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Water-soluble and amphiphilic polymers

6. A study on the surface composition of cast films of PSt/PMAA and PEO-PSt-PEO block polymers by XPS

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SUMMARY

Thin films of PSt/PMAA and PEO-PSt-PEO block polymers were deposited on a polystyrene substrate by solution adsorption (with or without solvent treatment) , and the film surfaces were characterized by means of XPS. Direct solvent - casting of PEO-PSt-PEO from benzene solutions resulted in PSt-rich surfaces, whereas PMAA richer surfaces were obtained for PSt/PMAA films cast from DMF solutions. Moreover, solvent treatment after casting had profound effect on the film surface composition. Treatment with water markedly increased the surface concentration of polar PEO segments. In the case of PSt-PMAA block polymers, the PSt content on the surface increased in the order of water < ethanol < cyclohexane < petroleum ether , the last-named giving films with almost pure PSt surface. It is well worth noticing that the bulk composition had little to do with the surface composition for both PSt/PMAA and PEO-PSt-PEO block polymers within the composition range investigated when subsequent solvent treatment was applied.

INTRODUCTION

The surface properties of polymers are essential in many applications. A knowledge of the chemical composition of the outermost layer is of prime importance for the understanding and prediction of surface properties. A number of techniques have been used to examine polymer surfaces, and among these, X-ray photoelectron spectroscopy (XPS, also called ESCA) has become a valuable tool. XPS analysis provides two types of information about the top 5 nm of the sample surface:(a) the atoms present at the surface and their chemical environment; (b) the stoichiometry of the sample.

Block polymers have been the subject of surface analysis by means of XPS. Clark and Peeling (1) used XPS to study the surface composition of polystyrene(PSt)/poly(dimethylsiloxane) (PDMS) diblock polymers and found PDMS predominant overlayers. Thomas and

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O'Malley investigated the surfaces of PSt/poly(ethylene oxide)(PEO) diblock (2) and triblock (3) polymers, and found that the surface composition of the polymers was higher in PSt than the bulk composition. The important conclusion so far obtained is: the lower surface free energy component will become richer on the surface. This conclusion has been supported by a variety of block polymer systems, including poly(bisphenol A-carbonate)(PC)/PDMS(4-6), PC/polysulfone (PSF) (4), poly (p-hydroxystyrene)/PSF/PDMS (7), urethane (8-11), PEO/poly(pivalolactone) (12), polypeptide/polybutadiene (13) and poly(ethylene terephthalate)/ perfluoro polyether (14). The " low free energy component surface enrichment " phenomenon also holds in other multiphase polymer systems, even in ethylene/chlorotrifluoroethylene alternating copolymer (11).

Amphiphilic polymers can be used to improve surface hydrophilicity of hydrophobic polymers, for example PSt. This paper involves a study of the surface composition of polystyrene/poly(methacrylic acid)(PSt/PMAA) and PEO-PSt-PEO block polymers dip-coated on a PSt substrate, and emphasizes the influence of solvent treatment.

EXPERIMENTAL

Materials --- The PSt/PMAA block polymers were prepared by radical polymerization by using a polyazoester as an initiator(15). The synthesis of PEO-PSt-PEO triblock polymers was described in a previous paper (16). A reference PSt homopolymer was synthesized by anionic polymerization by using sodium naphthalene as the initiator. The homo-PMAA sample was obtained by AIBN initiated polymerization. The characteristics of these polymers are given in Table 1.

N,N-dimethylformamide (DMF), ethanol, cyclohexane, petroleum ether and benzene used were A. R. grade solvents. Water was twice-distilled.

XPS Sample Preparation -- Thin films of PSt/PMAA block polymers were deposited from dilute DMF solutions (C=0.5 g/100 ml, for 4-5 sec.) on clean PSt substrates which had been prepared by dip-coating a PSt thin layer from a ~ 1 g/100 ml benzene solution on hot-pressed PSt plates (2 mm thick) to preclude oxygen contamination on the surface. When solvent treatment was applied the test specimen was subsequently dipped into a solvent for 5 min.

Films of PEO-PSt-PEO triblock polymers on clean PSt substrates were prepared by dip-coating from benzene solutions (C=1.0 or 0.5 g/100 ml, for 4-5 sec.), and then followed by three different procedures: (a) without solvent treatment, (b) subsequently treated with water overnight, and (c) dried overnight and then dipped in water overnight.

All test specimens were dried at room temperature in vacuum for at least two days before XPS study.

XPS Measurement --- XPS spectra were recorded on an ESCALAB MkII (VG Company) electron spectrometer using Mg $K\alpha_{1,2}$ exciting radiation, with a X-ray gun at 14 kV and 20 mA. All the XPS measurements were made by analyzing the photoemitted electrons normal to the surface of the samples. The value of 285.0 eV was used for the C_{1s} core level of the hydrocarbon. The calculation of C/O ratios was based on the experimental intensity ratios of C_{1s}/O_{1s}, and the relative photoionization sensitivity (2.97) of O_{1s}/C_{1s} obtained in our laboratory.

RESULTS AND DISCUSSION

The XPS core level spectra for PSt and PMAA homopolymers are shown in Fig. 1. A clean PSt surface shows a sharp peak from main photonization of the C_{1s} level at 285.0 eV, and a broad shake-up satellite at 291.7 eV arising from $\pi^* \leftarrow \pi$ transition in the benzene groups (2, 17). The surface of a clean PSt substrate contains little oxygen. The C_{1s} spectrum of PMAA exhibits double-peak structure: the smaller peak at 289.1 eV is easily identified as arising from its carbonyl carbon atoms, the position of which is in good

Table 1. Main characteristics of polymer samples

Sample	Composition *)		**) [η] (ml/g)
	PSt wt%	PSt mol%	
A (PSt/PMAA)	72.3	68.3	92.0
B (PSt/PMAA)	64.1	59.6	116.0
C (PSt/PMAA)	41.5	37.0	167.0
D (PMAA)	0	0	112.0
E (PEO-PSt-PEO)	88.2	76.0	28.4
F (PEO-PSt-PEO)	87.2	74.2	27.0
G (PEO-PSt-PEO)	58.8	37.3	28.4
H (PEO-PSt-PEO)	55.7	34.7	27.3
I (PSt)	100	100	30.9

*) determined by ^{1}H-NMR

**) measured at 30.0℃ in DMF for samples A-D, at 25.0℃ in toluene for E-I

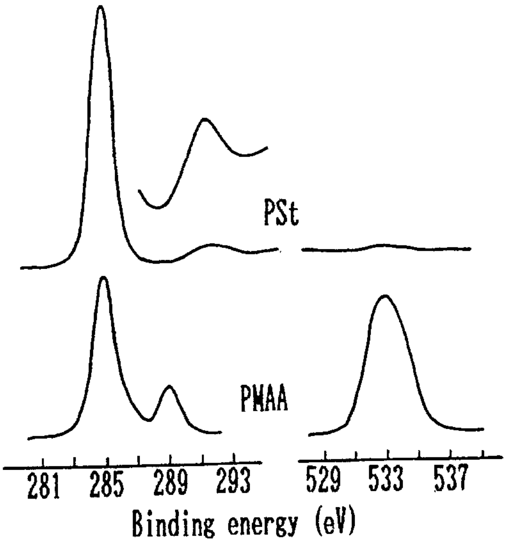

Figure 1. XPS spectra of PSt and PMAA homopolymers

agreement with the literature data for poly(acrylic acid) (18). The broad peak at ~ 533 eV is contributed by the two carboxyl oxygen atoms in different chemical environments (18).

In Fig. 2, we present the spectra of PSt/PMAA block polymer B, without and with subsequent solvent treatment. The line-shape analysis of the total C_{1s} envelope (except for that treated with petroleum ether) reveals the presence of three components at 285.0, 289.1, and 291.7 eV, respectively. The calculated surface composition data are listed in Table 2.

Table 2. Variation of surface composition of PSt-PMAA films with solvent treatment

Sample	mol% PSt at surface				
	no solvent treatment	solvent treatment with			
		water	ethanol	cyclohexane	petroleum ether
A	44.0	55.2	61.0	81.9	93.1
B	46.4	50.1	63.0	82.7	97.7
C	35.6	54.8	---	87.2	98.0

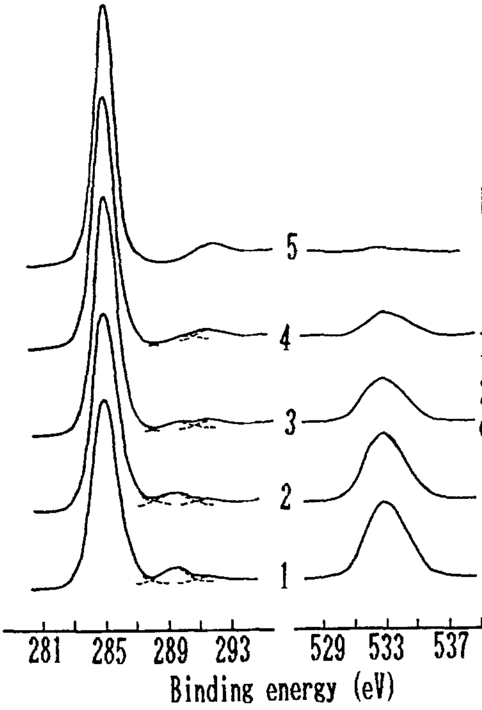

Figure 2. XPS spectra of PSt/PMAA films (sample B)

1--direct casting from a DMF solution
2 to 5--treated with water, ethanol cyclohexane, and petroleum ether,resp.

It is of interest to note that the subsequent solvent treatment has a profound effect on the film surface composition. The PSt content on the surface increases in the order of water < ethanol < cyclohexane < petroleum ether, the last named giving films with almost pure PSt surface. The effect of solvent treatment is in good consistence with the solubility parameter of the solvent used. The more polar the solvent is, the lower the PSt content on the surface.

As previously stated, the conclusion so far drawn is that the lower free energy component always concentrates on the surface of multiphase polymer systems. This is connected with the polymer-air interface and caused by a thermodynamic reason. The less polar segment would tend to transfer towards the surface to reduce the surface energy. The solvent treatment has changed the polymer-air interface to polymer-solvent (in fact, nonsolvent or precipitant) interface, which may apparently induce changes in the polymer chain arrangement to fit the surface energy requirement under the specific interface situation. Non-polar solvents would favor movement of the lower free energy segments to the polymer surface, while the polar solvents would attract the polar segments towards the surface.

For similar reason, nature of the solvent used for the cast solution would influence the surface stoichiometry of the solvent-cast films of multiphase polymer systems. It is interesting to note from the data in Table 2 that we have obtained surfaces richer in higher free energy component PMAA than the bulk by direct solvent-casting from dilute DMF solutions of PSt/PMAA block polymers.

Fig. 3 and Table 3 show the surface composition for PEO-PSt-PEO triblock polymers. Direct casting from benzene solutions results in PSt-rich surfaces, which is very similar with the results obtained by Thomas and O'Malley (2,3) for PEO/PSt di- and tri- block polymers cast from solutions of chloroform which has similar solubility parameter as benzene. Thomas and O'Malley also studied the surface composition of PEO/PSt diblock polymers cast from ethylbenzene or nitromethane solutions (2). It seems that the di- or tri- block structure and the molecular weight don't have apparent influence on the surface composition of the solvent-cast films, which is mainly governed by the bulk composition and the solvent used. Taking PEO/PSt block polymers with the same composition (say, 50 mol % PSt) for comparison and putting the results of Thomas et al. and ours together in Table 4, we can see that the surface composition of PEO/PSt block polymers is strongly solvent-dependent. The polar solvent favors the enrichment of high free energy segment on the surface.

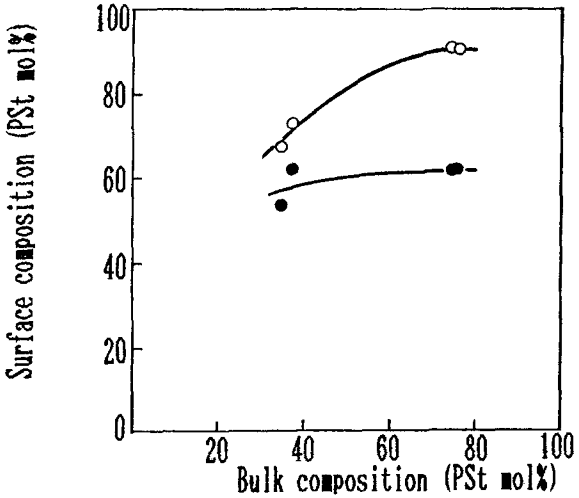

Figure 3. Surface vs. bulk composition of PEO-PSt-PEO films
○ direct casting from benzene solutions (C=0.5 g/100 ml)
● subsequently treated with water overnight

Table 3. PSt mole % content on the surface of PEO-PSt-PEO films

Sample	*) Conc.	Procedure**)		
		a	b	c
E	1.0	85.7	59.2	70.8
	0.5	90.5	61.9	77.1
F	1.0	83.3	61.7	80.8
	0.5	90.9	61.7	76.7
G	1.0	66.8	62.8	60.4
	0.5	72.5	61.7	68.1
H	1.0	56.3	64.0	61.9
	0.5	67.2	53.5	69.6

*) g polymer/100 ml benzene
**) see the part of experimental

As shown in Fig. 3 and Table 3. water treament markedly increases the concentration of PEO segment on the surface,and water treatment may cause the rearrangement of the PEO/PSt surface after the sample has been dried.

Moreover, it is well worth notice from Fig. 3 and Table 2 that the composition of the block polymers has little to do with the surface composition for both PEO-PSt-PEO and PSt/PMAA block polymers whithin the composition range investigated when subsequent solvent treatment is applied.

Table 4. Surface composition of PEO/PSt block polymers cast from different solvents *)

Solvent	Solubility parameter $\times 10^3$ $(J/m^3)^{1/2}$	Surface composition (PSt mol %)
ethylbenzene	18.0	88 (2)
chloroform	19.1	83 (2,3)
benzene	18.9	82
nitromethane	26.0	49 (2)

*) Bulk composition is referenced to 50 mol% of PSt.

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