polymer reports

The surface characterization of model charged and sterically stabilized polymer colloids by SSIMS and X.p.s.

A. Brindley, M. C. Davies*, R. A. P. Lynn and S. S. Davis
Department of Pharmaceutical Sciences, University of Nottingham, University Park,
Nottingham NG7 2RD, UK

and J. Hearn
Department of Chemistry and Physics, Nottingham Polytechnic, Clifton Lane,
Nottingham NG11 8NS, UK

and J. F. Watts
Department of Materials Science and Engineering, University of Surrey, Guildford,
Surrey GU2 5XH, UK

(*Received 2 May 1991; revised 20 August 1991*)

X-ray photoelectron spectroscopy (X.p.s.) and static secondary ion mass spectrometry (SSIMS) have been applied to the surface chemical analysis of charged and sterically stabilized polymer colloids. The techniques provide complementary evidence for the surface orientation of both the charged polymer end groups and polymer chains responsible for the steric barrier. The findings are discussed in terms of the particle formation mechanisms and the biological interactions of such colloid systems.

(Keywords: static secondary ion mass spectrometry; X-ray photoelectron spectroscopy; polymer colloid; steric stabilization; surface analysis)

INTRODUCTION

Polymer colloids have found applications in a wide range of scientific fields including use as cell markers[1], in agglutination tests[2], colloid chemistry research[3] and in drug delivery system development[4]. In many areas the potential use of a colloidal system is dependent upon its surface properties. These may be tailored to produce desired particle characteristics by employing different monomers, with a range of physicochemical properties and, of interest to this report, various stabilizing species.

In a previous work[5] the surface composition of colloidal particles prepared using charged stabilization has been studied using the surface specific techniques static secondary ion mass spectrometry (SSIMS) and X-ray photoelectron spectroscopy (X.p.s.). In this report, we extend these studies to demonstrate the potential of these surface analytical techniques to the characterization of the interfacial polymer composition of polystyrene (PS) latices stabilized with poly(ethylene glycol) (PEG) chains designed to induce steric stabilization.

The synthesis of PEG stabilized polymer colloids has been outlined in detail previously[6]. Sterically stabilized particles have been prepared by the surfactant-free copolymerization of a hydrophobic monomer, styrene with a comonomer/stabilizer (macromonomer) methoxypoly(ethylene glycol) methacrylate (MeOPEGMA) in the absence of an added emulsifier in a similar manner to that described previously by Ottewill and Satgurunathan[6]. In addition, an identical monomer formulation has been prepared with persulphate initiation to allow the formation of colloid stabilized by both charged species and PEG chains. For comparison, a charged-stabilized latex was prepared by the polymerization of styrene alone, again in the absence of emulsifier[7].

EXPERIMENTAL

The charged PS (PS^{c}) latex was prepared by surfactant-free oil-in-water emulsion polymerization[7]. Styrene, purified by distillation, (0.909% w/v) was added to a sufficient quantity of double distilled quality water to give a final reaction volume of 50 ml. The potassium persulphate initiator (recrystallized twice from double distilled quality water) was added at a concentration of 0.05% w/v. A PS–MeOPEGMA (PS–PEG^{c}, i.e. charged) latex was prepared by the copolymerization of styrene (0.909% w/v) with MeOPEGMA (molecular weight 750) (0.029% w/v) using potassium persulphate initiation at a concentration of 0.005% w/v in a final reaction volume of 50 ml. A further PS–MeOPEGMA (PS–PEG^{uc}, i.e. uncharged) latex was prepared by the copolymerization of the same quantities of styrene and MeOPEGMA (molecular weight 750) but initiating the polymerization with hydrogen peroxide (0.005% w/v) and ascorbic acid (0.01% w/v) in a final reaction volume of 50 ml.

The polymerizations were carried out for 24 h at 70°C under constant nitrogen gas flow, being stirred throughout. The resulting latices were extensively dialysed against double distilled quality water for 14 days, the dialysate being replaced daily until the conductivity was almost equal to that of water. The particle sizes of

---

* To whom correspondence should be addressed

0032-3861/92/051112-04

Table 1 Elemental ratios and carbon envelope ratios from X.p.s. analysis of PS^c, $PS-PEG^c$ and $PS-PEG^{uc}$ latex films

	Elemental ratios (%)			Carbon 1s envelope ratios (%)	
Latex	C	O	S	$\underline{C}-C/\underline{C}-H$	$\underline{C}-O$
PS^c	91.4	8.0	0.6	94	6
$PS-PEG^c$	90.4	9.0	0.5	88	12
$PS-PEG^{uc}$	86.2	13.8	-	82	18

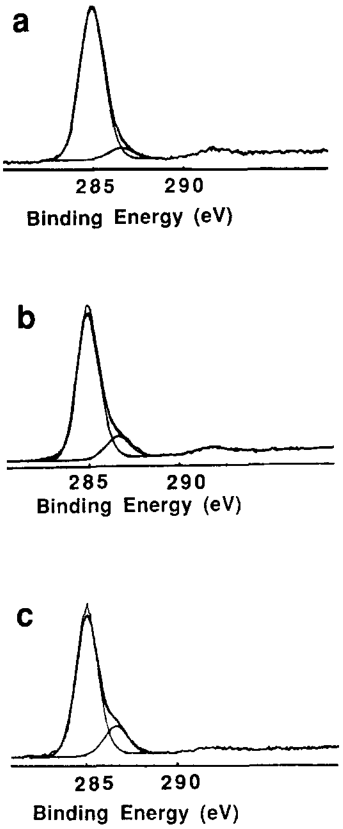

Figure 1 Carbon 1s envelopes from X.p.s. analysis for (a) PS^c, (b) $PS-PEG^c$ and (c) $PS-PEG^{uc}$ latex films

the latices were determined by photon correlation spectroscopy to be 193, 176 and 383 nm for PS^c, $PS-PEG^c$ and $PS-PEG^{uc}$, respectively. The surface orientation of the PEG from the macromonomer was confirmed by the stability of the $PS-PEG^c$ and $PS-PEG^{uc}$ colloids to divalent ions, as noted previously by Ottewill and Satgurunathan[6]. As anticipated, the charge stabilized PS^c latex flocculated at low concentrations of the divalent cations.

SSIMS and X.p.s. spectra were obtained using methodology described in detail previously[5]. Briefly, positive and negative SSIMS spectra were obtained using a Vacuum Generators SIMSLAB 3B spectrometer. The sample was irradiated with 2 keV argon atoms under non-damaging conditions[8] utilizing a non-damaging total atom dose (i.e. $< 10^{13}$ atoms cm^{-2}). X.p.s. spectra were obtained using a Vacuum Generators ESCALAB Mk2 spectrometer using $MgK\alpha_{1,2}$ X-rays with a power of 200 W. Peak fitting was performed using a VG data system and software package. Chemical shifts were referenced to hydrocarbon at 285 eV.

Samples for SSIMS and X.p.s. analysis were prepared by casting the colloidal solutions onto cleaned aluminium substrates and then allowing to dry at ambient temperatures. For comparative purposes, a small quantity of cleaned latex was dried, dissolved in chloroform and spin cast onto the same substrate.

RESULTS AND DISCUSSION

From X.p.s. analysis, the survey scans of all the latices confirm the presence of carbon, oxygen and in the case of PS^c and $PS-PEG^c$, sulphur in the surface layers. The elemental ratios are shown in *Table 1*. For PS^c and $PS-PEG^c$ the presence of sulphur originates from the sulphate groups terminating the polymer chains which provide colloidal stability and surface charge. In the case of PS^c latex, the oxygen signal arises from these charged groups whereas the oxyethylene repeat unit of the PEG accounts for the oxygen (and carbon) levels in the surface of both PS-PEG latices. It is apparent that the surface oxygen is highest for the $PS-PEG^{uc}$ possibly reflecting a higher level of PEG at the latex surface.

The C1s core levels from the X.p.s. analysis for PS^c, $PS-PEG^c$ and $PS-PEG^{uc}$ latices are shown in *Figures 1a, b* and *c*, respectively and illustrate the change in surface composition with the introduction of steric stabilizing polyoxyethylene chains into the PS^c interface. Two main carbon environments are observed at 285 and 286.6 eV corresponding to hydrocarbon carbon, $\underline{C}-C/\underline{C}-H$ and ether carbon, $\underline{C}-O$, respectively. The former environment arises predominantly from the PS backbone. In the case of PS^c latex, the $\underline{C}-O$ bonds arise from the terminal carbon on the PS chain bound to sulphate end groups[5]. In the case of $PS-PEG^c$ latex, this ether environment is likely to contain an additional major contribution from the PEG surface molecules. Naturally, for the $PS-PEG^{uc}$ system, the $\underline{C}-O$ should arise from the PEG chains alone. All systems show a small $\pi-\pi^*$ shake-up satellite at 291.6 eV arising from the aromatic ring of PS which falls in intensity with the introduction of the PEG chains into the colloid surface.

The data from the peak deconvolution of the C1s core levels is shown in *Table 1*. While the elemental ratios are similar, there is a significant increase in the ether carbon for $PS-PEG^c$ latex relative to the PS^c system reflecting the introduction of the PEG chains to the colloid surface. The further increase in the level of the ether carbon for the $PS-PEG^{uc}$ latex is paralleled by an increase in the surface oxygen implying that the surface density of PEG

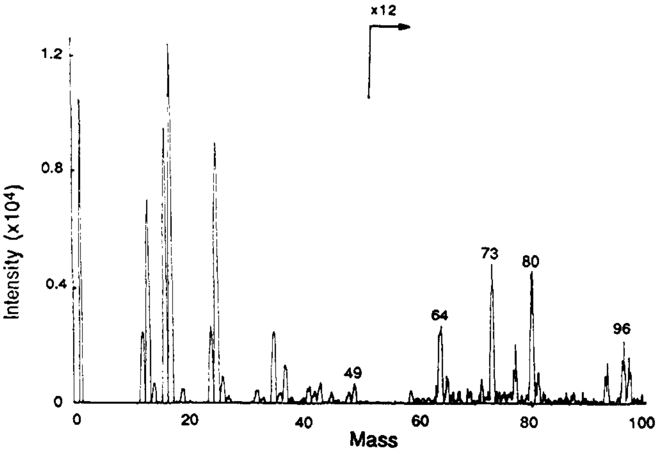

Figure 2 Negative ion SSIMS spectrum (m/z 0–100) for PS^c latex film

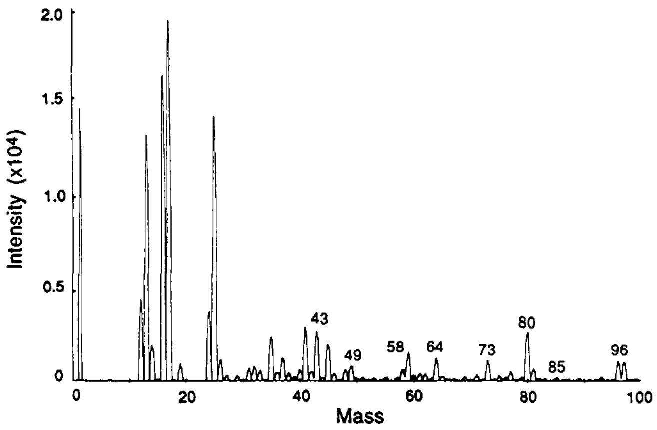

Figure 3 Negative ion SSIMS spectrum (m/z 0–100) for PS–PEG^c latex film

in this sterically stabilized system is higher than for PS–PEG^c. Hence these X.p.s. studies clearly demonstrate the increase in the ether carbon environment reflecting the surface presence of the PEG chains in the sterically stabilized latices.

The negative ion SSIMS spectra of PS^c and PS–PEG^c in *Figures 2* and *3* further demonstrate the clear differences in molecular structure in the surface of the latices. Anions which are observed in pure PS films[8] at m/z 37, 49, 62 and 73 which have been assigned to C_3H^-, C_4H^-, $C_5H_2^-$ and C_6H^- are present in all three latex spectra. Similarly, the presence of the surface oriented charged polymer end groups is confirmed by the detection of the sulphate-derived peaks at m/z 64 (SO_2^-), 80/81 (SO_3^-/HSO_3^-) and 96/97 (SO_4^-/HSO_4^-) for both PS^c and PS–PEG^c. There are a number of peaks detected within *Figure 3* (absent in *Figure 2* for the PS^c latex) which are observed in the PEG homopolymer spectrum[8] and hence may be attributable to the PEG portion of the surface, i.e. anions at m/z 59, 61 and 85 which have been assigned[8] to $HO\text{-}CH{=}CH\text{-}O^-$, $HO\text{-}CH_2\text{-}CH_2\text{-}O^-$, and $CH_2{=}CH\text{-}O\text{-}CH{=}CH\text{-}O^-$, respectively. In the negative ion SSIMS spectrum of PS–PEG^{uc} latex, the PEG diagnostic peaks are also observed together with those of the PS backbone. Naturally, for this colloid prepared without charged polymer end groups, no surface sulphate groups were detected.

The positive ion SSIMS spectrum of the PS^c latex in *Figure 4a* (m/z 40–100) is typical of that observed for pure PS films[8] where many of the peaks are readily assigned to hydrocarbon fragments, e.g. cations at m/z 51, 63, 77 and 91 are thought to correspond to $C_4H_3^+$, $C_5H_3^+$, $C_6H_5^+$ and $C_7H_7^+$, respectively[8]. Similarly these PS-derived peaks are also observed in both the positive ion SSIMS spectra for PS–PEG^c and PS–PEG^{uc} latices shown in *Figures 4b* and *c*, respectively (m/z 40–100). A number of additional signals at m/z 43, 45, 59, 73 and 89 are prominent in the positive ion SSIMS spectra for the PS–PEG^c and PS–PEG^{uc} but not for the PS^c latex. These ions also dominate the pure PEG spectrum[8] and are assigned to the following ions, respectively: $CH_2{=}C{=}OH^+$, $CH_3\text{-}CH{=}OH^+$, $HO\text{-}CH_2\text{-}C^+{=}O$, $CH_3\text{-}O\text{-}CH_2\text{-}C^+{=}O$ and $CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH{=}OH^+$. The ratios of the ion intensities of m/z 45 (diagnostic of PEG) to 91 (diagnostic of PS) for the PS^c PS–PEG^c and PS–PEG^{uc} latices are 0.14, 1.10 and 2.38, respectively, reflecting the gradual increase in the surface PEG as observed in the X.p.s. studies.

The X.p.s. and SSIMS spectra of all the chloroform-dissolved latices show a drastic reduction in the sulphate and PEG signals and in many respects, are virtually identical to data obtained for the pure PS homopolymer.

CONCLUSIONS

This paper clearly demonstrates that SSIMS and X.p.s. may provide a detailed insight into the surface structure of model colloids. These complementary techniques are able to distinguish between the polymer backbone, the

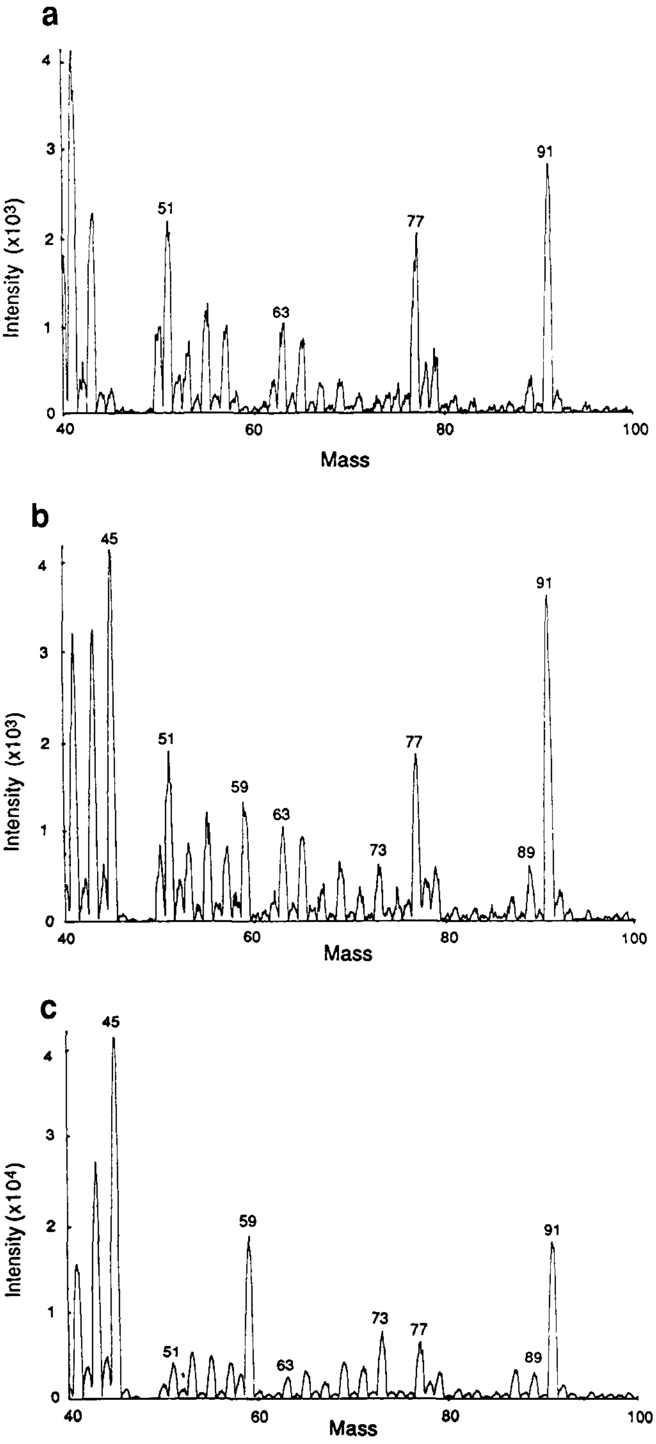

Figure 4 Positive ion SSIMS spectra (m/z 40–100) for (a) PS^c, (b) PS–PEG^c and (c) PS–PEG^{uc} latex films

charged surface groups (as noted previously in ref. 5) and for the first time, the presence of PEG polymers designed to form the steric barrier for colloid stability. In particular, the increase in the $\underline{C}$–O component within the C1s core spectrum for PS–PEG^c and PEG–PEG^{uc} colloid over the control PS^c latex coupled with the emergence of ions diagnostic of the molecular structure of PEG within the SSIMS spectra for the PS–PEG particles, provides evidence of the surface orientation of the macromonomer, despite its low monomer ratio. This surface orientation of the macromonomer in the PS–PEG^c latex facilitates colloid formation despite the use of a lower persulphate initiator concentration compared to the PS^c latex. Additional proof of the surface orientation of the macromonomer is provided from the X.p.s. and SSIMS spectra of the chloroform-dissolved particles where the colloid surface chemistry is totally disrupted and there may be a more random distribution of the PEG chains and the polymer end groups within the bulk phase. It is important to note that the confirmation of the surface PEG chains mirrors the reported stability of the PS–PEG colloids in the presence of divalent cations.

This work further confirms the potential of the surface analytical techniques in the characterization of colloid interfacial structure. Future studies will address the changes in the surface density of macromonomer with changing copolymerization ratios and the *in vitro* and *in vivo* biological fate of such carefully characterized model colloids.

ACKNOWLEDGEMENTS

The authors would like to thank SERC for the receipt of an Instant postgraduate research award to AB and a major equipment grant to MCD contributing to a SIMS instrument. The technical assistance of Mr S. Greaves at the University of Surrey is also acknowledged.

REFERENCES

1 Rembaum, A., Yen, S. P. S. and Molday, R. S. *J. Macromol. Sci. Chem.* 1979, **A13**, 603

2 Hechemy, K. E. and Michaelson, E. E. *Lab. Management* 1984, **22** (6), 27 (Pt 1); 22 (7), 26 (Pt2)

3 Ottewill, R. H. and Shaw, J. N. *Kolloid Z.Z. Polym.* 1966, **215**, 161

4 Davis, S. S. and Illum, L. I. in 'Site-Specific Drug Delivery' (Eds E. Tomlinson and S. S. Davis), Wiley, Chichester, 1986, pp. 93–110

5 Lynn, R. A. P., Davis, S. S., Short, R. D., Davies, M. C., Vickerman, J. C., Humphrey, P., Johnson, D. and Hearn, J. *Polym. Commun.* 1988, **29**, 365

6 Ottewill, R. H. and Satgurunathan, R. *Colloid Polym. Sci.* 1987, **265**, 845

7 Kotera, A., Furusawa, K. and Takeda, Y. *Kolloid Z.Z. Polym.* 1970, **239**, 677

8 Briggs, D., Brown, A. and Vickerman, J. C. 'Handbook of Secondary Ion Mass Spectrometry', Wiley, Chichester, 1989