

Surface characterization of poly(styrene-*co-p*-hexafluorohydroxyisopropyl- α -methyl styrene) copolymers by ToF-SIMS, XPS and contact angle measurements

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A series of spin-cast films of poly(styrene-*co-p*-hexafluorohydroxyisopropyl- α -methyl styrene) (poly(St-*co*-HFMS)) copolymers were analysed by x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and contact angle measurements. The XPS results showed that the surface chemical composition of the copolymers was the same as that of the bulk. The water contact angle decreased slightly with the HFMS content, indicating that there was no fluorine segregation on the surface. This result showed that the decrease of the surface energy due to the presence of the fluorinated groups was offset by the presence of the polar hydroxyl group. The characteristic peaks of poly(St-*co*-HFMS) could be distinguished from those of polystyrene in both positive and negative ToF-SIMS spectra. Our analyses have demonstrated that normalized peak intensities and relative intensities of the characteristic peaks can produce useful quantitative results. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: ToF-SIMS; XPS; contact angle; copolymer

INTRODUCTION

Copolymers of styrene with *p*-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)- α -methyl styrene (poly(St-*co*-HFMS)) have been studied with considerable interest in miscibility enhancement via hydrogen bonding interaction.^{1–3} *p*-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropyl)- α -methyl styrene (HFMS) has been shown to be effective for introducing hydrogen bonds in polymer blends. Only a small amount of HFMS is needed in poly(St-*co*-HFMS) to make it miscible with one of the proton-acceptor-containing polymers such as poly(methyl methacrylate),^{1,2} poly(butyl methacrylate),³ poly(ethylene oxide),⁴ polycarbonate⁵ and poly(4-vinyl pyridine) (details available from the author upon request).

The fluorinated methyl group, which has a strong electron-drawing ability, is intentionally chosen to be located next to the hydroxyl group in HFMS, making it more acidic. The presence of the fluorinated methyl side

group, which is known to be a low surface energy component, can have a significant effect on the surface chemical composition of poly(St-*co*-HFMS). Because of the low surface energy of the fluorinated methyl groups, there is a strong thermodynamic driving force for the HFMS to segregate to the surface. However, this situation is complicated by the presence of the polar hydroxyl group, which is a high surface energy component. It is of interest to study the effects of these two counterbalancing forces on the surface chemical composition of poly(St-*co*-HFMS) copolymers as the HFMS content in the copolymer varies.

X-ray photoelectron spectroscopy (XPS) is a popular surface characterization technique that has been used extensively to study the surface chemical composition of polymers.^{6–8} Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has also gained importance in the past 10 years in the characterization of polymer surfaces due to its high molecular specificity, extreme surface sensitivity and high mass resolution.^{6–11} However, compared with XPS, SIMS has a main drawback in its ability to yield quantitative results because the mechanisms of the formation and emission of the secondary ions are not well understood yet. Nevertheless, quantification by SIMS has gained popularity in the past few years. It has been shown that quantitative analyses can be performed with static SIMS on certain polymers and copolymers, such as nylon 6/6,^{12,13} poly(ethyl methacrylate/hydroxyethylmethacrylate),¹⁴ poly(methyl methacrylate/ethyl methacrylate),¹³ poly(styrene/*p*-hydroxystyrene),¹⁵ poly(styrene/butadiene),¹⁶ poly(styrene/*p*-methyl styrene),¹⁷ poly(methyl methacrylate/

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(ethylene glycol) methacrylate),^{18,19} poly(ethylene/propylene),²⁰ ethylene/methyl acrylate,²¹ and poly(ethylene/vinyl acetate),²² as well as polymer blends, such as polystyrene/poly(vinyl ethyl ether),²³ polycarbonate/poly-styrene²⁴ and polycarbonate/poly(methyl methacrylate).²⁵ In the above systems, the intensities of some SIMS characteristic peaks unique to each component were shown to be related to the bulk composition or the surface composition determined by XPS. In these few cases, the strong relationship between these SIMS intensities and the copolymer or polymer blend composition showed that SIMS can be used as a quantitative technique. However, such a conclusion cannot be generalized until more polymer systems are analysed.

The objective of the present work is to study a series of poly(St-co-HFMS) copolymers with various amounts of HFMS and to investigate whether quantitative information can be obtained from SIMS data. However, the possibility of HFMS migrating to surface can make the SIMS quantification more difficult. Both XPS and contact angle measurements were first used to determine the surface chemical composition of the copolymers. Then, high-resolution ToF-SIMS was used to characterize the surface of a series of poly(St-co-HFMS). The ToF-SIMS results were compared with the XPS and contact angle measurement results.

EXPERIMENTAL

Sample preparation

Styrene and *p*-chloro- α -methyl styrene were purified and vacuum-distilled in the presence of calcium hydride or/and sodium mirror just before use. The hydroxyl-containing monomer HFMS was synthesized from *p*-chloromethylstyrene via the Grignard reaction with hexafluoroacetone.

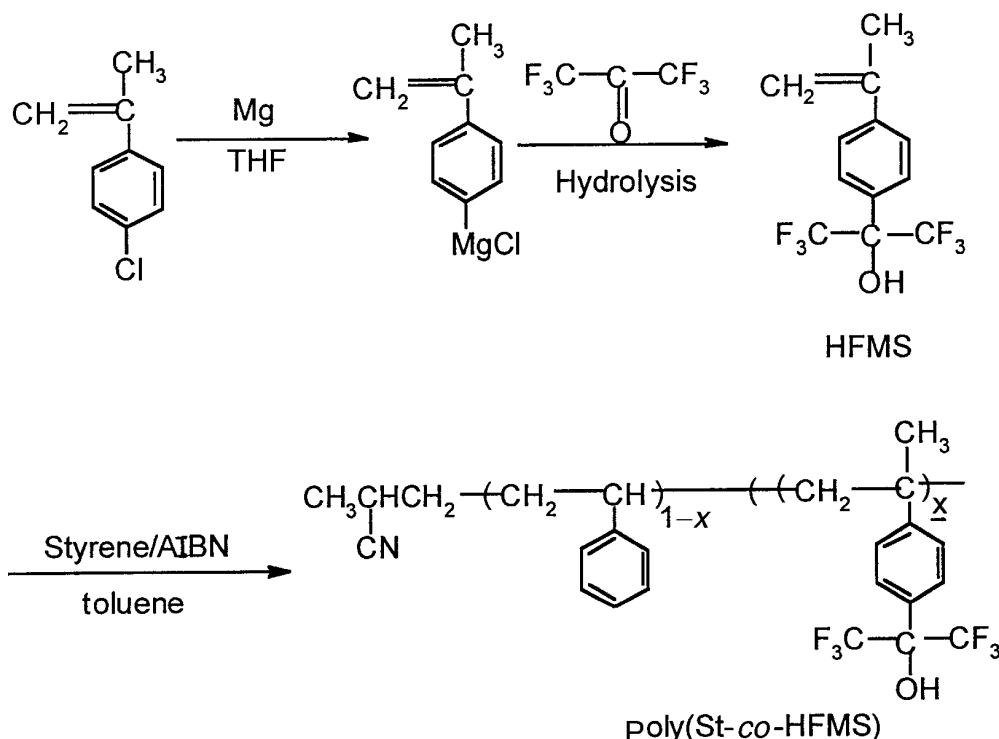
A general scheme for preparing the HFMS monomer is shown in Scheme 1.

Copolymers of styrene and HFMS were prepared by solution copolymerization in benzene at 60 °C using 2,2-azoisobutyronitrile (AIBN) as initiator. The products were purified by precipitation from a dichloromethane/petroleum ether mixture. By varying the feed composition, a series of poly(St-co-HFMS) copolymers with various HFMS contents in the range of 1–50 mol.% were obtained. The purified products were analysed by size exclusion chromatography using a polystyrene standard and the results are shown in Table 1. Their structures were verified by Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. Each HFMS unit is expected to be linked mostly with the styrene units during copolymerization because it is difficult to find a long block of HFMS owing to the difficulty in homopolymerizing α -methylstyrene in free-radical polymerization due to its low ceiling temperature. The HFMS content in the copolymers was determined by the fluorine content as measured by elemental analysis and the results are summarized in Table 1.

Poly(St-co-HFMS) copolymers were dissolved in CHCl₃ and the concentration of the solutions was

Table 1. The physical properties of poly(St-co-HFMS)

Sample	HFMS content	$M_n/10^4$	M_w/M_n
Poly(St-co-HFMS)-1	1	3.68	1.51
Poly(St-co-HFMS)-3	3.2	4.66	1.31
Poly(St-co-HFMS)-5	5.1	3.22	1.48
Poly(St-co-HFMS)-8	8.3	3.87	1.52
Poly(St-co-HFMS)-12	12.4	3.41	1.27
Poly(St-co-HFMS)-21	20.6	2.54	1.83
Poly(St-co-HFMS)-34	33.8	1.33	1.52
Poly(St-co-HFMS)-49	49.2	1.05	1.61
Polystyrene	—	4.70	1.04



Scheme 1. Reaction scheme for preparation of poly(St-co-HFMS).

2.5 g dl⁻¹. The solutions were spin-cast on silicon wafers to prepare uniform films suitable for contact angle measurements as well as for XPS and ToF-SIMS experiments.

Surface characterization

The surface properties of a series of poly(St-co-HFMS) copolymers were studied by XPS, ToF-SIMS and contact angle measurements. The XPS spectra were obtained with a PHI 5600 multi-technique system equipped with a monochromatic Al K α x-ray source. A pass energy of 23.4 eV was used. All core-level spectra were referenced to the C 1s neutral carbon peak at 285.0 eV. The emission angle (the angle between the surface normal and the axis of the analyser) of the photoelectron was 45°, corresponding to a sampling depth of ~ 45 Å. Contact angles were measured on a Kruss goniometer at room temperature, using HPLC water. The volume of the water droplet was 15 μ L. An average value was obtained from five to seven measurements for each sample.

The ToF-SIMS measurements were performed on a Physical electronics PHI 7200 ToF-SIMS spectrometer. The primary ions were generated from a Cs ion source (8 kV). The scanned area was 200 μ m \times 200 μ m and the total ion dose for each spectrum acquisition was $< 4 \times 10^{11}$ ions cm⁻². Charge compensation was realized by low-energy (0–70 eV) flooding electrons being pulsed out of phase in the primary ion beam. Both positive and negative high-resolution mass spectra of poly(St-co-HFMS) copolymers were recorded.

RESULTS AND DISCUSSION

X-ray photoelectron spectroscopy and contact angle measurements

The XPS results on all poly(St-co-HFMS) copolymer films show the presence of only three elements: carbon, oxygen and fluorine. No signal from the silicon substrate or contaminants is detected, indicating that the copolymers are clean and the film thickness is uniformly more than ~ 100 Å. Typical C 1s spectra of poly(St-co-HFMS)-49 and poly(St-co-HFMS)-21 are shown in Fig. 1(a) and 1(b), respectively. The C 1s spectrum can be resolved into four component peaks representing different chemical environments. The four components include the hydrocarbon peak at 285.0 eV, the $\text{C}-(\text{CF}_3)_2\text{OH}$ peak at 288.6 eV, the $\pi-\pi^*$ shake-up satellite peak at 291.6 eV and the CF_3 peak at 293.4 eV. For poly(St-co-HFMS) copolymers with a very low HFMS content, the C 1s spectrum is similar to that of polystyrene.

The F/O atomic ratio is 6, which is in good agreement with the chemical structure of the poly(St-co-HFMS) copolymers, suggesting that the surface of the copolymers does not contain any contaminants. The surface chemical composition of the copolymers was determined using the following equation

$$\phi_{\text{HFMS}} = \frac{8R_{\text{F/C}}}{6 - 4R_{\text{F/C}}} \quad (1)$$

where ϕ_{HFMS} is the surface mole fraction of HFMS and $R_{\text{F/C}}$ is the atomic ratio of fluorine to carbon. Figure 2

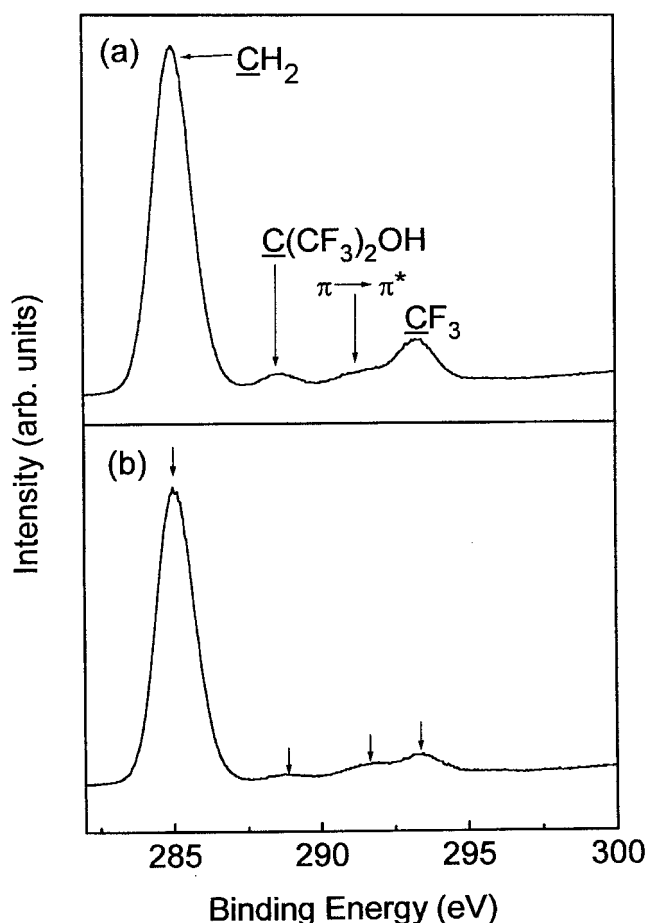


Figure 1. Carbon 1s spectra of (a) poly(St-co-HFMS)-49 and (b) poly(St-co-HFMS)-21.

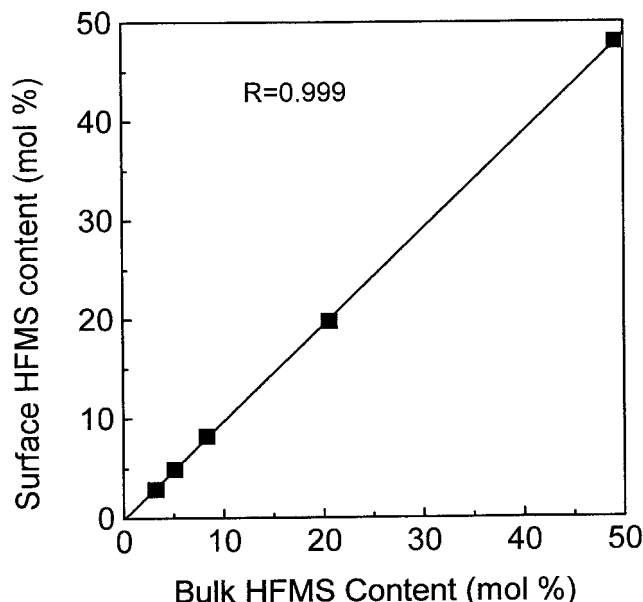


Figure 2. Surface HFMS content determined by XPS vs. the bulk HFMS content.

shows a plot of the surface HFMS content determined by XPS as a function of its bulk content for five copolymers. The results shown in Fig. 2 indicate that the surface chemical composition of the copolymers is more or less identical to the bulk. The presence of two trifluoromethyl groups in

HMFS could be a driving force for the HMFS segments to migrate to the surface. However, the XPS results indicate that there is no surface segregation of the HMFS segments. This is probably the result of having a high surface energy hydroxyl group in HMFS, offsetting the effect of the two low surface energy trifluoromethyl groups.

Because the sampling depth of XPS is $\sim 40\text{--}50$ Å, it is worth checking whether HFMS segments have been segregated to the topmost layer by contact angle measurement, which is sensitive to chemical changes at the topmost layer of a surface. If HFMS has been segregated at the topmost surface, changes in the water contact angle should be observed on the poly(St-co-HFMS) films as the HFMS content increases. Figure 3 shows the static contact angle of water on the surface of poly(St-co-HFMS) films as a function of the HFMS content. The water contact angles on the poly(St-co-HFMS) films with a low HFMS content are slightly larger than that on polystyrene. Then the contact angle decreases and stays relatively constant when the HFMS content is above 15 mol.%. From the XPS and contact angle results, we may conclude that the surface chemical composition of the films is very similar to the bulk and the surface energy of the HFMS is not too different from that of pure polystyrene. The slight decrease in the water contact angle may indicate a small increase in the surface energy for films with a high HFMS content.

Time-of-flight SIMS spectrum analysis

A typical positive SIMS spectrum of poly(St-co-HFMS)-49 is shown in Fig. 4. The characteristic peaks of polystyrene, e.g. $m/z = 27, 39, 51, 77, 91, 103, 105, 115, 128, 141, 152, 165, 178$ and 193 , are also present in the spectrum of the poly(St-co-HFMS)-49 copolymer. The largest peak in the spectra of poly(St-co-HFMS) with HFMS content varying from 1 to 49 mol.% is also at $m/z = 91$. The structure of these ions has been proposed previously.²⁶ At the same time, positive ions from poly(St-co-HFMS) that are distinguished from that of polystyrene are at $m/z = 19(\text{F}^+)$, $31(\text{CF}^+)$, $69(\text{CF}_3^+)$, $109, 172, 257, 271, 285$ and 373 . The proposed secondary ion structures of some of these ions are shown below. The peaks at $m/z = 15$ and 105 are also considerably larger relative to the peaks at $m/z = 27$ and 103 ,

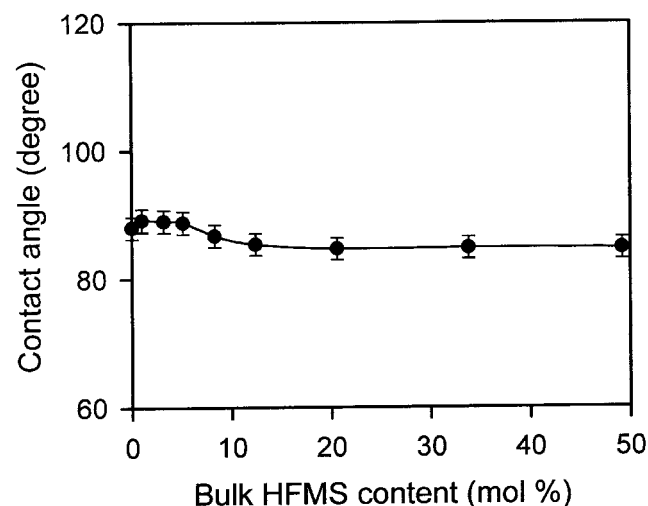


Figure 3. Water contact angle of poly(St-co-HFMS) films as a function of the HFMS content.

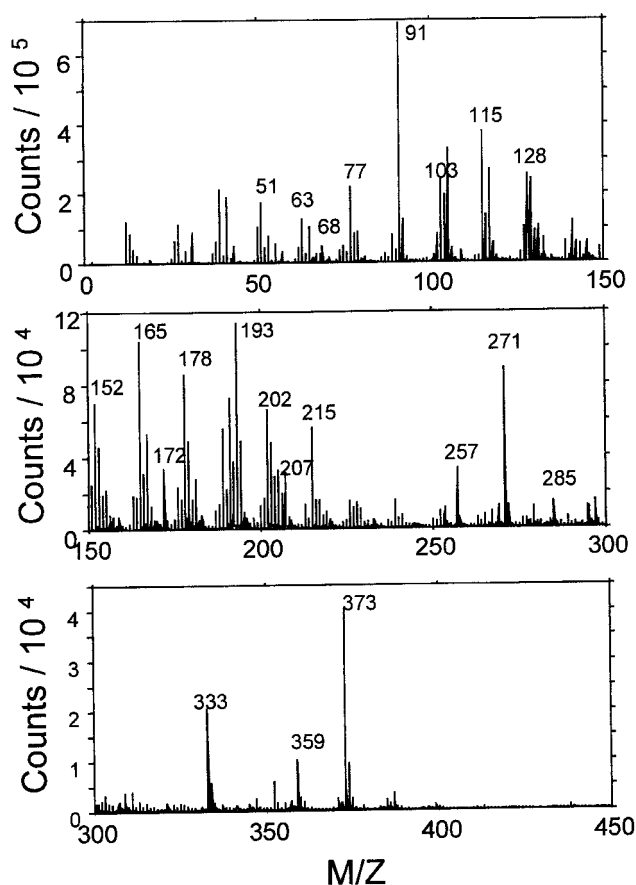


Figure 4. Positive ToF-SIMS spectra of poly(St-co-HFMS)-49 copolymers for $m/z = 0\text{--}450$.

respectively. The enhancement of the peak at $m/z = 15$ is due to the CH_3 group associated with HFMS. Among the peaks from poly(St-co-HFMS), the peaks at $m/z = 68$ and 172 are derived from the initiator and the initiator plus a polystyrene repeat unit, respectively. The peaks at $m/z = 257, 271$ and 285 are directly associated with the structure of HFMS. Among these three peaks, the peak at $m/z = 271$ is the most intense, probably due to the fact that the formation of this ion requires the least number of bond cleavages and hydrogen transfers. The peak at $m/z = 373$ is associated with styrene-HFMS (AB) units.

Figure 5 shows the negative ion spectrum of poly(St-co-HFMS)-49. Except for the peaks such as $m/z = 13(\text{CH}^-)$, $25(\text{C}_2\text{H}^-)$, $37(\text{C}_3\text{H}^-)$, $49(\text{C}_4\text{H}^-)$, $62(\text{C}_5\text{H}_2^-)$ and $73(\text{C}_6\text{H}^-)$, which are also present in the negative spectrum of polystyrene, poly(St-co-HFMS) can be distinguished from polystyrene by the presence of peaks at $m/z = 19(\text{F}^-)$, the largest peak in the spectrum), $31(\text{CF}^-)$, $43(\text{C}_2\text{F}^-)$, $69(\text{CF}_3^-)$, $93(\text{C}_3\text{F}_3^-)$, $147, 166, 195, 199, 201, 214, 227$ and 283 . The proposed secondary ion structures of some of these ions are shown below.

Quantitative analysis by ToF-SIMS

Positive spectrum. X-ray photoelectron spectroscopy and contact angle measurements show that the surface composition of poly(St-co-HFMS) copolymers is very similar to the bulk. Because the surface chemical composition of the copolymer films is known, the ToF-SIMS data were analysed to test whether these data can be used in quantitative

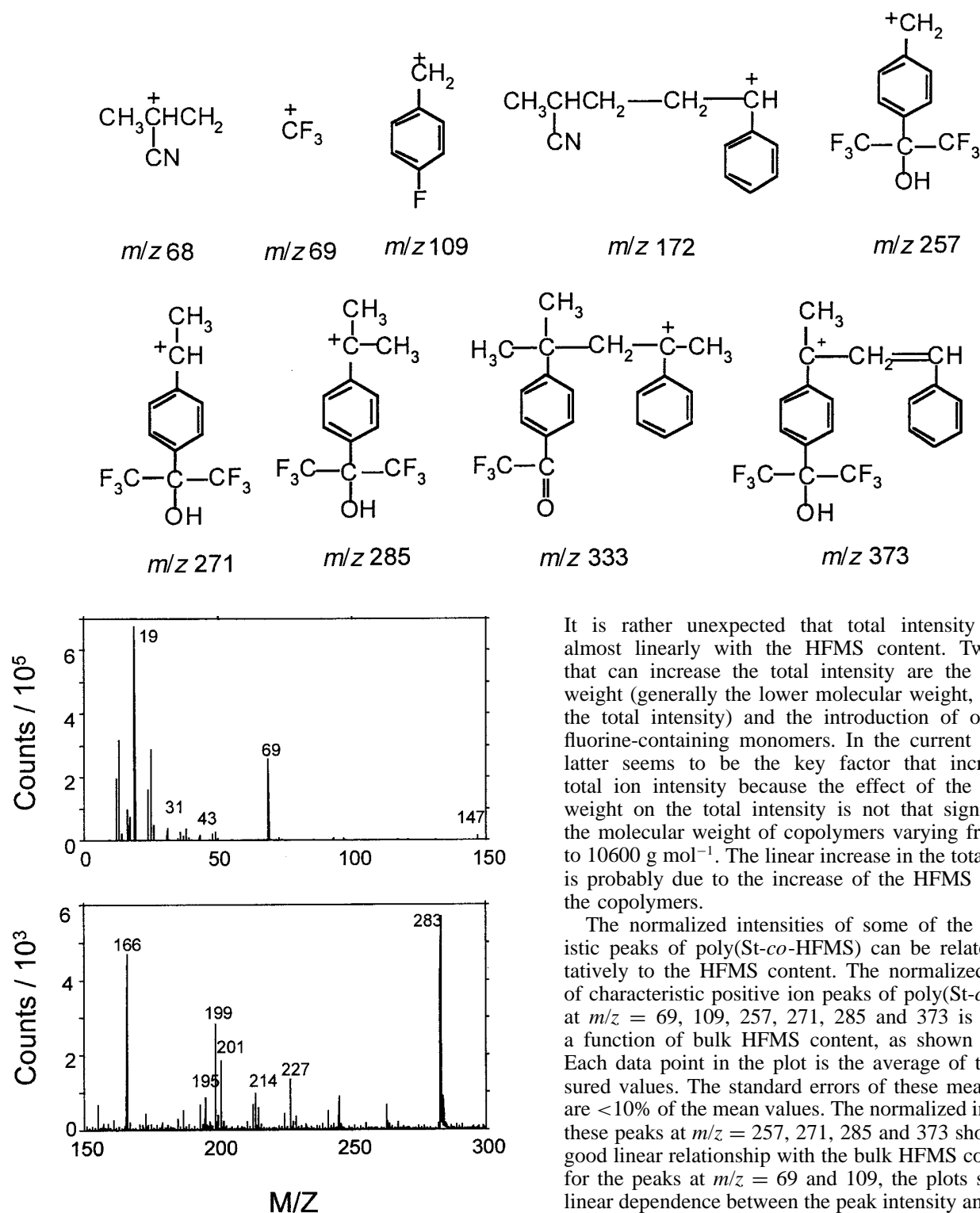


Figure 5. Negative ToF-SIMS spectra of poly(St-co-HFMS)-49 copolymers for $m/z = 0-300$.

analyses. The selection of characteristic peaks is the most crucial step in the quantitative analysis procedure. Both normalized peak intensities and the ratios of the intensities of two peaks unique to the two monomer units in the poly(St-co-HFMS) copolymers were used. The normalized intensity is the intensity of a peak normalized by the total intensity.

Figure 6 shows a plot of the total intensity of the positive ions as a function of the HFMS content.

It is rather unexpected that total intensity increases almost linearly with the HFMS content. Two factors that can increase the total intensity are the molecular weight (generally the lower molecular weight, the higher the total intensity) and the introduction of oxygen- or fluorine-containing monomers. In the current study, the latter seems to be the key factor that increases the total ion intensity because the effect of the molecular weight on the total intensity is not that significant for the molecular weight of copolymers varying from 46500 to 10600 g mol^{-1} . The linear increase in the total intensity is probably due to the increase of the HFMS content in the copolymers.

The normalized intensities of some of the characteristic peaks of poly(St-co-HFMS) can be related quantitatively to the HFMS content. The normalized intensity of characteristic positive ion peaks of poly(St-co-HFMS) at $m/z = 69, 109, 257, 271, 285$ and 373 is plotted as a function of bulk HFMS content, as shown in Fig. 7. Each data point in the plot is the average of three measured values. The standard errors of these measurements are $<10\%$ of the mean values. The normalized intensity of these peaks at $m/z = 257, 271, 285$ and 373 shows a very good linear relationship with the bulk HFMS content. But for the peaks at $m/z = 69$ and 109 , the plots show non-linear dependence between the peak intensity and the bulk HFMS content. From the chemical structure of the ions at $m/z = 257, 271, 285$ and 373 , these ions are produced by fragmentation at the backbone of the poly(St-co-HFMS) chains. But the production of ions at $m/z = 69$ and 109 has to involve cleavage of the fluorine-carbon bonds, therefore it is reasonable that the normalized intensity of the peaks at $m/z = 257, 271, 285$ and 373 is linearly related to the HFMS content of the poly(St-co-HFMS) copolymers. From these, it can be concluded that better quantification results would be obtained if characteristic peaks that are directly associated with the monomer structure are used.

The relative intensities of the characteristic peaks that are related to the monomer units of the copolymer can

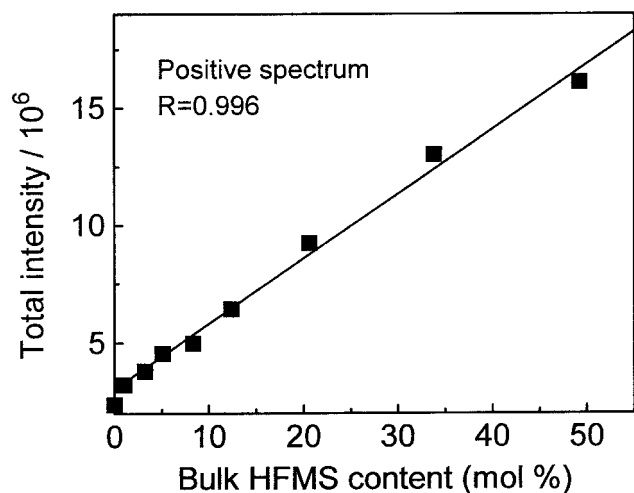
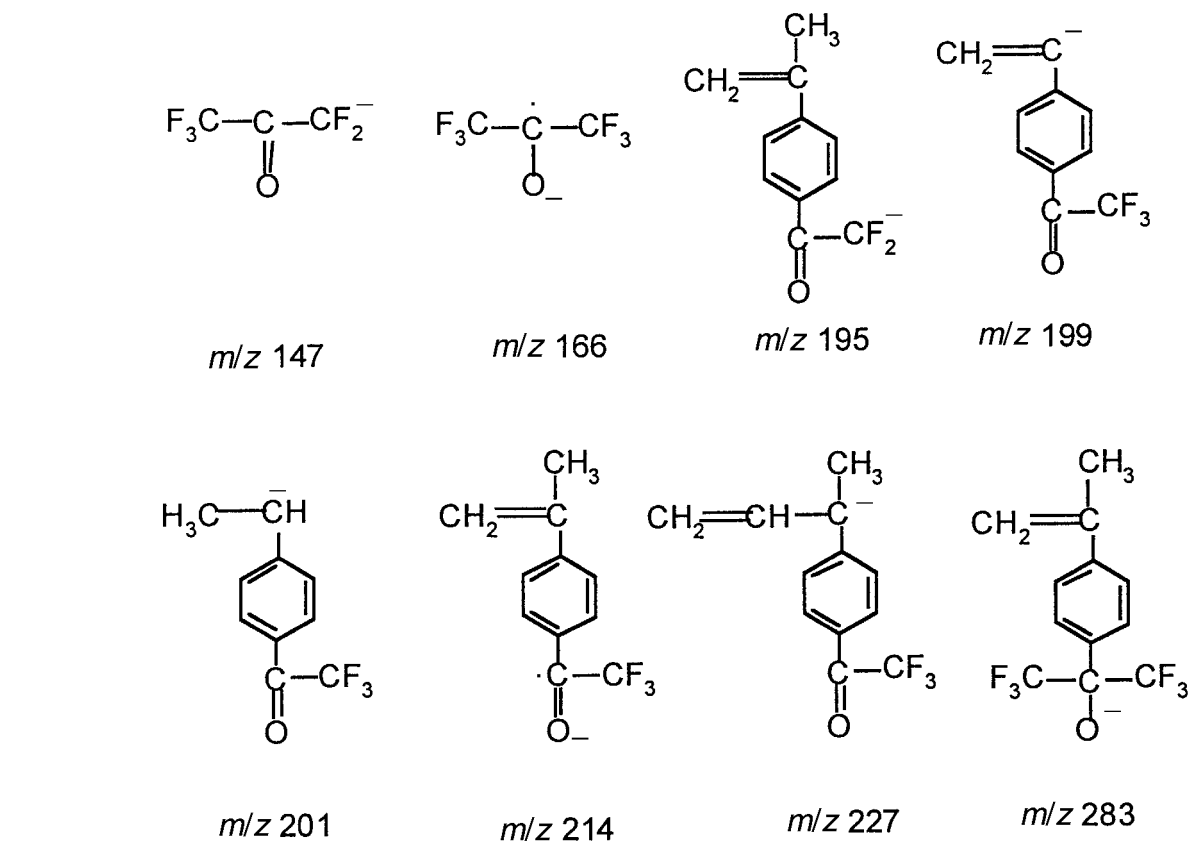


Figure 6. Total intensity of the positive ions versus the bulk HFMS content.

also be used in quantitative analysis. This method should be more reliable compared with the previous one when the samples have some contaminants that can have a significant effect on the total peak intensity. The peaks at $m/z = 257, 271, 285$ and 373 have been identified as the characteristic peaks of the HFMS monomer units, whereas the peaks at $m/z = 91, 103$ and 115 are identified as the characteristic peaks of polystyrene. Some of the characteristic peaks of polystyrene at $m/z = 51, 77, 165$ and 193 are not good choices owing to interference of the ions derived from HFMS, because the HFMS repeat units would also contribute to these peaks due to the presence of CHF_2^+ ($m/z = 51$) $\text{C}_3\text{H}_3\text{F}^+$ ($m/z = 77$) $\text{C}_{10}\text{H}_7\text{F}_2^+$ ($m/z = 165$) and $\text{C}_5\text{H}_3\text{F}_6\text{O}^+$ ($m/z = 193$) ions.

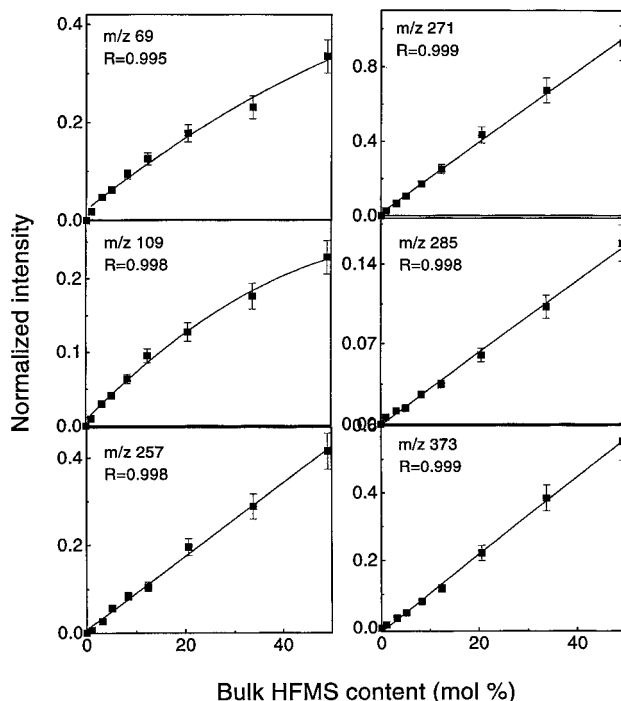


Figure 7. Normalized intensity of the positive ion peaks at $m/z = 69, 109, 257, 271, 285$ and 373 versus the bulk HFMS content.

The plots of $I_{m1}^{\text{HFMS}} / (I_{m1}^{\text{HFMS}} + I_{m2}^{\text{PS}})$ as a function of the HFMS content are shown in Fig. 8; I_{m1}^{HFMS} and I_{m2}^{PS} are the intensities of characteristic peaks of the HFMS and polystyrene (PS) units at $m/z = m1$ and $m2$, respectively. In Fig. 8, the peaks at $m/z = 271$ and 373 are used for HFMS and the peaks at $m/z = 91, 103$ and 115

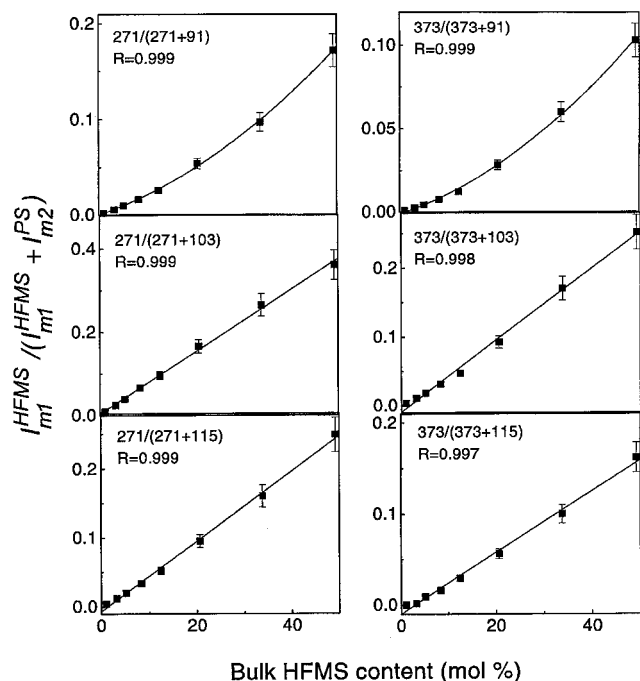


Figure 8. Intensity ratios of several positive ion peaks as a function of bulk HFMS content: 271/(271 + 115), 271/(271 + 103), 271/(271 + 91), 373/(373 + 115), 373/(373 + 103) and 373/(373 + 91).

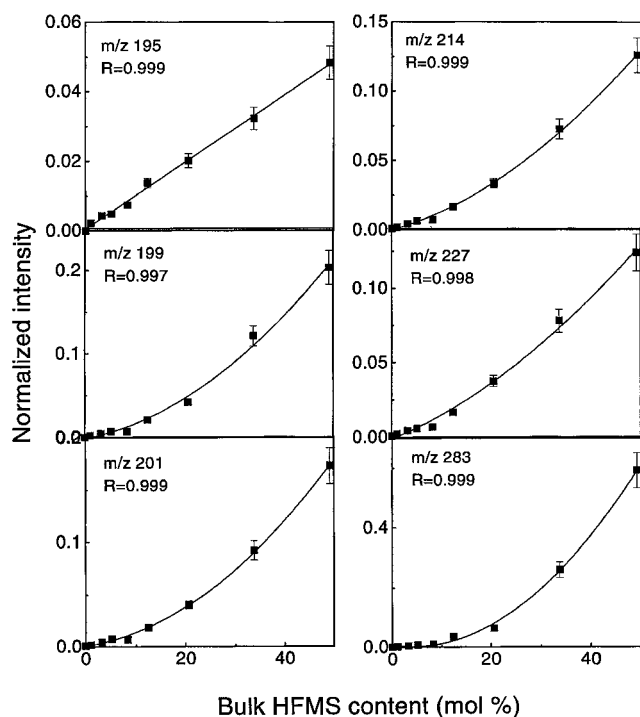


Figure 9. Normalized intensity of the negative ion peak at $m/z = 195, 199, 201, 214, 227$ and 283 versus the bulk HFMS content.

are used for styrene. The use of the polystyrene peaks at $m/z = 103$ and 115 gives very good linear fits, whereas the use of the peaks at $m/z = 91$ produces a non-linear curve. All the plots shown in Fig. 8 can be used in quantitative analyses because $I_{m1}^{HFMS} / (I_{m1}^{HFMS} + I_{m2}^{PS})$ increases monotonically with the HFMS content. These results are in agreement with the results of Weng *et al.* on the quantification of styrene-butadiene random copolymers¹⁶

and the tandem mass spectrometry study on polystyrene.²⁷ The peaks at $m/z = 115$ and 103 can be explained from the same fragmentation sequence of polystyrene, but the peak at $m/z = 91$ is less characteristic of polystyrene, i.e. it may come from several precursors.

Negative spectrum. Some of the characteristic peaks of the negative SIMS spectra of poly(St-co-HFMS) are $m/z = 195, 199, 201, 214, 227$ and 283 . Figure 9 shows the intensity of these peaks as a function of HFMS content. It is clear that the intensity of all these peaks except the one at $m/z = 195$ shows a non-linear relationship with the HFMS content. The intensity of these peaks cannot be used to perform quantitative analysis at low HFMS contents because the change of intensity is fairly insensitive to the HFMS content. This is because the dominating negative ion species is F^- , which is a very stable negative ion and its intensity is extremely high, which may saturate the detector. Consequently, its contribution to the total intensity of the negative ion peaks is no longer linearly related to the surface composition of the sample, leading to errors in calculating the normalized intensities. The intensity for peaks with $m/z < 30$ was not included in the calculation of the total intensity of the negative ions. Then the normalized intensity of the ions considered in Fig. 9 was recalculated with the new total ion intensity. The results are shown in Fig. 10. The intensity of the peaks at $m/z = 199, 201, 214$ and 227 show a linear relationship with the HFMS content. However, the intensity of the peak at $m/z = 195$ now shows a non-linear relationship with the HFMS content and no significant change is observed for the peak at $m/z = 283$. Based on these results, we may conclude that the exclusion of the intensity of the peaks for $m/z < 30$ tends to produce a linear relationship between the intensity of the ion and the HFMS content, confirming the saturation effect of the F^- ions.

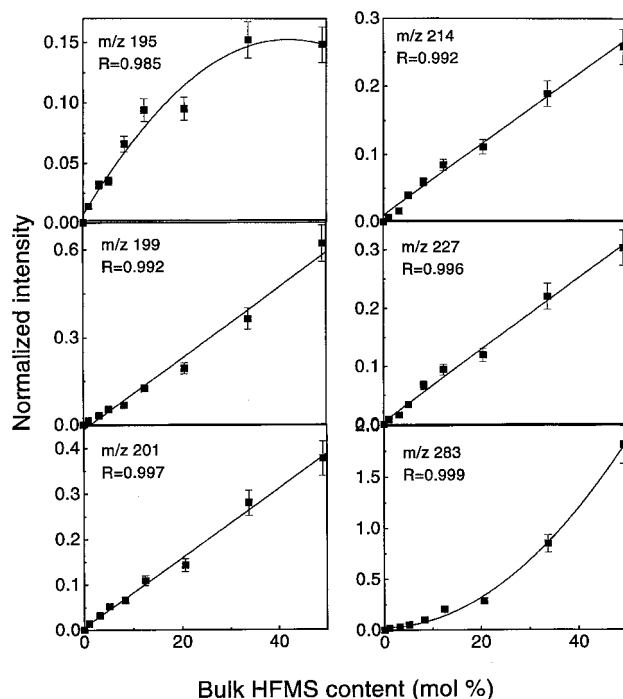


Figure 10. Normalized intensity of the negative ion peak at $m/z = 195, 199, 201, 214, 227$ and 283 versus the bulk HFMS content. In the calculation of the total intensity of the negative ions, the intensity of the peaks for $m/z < 30$ was excluded.

CONCLUSIONS

A detailed analysis of a series of spin-cast films of poly(St-co-HFMS) copolymers by XPS, SIMS and contact angle measurements was performed. The XPS results indicate that the surface chemical composition of these polymers is almost identical to the bulk. The water contact angle decreases slightly with the HFMS content, indicating a small increase of surface energy. Both XPS and contact angle measurement results show that there is no fluorine segregation on the surface. This indicates that the decrease

in the surface energy caused by the presence of the two trifluoromethyl groups has been offset by the presence of the hydroxyl group. The characteristic peaks of poly(St-co-HFMS) can be distinguished from that of polystyrene in both positive and negative ToF-SIMS spectra. Using characteristic ion peaks of HFMS and polystyrene, quantitative analyses can be performed.

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REFERENCES

1. Jiang M, Qiu XP, Qin W, Fei L. *Macromolecules* 1995; **28**: 730.
2. Qiu X, Jiang M. *Polymer* 1994; **35**: 5084.
3. Qiu X, Jiang M. *Polymer* 1995; **36**: 3601.
4. Pearce E, Kwei TK, Min B. *J. Macromol. Sci. Chem.* 1984; **A21**: 1181.
5. Ting SP, Bulkin BJ, Pearce EM. *J. Polym. Sci., Polym. Chem. Ed.* 1981; **19**: 1451.
6. Chan CM. *Polymer Surface Modification and Characterization*. Hanser: New York, 1994.
7. Briggs D, Fletcher IW, Reichlmaier S, Agulo-Sanchez JL, Short RD. *Surf. Interface Anal.* 1996; **24**: 419.
8. Briggs D. *Surface Analysis of Polymers by XPS and Static SIMS*. Cambridge University Press: Cambridge, 1998.
9. Briggs D. In *Practical Surface Analysis*, vol. 2, Briggs D, Seah MP (eds). Wiley: Chichester, 1992; 367.
10. Benninghoven A. *Surf. Sci.* 1994; **299/300**: 246.
11. Vickerman JC. *Analyst* 1994; **119**: 513.
12. Briggs D. *Surf. Interface Anal.* 1986; **9**: 391.
13. Lub J, van Vroonhoven FCBM, van Leyen D, Benninghoven A. *J. Polym. Sci. B* 1989; **27**: 2071.
14. Briggs D, Ratner BD. *Polym. Commun.* 1986; **29**: 6.
15. Chilkoti A, Castner DG, Ratner BD, Briggs D. *J. Vac. Sci. Technol. A* 1990; **8**: 2273.
16. Weng LT, Bertrand P, Lauer W, Zimmer R, Busetti S. *Surf. Interface Anal.* 1995; **23**: 879.
17. Affrossman S, Hindryckx F, Pethrick RA, Stamm M. In *Proc. First Conference on Polymer-Solid Interface*, Pireaux JJ, Bertrand P, Bredas JL (eds). Institute of Physics Publishers: Bristol, 1992; 337.
18. Shard AG, Davies MC, Tendlar SJB, Nicholas CV, Purbrick MD, Watts JF. *Macromolecules* 1995; **28**: 7885.
19. Briggs D, Davies MC. *Surf. Interface Anal.* 1997; **25**: 725.
20. Bhatia QS, Burrell MC. *Surf. Interface Anal.* 1990; **15**: 388.
21. Thompson PM. *Anal. Chem.* 1991; **63**: 2447.
22. Lhoest J-B, Bertrand P, Weng LT, Dewez J-L. *Macromolecules* 1995; **28**: 4631.
23. Galsuka AA. *Surf. Interface Anal.* 1997; **25**: 1.
24. Galsuka AA. *Surf. Interface Anal.* 1996; **24**: 380.
25. Galsuka AA. *Surf. Interface Anal.* 1994; **21**: 703.
26. van Ooij WJ, Brinkhuis RHG. *Surf. Interface Anal.* 1988; **11**: 430.
27. Leggett GJ, Vickerman JC, Briggs D, Hearn MJ. *J. Chem. Soc. Faraday Trans* 1992; **88**: 297.