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An analysis of the surface chemical structure of polymethacrylate (Eudragit) film coating polymers by XPS

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Summary

The surface chemical composition of a range of polymethacrylate films has been examined in the solid state using X-ray photoelectron spectroscopy (XPS or ESCA). A good correlation between experimental and theoretical values was observed for both surface elemental ratios and the differing carbon environments within the C-1s envelope. The data suggest that for this series of polymers, the surface composition reflects that of the bulk. The XPS results are discussed in the light of previous surface analysis studies and the technique appears to have potential for the future study of pharmaceutical film coatings.

Introduction

At the present time, the majority of polymers in use as pharmaceutical film-coatings are substituted celluloses or methacrylate copolymers. The different methacrylate copolymers (Eudragit series) offer a range of physico-chemical properties and are utilised in a variety of controlled release applications. The type and frequency of the ester substituents in these polymers determines their water permeability (Okor, 1988) and pH-solubility characteristics (Lehmann, 1968) and therefore different members of the series may be employed as taste-masking or enteric coating agents, or as rate-controlling membranes in sustained release dosage forms. The surface chemistry of the polymers is important in terms of their dissolution and coating behaviour and hence, further knowledge of the polymer surface chemical structure may aid in the understanding of the interface phenomena of film coating.

X-ray photoelectron spectroscopy (XPS) has proved a potent tool for the characterisation of polymer surfaces and it has made a significant contribution to the analysis of biomedical polymers (Clark, 1978; Andrade, 1985). The technique is reviewed in detail elsewhere (Clark, 1978; Andrade, 1985), but in essence it provides a quantitative elemental analysis (except for hydrogen and helium), and also information on the chemical bonding within the surface layers of the polymer. In this paper we report on the applica-

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TABLE 1

Methacrylate copolymers used in this study

Trade name	IUPAC name
Eudragit™ S	Poly(methacrylic acid, methyl methacrylate)
Eudragit™ L	Poly(methacrylic acid, methyl methacrylate)
Eudragit™ E	Poly(butyl methacrylate, (2-dimethyl aminoethyl) methacrylate, methyl methacrylate)
Eudragit™ RS	Poly(ethyl acrylate, methyl methacrylate) trimethylammonioethyl methacrylate chloride

tion of XPS to investigate the surface properties of Eudragit polymer films.

Materials and Methods

Materials

The methacrylate polymers examined are listed in Tables 1 and 2 and were used as supplied from Rohm-Pharma (Darmstadt). Methanol (Analar grade, BDH, Poole) was double-distilled.

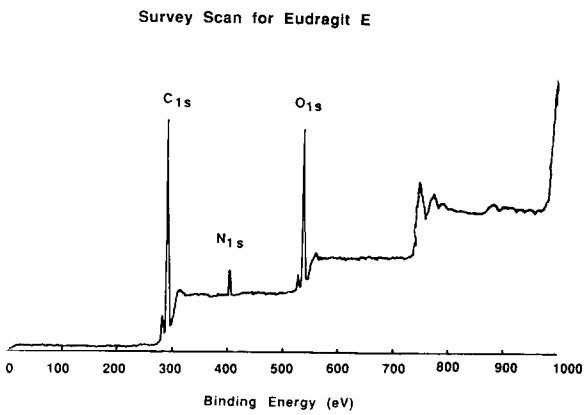


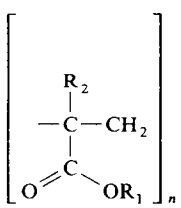
Fig. 1. Wide-scan spectrum for Eudragit E.

X-ray photoelectron spectroscopy

The polymers were studied as thin films (approx. 5–10 μm in thickness), spin-cast from a 1% solution in methanol onto a clean aluminium substrate. Samples were analysed within 60 min of casting using a VG Scientific ESCALAB Mk II spectrometer employing Mg κ_α X-rays ($h\nu$ = 1253.6 eV). The X-ray gun was operated at 120 W and spectra recorded at an electron take-off angle of 45°, corresponding to a depth of analysis of about 50 Å. A survey or wide scan spectrum (0–1000 eV), and also narrow (high-resolution) scans in the C-1s and O-1s regions were recorded

TABLE 2

Copolymer structure and composition



Type and relative residue frequency of side group R_1

Eudragit™	H	CH_3	C_2H_5	C_4H_9	$CH_2CH_2N(CH)_3$	$CH_2CH_2N^+(CH_3)_3$
S	1	2	–	–	–	–
L	1	1	–	–	–	–
E	–	1	–	1	2	–
RS	–	2	1 *	–	–	0.1

$R_2 = CH_3$ except for * when R_2 = H.

for all samples. The analyser was operated in fixed transmission mode with a pass energy of 50 eV for wide scans, and 20 eV for the high-resolution scans. Data acquisition and analysis was performed using a VGS 5000-S data system based on a DEC PDP 11/73 computer. A series of peaks, corresponding to shifts due to different chemical bonding, were fitted to the O-1s and C-1s envelopes using methodology described elsewhere (Sherwood, 1985). The recorded spectra were corrected for sample charging with reference to C–H/C–C at 285 eV in the C-1s envelope.

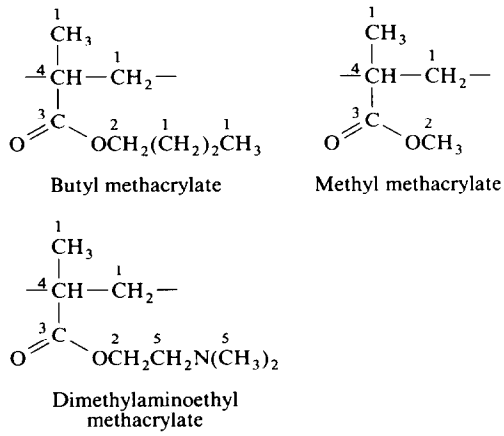
Results and Discussion

The wide scan spectra (e.g., see Fig. 1) showed that the samples appeared to be free from significant extraneous elemental contamination. The absence of an aluminium peak indicated that the films were both continuous and free from pinholes.

The surface elemental ratios determined experimentally by XPS are shown in Table 3 and are compared with anticipated theoretical values derived from the structural formulae. It can be seen that the experimental results show very good agreement with the anticipated theoretical values.

To aid the understanding of the following discussion, the structural formulae of the three component monomer residues comprising Eudragit E (as an example) are shown in Scheme 1. The different bonding environments for each of the carbon atoms are indicated by numbers.

High-resolution C-1s and O-1s peaks are shown in Fig. 2 for Eudragits E, RS and L. Curves



Scheme 1.

corresponding to four main chemical shifts were fitted to the C-1s peak envelopes.

The major C-1s component corresponds to the C–H/C–C carbon environment (indicated by no. 1 in Scheme 1). This arises from carbon atoms both from within the polymer backbone and also

TABLE 3

Elemental analysis of Eudragit copolymers by XPS

Sample	Atomic %		
	Carbon	Nitrogen	Oxygen
Eudragit S	70.7 (70.0) *	0 (0)	29.3 (30.0)
Eudragit L	70.3 (69.2)	0 (0)	29.7 (30.8)
Eudragit E	77.6 (74.4)	3.8 (5.1)	18.6 (20.5)
Eudragit RS	72.8 (71.6)	0.3 (0.5)	26.9 (27.9)

* Values in parentheses are theoretical values calculated from the structural formulae.

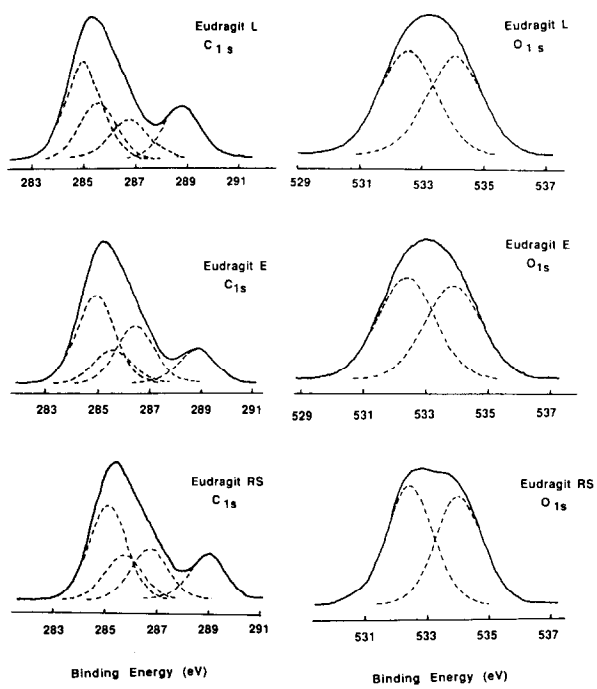


Fig. 2. High-resolution C-1s and O-1s envelopes for Eudragit E, L and RS.

TABLE 4

Experimental and theoretical percentages for chemical shifts within the C-1s envelope for Eudragit copolymers

(a) Sample	% C-1s envelope			
	C–C	O–C = O	C–COO (β)	C–O + C–N
	285 eV	289.2 eV	285.7 eV	286.6 eV
Eudragit S	45.0	21.0	21.0	13.0 *
Eudragit L	45.0	21.0	21.0	13.0 *
Eudragit E	39.0	14.0	15.0	33.0
Eudragit RS	40.0	19.0	19.0	21.0
* C–O only				

(b)	C–C	O–C = O	C–COO (β)	C–O	C–N	C–O + C–N
Eudragit S	42.9	21.4	21.4	14.3	0	14.3
Eudragit L	44.4	22.2	22.2	11.1	0	11.1
Eudragit E	37.9	13.8	13.8	13.8	20.7	34.5
Eudragit RS	39.2	19.6	19.6	19.6	1.9	21.5

from the ester side chains. The carbon peak at 286.6 eV corresponds to carbon singly bonded to oxygen C–O (no. 2, Scheme 1) which is generated from the alkyl ester side chain. The C-1s contribution at 289.2 eV, from carbon bonded to two oxygen species (no. 3, Scheme 1), arises solely from the acrylate function of the polymer backbone. In addition, a secondary chemical shift of 0.7 eV, as proposed by Pijpers and Donners (1985), is used for the carbon α to the ester linkage (no. 4, Scheme 1). The dimethylaminoethyl group of Eudragit E is fitted with C–N at 286.5 eV (no. 5, Scheme 1).

The theoretical and experimental values for the % ratio of the different carbon environments, derived from the shifts fitted to the C-1s peaks are presented in Table 4. There appears to be good correlation between the two sets of data. The close proximity of the chemical binding energies for the CH_3–N and C–O shifts (285.5 and 285.6 eV, respectively) prevents the separation of their individual contribution to the C-1s envelope and as a consequence, the results have been pooled. The good correlation between the theoretical and experimentally determined % composition appears to indicate that the near-surface chemistry of Eudragit films reflects closely that of the bulk chemical composition, and it is concluded that there is no preferential surface orientation of one or more of the monomer residues. More generally, the results show that this technique can both individually distinguish and resolve the surface chemical state of these methacrylate/acrylate copolymers and as such, appears to be a potent tool for the analysis of their surface composition both in a qualitative, and more importantly, in a quantitative manner. In a previous paper in this series (Wilding et al., 1989), we examined the surface structure of these polymers using a complementary surface chemical technique, static secondary ion mass spectrometry (SSIMS). The results demonstrated that the high degree of molecular specificity possible with SSIMS enabled the identification of specific diagnostic ions attributable to either the polymer backbone or the different ester substitutions. However, SSIMS information is essentially qualitative and the relative intensities of the ions do not always reflect the surface composition. It would appear therefore that the most advantageous approach is to combine the qualitative molecular specificity of SSIMS with the quantitative elemental and chemical state information obtained from XPS.

This combined approach should have significant potential for the study of pharmaceutical film coats and their performance. For example, XPS may permit the study of the changes in Eudragit polymer surfaces as a result of dissolution processes or additive incorporation. The combined use of XPS and SSIMS may allow the specific

identification of the film coating material on dosage forms, providing there is no significant contamination and that the complexity of the formulation is minimized. In addition, XPS may play a significant role in establishing polymer purity (Ratner, 1988), a strong pre-requisite for any material which is employed in pharmaceutical systems.

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