) Dimethylene ether structure essentially in gel form:

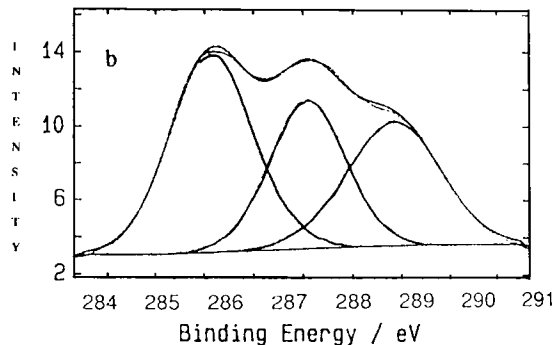
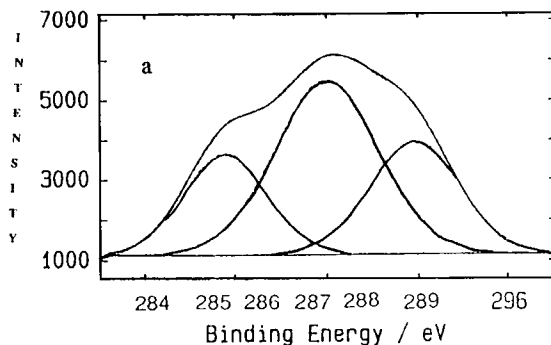
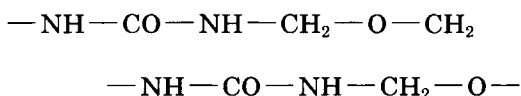
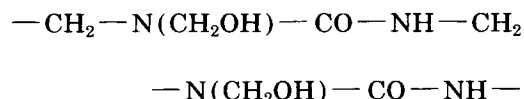


Figure 3 The C_{1s} core-level spectra for (a) gel and (b) film.

- (b) Diaminomethylene structure essentially in the film form:



We can note that in dimethylene ether there are mainly two different carbons, i.e., N—CH₂—O and N—CO—N, which will be called, respectively, C₂ amino ether and C₃ carbonyl. In the diaminomethylene structure, we can distinguish three different carbons: Two correspond to the C₂ and C₃ atoms observed in the dimethylene ether structure, and the third one, called C₁ diamino, which is linked to two nitrogens N—CH₂—N. Therefore, three carbon types have to be considered:

Table II The Binding Energies and Amounts of Atoms Present on the Surface of Gel-DMU and Film-DMU

	Binding Energies (eV)			Proportions (%)			
	C	N	O	C	N	O	C/N
Gel-DMU	287.2	400	531.9	53.1	28.3	18.6	1.8
Film-DMU	287	400.3	532.5	52.4	28.2	19.4	1.8

Table III Binding Energies and Amounts of Carbon Present on the Surface of Gel-DMU and Film-DMU: Comparison with Theoretical Values

	Binding Energies (eV)			Proportions (%)			
	C ₁	C ₂	C ₃	C ₁	C ₂	C ₃	C ₂ /C ₃
Gel-DMU	285	287.2	289.2	23	49	28	1.75
Film-DMU	285.4	287.4	289.1	42	28	30	0.9
Theoretical gel				0	66	33	2
Theoretical film				33	33	33	1

C₁: N—CH₂—N diamino carbon

C₂: N—CH₂—O amino ether carbon

C₃: N—CO—N carbonyl carbon

The binding energies of these three carbon atoms can be estimated from Wagner et al.¹⁶ considering the chemical displacement due to different groups linked to these atoms. Then, the binding energies are estimated at

- −286 eV for C₁
- −287.1 eV for C₂
- −289 eV for C₃

The binding energies of C₂ and C₃ are close to the experimental values, which are 287.2–287.4 eV for C₂ and 289.2–289.1 eV for C₃ obtained both with gel and film XPS analysis. This effectively indicates that there are N—CO—N and O—CH₂—N carbon in the gel and film. But the carbon peak C₁ at 285–285.4 eV obtained by XPS is only characteristic of aliphatic carbons that are due to contamination coming from XPS vacuum pumping or sample preparation, because neither dimethylene ether nor diaminomethylene structures contain aliphatic carbons. This contamination can be seen in the ratio C/N, which is greater (1.8) than the one obtained by chemical analysis (1.1–1.3) (Table I). Therefore, we can explain the presence of C₁ peaks in the gel spectra essentially by contamination.

But the film spectra should theoretically show the presence of diamino carbon N—C—N at 286 eV, whereas a peak is observed at 285.4 eV. This result can be explained by considering the diamino carbon N—C—N to be shifted to 285.4 eV by overlapping with the aliphatic carbon peak. We have shown by XPS that the two forms have the same binding energy for the three carbons. But as can be seen in Table III, the two forms present different

amounts of each component, which correspond to different chemical structures.

Theoretically, if we only consider carbons C₂ and C₃ of structures (a) and (b), we can note that the C₂ to C₃ ratio is equal to “2” for the dimethylene ether structure (gel-DMU) and to “1” for the diaminomethylene structure (film-DMU). This XPS study shows that the C₂-to-C₃ ratio is equal to “1.75” for the gel and “0.9” for the film. These values are close to the theoretical ones. Therefore, we can deduce that the structure of the gel is composed mainly of dimethylene ether groups, whereas in the film-DMU, there are essentially diaminomethylene groups.

CONCLUSION

We have shown by XPS that gel and film DMU polymer forms present different chemical structures. XPS can therefore be used for chemical structure determination as well as the usual methods like NMR, Raman spectroscopy, and so on and not just for surface characterization. Furthermore, this study can help us to understand the XPS analysis of polysulfone ultrafiltration membranes superficially modified by DMU polymers.

REFERENCES

1. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlson, I. Lindgren, and B. Lindberg, *ESCA Atomic Molecular and Solid State Structures Studied by Means of Electron Spectroscopy*, Almquist and Wiksells, Stockholm, 1967.
2. P. Zadorecki and T. Rönnhult, *J. Polym. Sci. Part A Polym. Chem.*, **24**, 737 (1986).
3. J. Hedmann, P. F. Heden, R. Norberg, C. Nordling,

- and B. J. Lindberg, *Spectrochim. Acta*, **26A**, 761 (1970).
4. J. A. Brydson, in *Plastics Materials*, 5th ed. Butterworths, London, 1989.
 5. J. I. De Jong and J. De Jonge, *Recueil*, **72**, 139 (1957).
 6. I. Svadjumovic, Z. Meic, and M. Bravar, *Nafta (Zagreb)*, **36**(12), 621 (1985).
 7. B. Tomita and H. Ono, *Netsu Kokasei Jushi*, **1**(1), 11 (1980).
 8. J. R. Ebdon, P. E. Heaton, T. N. Huckerby, W. T. S. O'Rourke, and J. Parkin, *Polymer*, **25**(6), 821 (1984).
 9. C. G. Hill, A. M. Hedren, G. E. Myers, and J. A. Koutsky, *J. Appl. Polym. Sci.*, **29**(9), 2749 (1984).
 10. B. Tomita, *J. Polym. Sci.*, **16**, 2509C (1978).
 11. B. Tomita and Y. Hirose, *J. Polym. Sci.*, **14**, 387 (1976).
 12. S. Chow and P. R. Steiner, *Holzforschung*, **29**, 4 (1975).
 13. P. R. Steiner, *Wood Sci.*, **7**, 99 (1974).
 14. E. Matthiasson, *J. Membr. Sci.*, **16**, 23 (1983).
 15. S. S. Jada, *J. Appl. Polym. Sci.*, **35**, 1573 (1988).
 16. C. B. Wagner, W. M. Riggs, L. E. Davis, J. S. Moulder, and G. E. Muilenberg, Eds., *Handbook of Perkin-Elmer Corp.*, 1979.

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