

# Surface Studies of Polymers with a Well-Defined Segmental Length by ToF-SIMS and XPS. Relationship between the Surface Chemical Composition and Segmental Length

Lin Li, Chi-Ming Chan,\* Shiyong Liu, Lijia An, and Kai-Mo Ng

Department of Chemical Engineering, Advanced Engineering Materials Facility, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

Lu-Tao Weng and Ka-Chun Ho

Materials Characterization & Preparation Facility, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

Received August 25, 1999; Revised Manuscript Received June 13, 2000

**ABSTRACT:** Two series of sequential polymers were synthesized by polymerization of 1,*n*-dibromoalkane (*n* = 4, 6, 8, 10, 12, 14, and 18) with 4,4'-(hexafluoroisopropylidene)diphenol (6FBA) and bisphenol A (BA). The flexible aliphatic segment length changes from 4 to 21 Å corresponding to 4–18 CH<sub>2</sub> groups. The influence of the flexible aliphatic segment length on the surface composition of BA and 6FBA sequential polymers was investigated by XPS and ToF-SIMS. The O 1s/C 1s peak ratios of the BA polymers indicated that the flexible segment was enriched on the BA polymer surface when the number of the CH<sub>2</sub> groups was larger than 14 (the length of the flexible segment ~17 Å). The F 1s/C 1s peak ratios of the 6FBA polymers showed that the length of the flexible segment on the surface was the same as the bulk. The ratios between the intensities of the characteristic peaks of the flexible and rigid segments displayed a linear dependence on the surface flexible segment length determined by XPS.

## Introduction

Surface properties of block copolymers are usually quite different from that of the bulk.<sup>1–9</sup> The difference in the surface free energy between the block components is a major reason that the blocks of lower surface free energy preferentially segregate to the surface.

Recently, much attention has been given to the study of the surface composition and morphology of block copolymers, because surface segregation of the lower surface free energy component can occur at a very low concentration. Therefore, it is possible to change the surface properties without any significant change in the bulk composition. More recently, great interest has been generated in the study of surface composition and properties of block copolymers containing a low surface energy component, such as poly(dimethylsiloxane) (PDMS).<sup>4,5,10–14</sup> McGrath et al.<sup>4</sup> studied surface and bulk segregation in polysulfone-*b*-PDMS block copolymers by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Their work suggested that the PDMS block length determined the extent of PDMS enrichment in the overlayer while the polysulfone block length influenced the gradient of the surface composition. Systematic studies were performed on block copolymer surfaces by Gardella, Jr., et al.,<sup>10–14</sup> using XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Their results suggested that the enrichment of the PDMS blocks in the near surface region could be found in the PDMS block copolymers, such as polyimidesiloxane copolymers with short PDMS segments.<sup>10</sup> Their angle-resolved XPS results indicated that the surface composition of those copolymers was defined by the siloxane segment length.

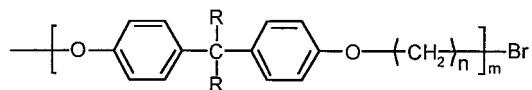
Clearly, the lower surface energy segments can segregate to the surface of the block copolymers. How-

ever, there is no general agreement on the effect of other factors, such as block or segment length, on the chemical composition of the copolymers.

ToF-SIMS has been shown to be very useful in surface characterizations of polymer materials.<sup>1,6,8,10–20</sup> The secondary fragments emitted from a polymer surface are directly related to the surface molecular structure.<sup>21–23</sup> However, there is no direct relationship between the surface chemical composition and the ToF-SIMS peak intensities. This limits the applications of ToF-SIMS in quantitative analysis of polymer surfaces. Only a few studies have been reported on the quantification of polymer surfaces by combining XPS and ToF-SIMS, such as copolymers<sup>24–26</sup> and polymer blends.<sup>27,28</sup> Briggs and Ratner<sup>24</sup> studied the random copolymers of ethyl methacrylate (EMA) and hydroxyethyl methacrylate (HEMA). The relative intensities of the characteristic fragment peaks from the EMA–HEMA copolymers were related to the bulk composition. Bertrand et al.<sup>27</sup> developed a method to estimate the surface concentration of polycarbonate (PC) and poly(methyl methacrylate) (PMMA) blends by using the relative intensities of characteristic ions of PC and PMMA. Their results had good agreement with that of XPS. However, there are still many issues that have to be resolved before ToF-SIMS can be applied routinely to the quantification of polymer surfaces.

To quantitatively study the influence of segment length on the surface composition, two series of sequential polymers with a well-defined segment length were synthesized. The surface chemical compositions, determined by XPS, were related to the length of the flexible aliphatic segment. A detailed study of this series of sequential polymers with a well-defined structure can help us obtain a better understanding of the effects of the surface flexible segment length on the

\* To whom correspondence should be addressed.

**Scheme 1. Structure of the BA and 6FBA Sequential Polymers**

R:  $-\text{CH}_3$  the BA polymers;  $-\text{CF}_3$  the 6FBA polymers

$n = 4, 6, 8, 10, 12, 14$  or  $18$

**Table 1. Binding Energies of C 1s, O 1s, and F 1s of the BA and 6FBA Polymers**

atom	functional groups	BA-Cn (eV)	6FBA-Cn (eV)
C 1s	$\text{CF}_3$		292.8 ( $\pm 0.07$ )
	$\pi \rightarrow \pi^*$ (shake-up)	291.4 ( $\pm 0.05$ )	291.4 ( $\pm 0.10$ )
	C-O	286.2 ( $\pm 0.10$ )	286.4 ( $\pm 0.08$ )
	$\text{CH}_2$ and aromatic C	284.8	284.8
O 1s	C-O	533.2 ( $\pm 0.06$ )	533.1 ( $\pm 0.04$ )
F 1s	$\text{CF}_3$		688.3 ( $\pm 0.04$ )

relative intensity ratios of the characteristic fragment ion peaks.

**Experimental Section**

**Sample Preparation.** BA and 6FBA polymers with a well-defined flexible segment length were prepared and characterized as previously reported.<sup>29</sup> The structure of the BA and 6FBA sequential polymers is shown in Scheme 1.

Thin films of the BA and 6FBA sequential polymers were prepared by solution spin-casting on silicon wafers. The solvents used for the BA and 6FBA sequential polymers were chloroform and tetrahydrofuran, respectively. The concentrations were normally in the range 10–30 mg mL<sup>-1</sup>. Approximately 40  $\mu\text{L}$  of each solution was spin-cast at 4000 rpm onto a silicon wafer of 10 mm  $\times$  10 mm. The silicon wafers were cleaned before use by being washed in acetone and *n*-hexane. All samples were free of additives, catalysts, and defects.

**ToF-SIMS and XPS.** XPS spectra were recorded on a PHI 5600 multitechnique system equipped with an Al monochromatic X-ray source. A pass energy of 58.7 eV was used. The spectra were obtained at a takeoff angle of 45°. The number of the  $\text{CH}_2$  group on the BA and 6FBA polymer surfaces was calculated from the O/C and F/C peak area ratios. All core-level spectra were referenced to the C 1s (C-C and C-H bonds) peak at 284.8 eV. The C 1s, O 1s, and F 1s binding energies of the BA and 6FBA sequential polymers are listed in Table 1.

The ToF-SIMS measurements were performed on a Physical Electronics PHI 7200 ToF-SIMS spectrometer. High-resolution mass spectra were obtained by using a Cs<sup>+</sup> primary ion source operating at 8 keV. The total ion dose was lower than 4  $\times$  10<sup>11</sup> ions/cm<sup>2</sup>. Three positive and three negative spectra were taken for each sample.

**Results and Discussion**

**XPS Results.** As an example, parts a and b of Figure 1 show the C 1s core-level spectra of the BA-C8 and 6FBA-C8 polymers, respectively. The difference in the C 1s core-level between the BA and 6FBA polymers is due to the presence of different side groups ( $\text{CH}_3$  and  $\text{CF}_3$ ). The C 1s binding energy of the ( $\text{CF}_3$ ) carbon is observed at 292.8 eV. The C 1s binding energies of the  $\text{CF}_3$ , and C-O carbons are similar to the values reported in the literature.<sup>16</sup> There is no change in the binding energy of the C 1s, O 1s, and F 1s core levels when the length of the flexible segment of the BA and 6FBA polymers increases.

The number of the  $\text{CH}_2$  groups at the surface of the BA polymers,  $n_s$ , was determined by the following equation:

$$n_s = \frac{2 - 15R_{\text{O/C}}}{R_{\text{O/C}}} \quad (1)$$

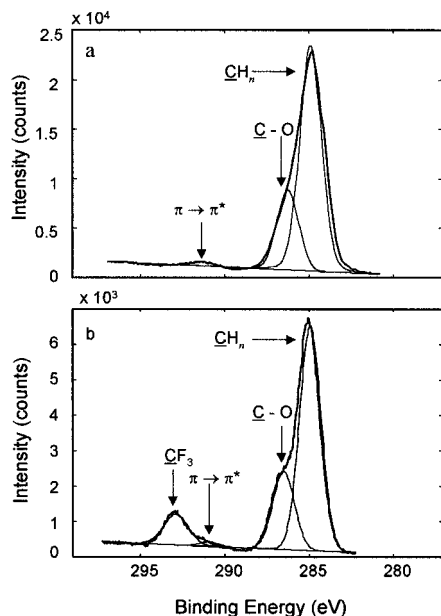
where  $R_{\text{O/C}}$  is the O-to-C atomic ratio. The number of the  $\text{CH}_2$  groups at the surface of the 6FBA polymers was determined by using the F-to-C atomic ratio,  $R_{\text{F/C}}$ .

$$n_s = \frac{6 - 15R_{\text{F/C}}}{R_{\text{F/C}}} \quad (2)$$

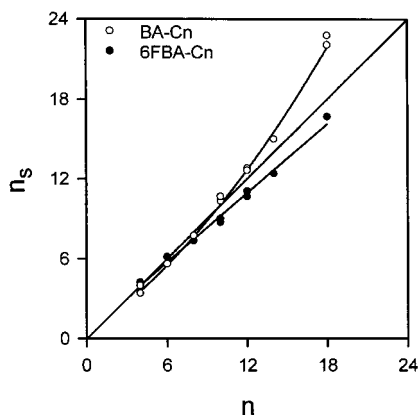
The atomic concentrations of O, C, and F were calculated by using the peak areas and the sensitivity factors provided by Physical Electronics. The number of the  $\text{CH}_2$  groups as a function of  $n$  is shown in Figure 2. The value of  $n_s$  for the 6FBA polymers exhibits a linear relationship with the value of  $n$  for  $n = 4$ –18. The value of  $n_s$  is slightly smaller than  $n$  as  $n$  increases, possibly indicating a slight surface excess of the rigid segments because of the presence of two  $\text{CF}_3$  groups in the rigid segments. However, for the BA polymers  $n_s$  determined by XPS is much larger than  $n$ , when  $n > 14$ . This suggests that the flexible segments segregate onto the surface of the BA polymers when the length of the flexible segment is long enough ( $n > 14$ , segment length  $\sim 17$  Å). Repeated measurement yielded similar results. A comparison between the XPS results of the BA and 6FBA polymers indicates that the effects of the flexible segment length on the surface composition are different even for the sequential polymers with a very similar structure. The difference in the surface free energy between the rigid and flexible segments is the driving force for the segregation of the low surface energy component to the surface. Because the BA and 6FBA polymers have a different side group ( $\text{CH}_3$  and  $\text{CF}_3$ ), the surface energy difference between the rigid and flexible segments is not identical for these two polymers.

The length of the flexible segment plays an important role in determining the surface composition of the polymers. In the BA polymers, the flexible segment obviously has a lower surface energy than the rigid segment. When the length of the flexible segment increases, the flexibility of the segment also increases. As a result, surface excess of the flexible segments occurs. But for the 6FBA polymers, the surface energy difference between the rigid and flexible segments may not be significant. Therefore, no significant surface excess of the flexible segments is observed even at  $n = 18$ .

**ToF-SIMS Results.** To simplify the analysis of the ToF-SIMS results, the characteristic ion fragments of the BA and 6FBA polymers are summarized in three series. (1) Flexible fragments,  $F_i$ , are mainly emitted from the flexible segment, such as  $\text{CH}_2^-$ ,  $\text{C}_2\text{H}_5^+$ ,  $\text{C}_3\text{H}_7^+$ , and  $\text{C}_4\text{H}_9^+$ , at  $m/z = 14, 29, 43,$  and  $57$ , respectively. (2) Rigid fragments,  $R_j$ , are mainly emitted from the rigid segment, such as  $\text{C}_7\text{H}_{11}\text{O}^+$  and  $\text{C}_{14}\text{H}_{13}\text{O}_2^+$ , at  $m/z = 135,$  and  $213$ , respectively, of the BA polymers and  $\text{C}_9\text{F}_6\text{H}_5\text{O}^+$ ,  $\text{C}_{14}\text{F}_3\text{H}_{10}\text{O}_2^+$ ,  $\text{C}_9\text{F}_5\text{H}_4\text{O}^-$ , and  $\text{C}_{14}\text{F}_3\text{H}_8\text{O}_2^-$  at  $m/z = 243, 267, 223,$  and  $265$ , respectively, of the 6FBA polymers. The possible structure of these ions is shown in Scheme 2. (3) Molecular fragments,  $\text{AB}_n$ , are directly related to the molecular structure of the BA and 6FBA repeat units, such as  $[\text{M}-\text{H}]^-$  at  $m/z = 281, 309, 337,$  ... with  $n = 4, 6, 8, \dots$  of the BA polymers. If the matrix effects can be neglected, the absolute intensity ratios,  $I(F_j)/I(R_j)$ , of the flexible fragments to the rigid fragments are related to the number of the  $\text{CH}_2$  groups at

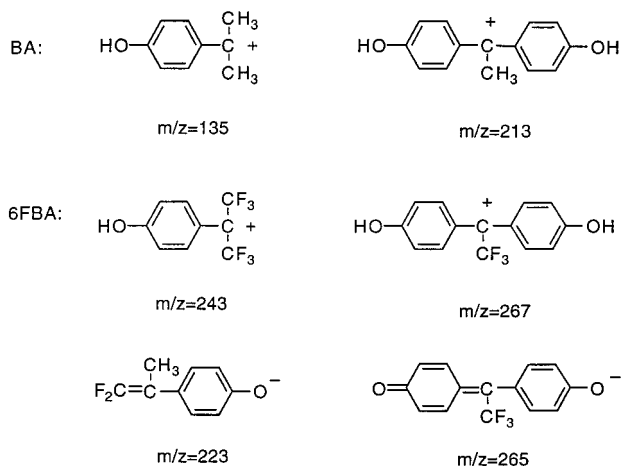


**Figure 1.** C 1s spectra of the BA and 6FBA polymers showing the carbon atoms at different environments.



**Figure 2.**  $n_s$  determined by XPS vs  $n$  of the BA and 6FBA polymers.

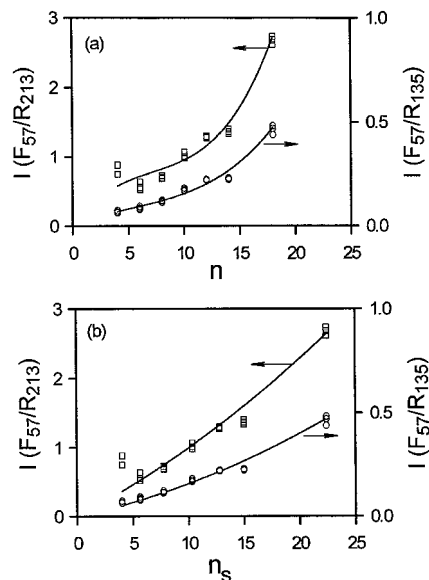
### Scheme 2. Structure of the Ions from the Rigid Fragments



the surface,  $n_s$ , as shown in eq 3.

$$\frac{I(F_j)}{I(R_j)} = \frac{S_i C(F)}{S_j C(R)} \propto K(ij) n_s \quad (3)$$

where  $I(F_j)$  and  $I(R_j)$  are the absolute intensities of the

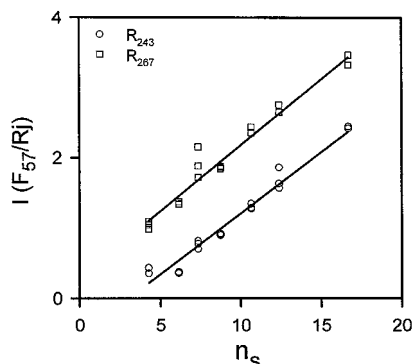


**Figure 3.** Positive ion intensity ratios of  $I(F_{57})/I(R_{135})$  and  $I(F_{57})/I(R_{213})$  of the BA polymers as a function of (a)  $n$  and (b)  $n_s$ .

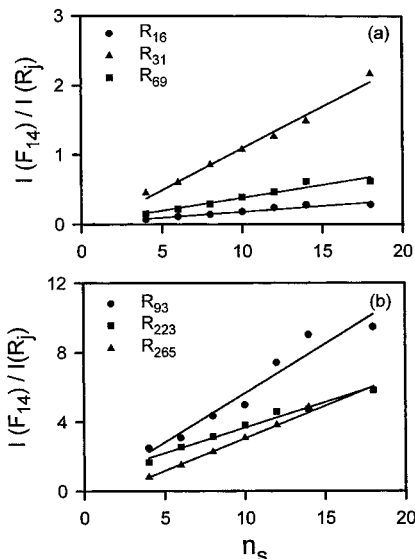
flexible and rigid segments, respectively.  $S_i$  and  $S_j$  are related to the sensitive factors of the ion fragments  $i$  and  $j$ , respectively.  $C(R)$  and  $C(F)$  are the molar concentrations of the flexible and rigid segments, respectively.  $K(ij)$  is a parameter related to the yield of fragments  $i$  and  $j$ .

The positive ion intensities of the flexible segments were examined using saturated aliphatic ions such as  $C_2H_5^+$ ,  $C_3H_7^+$ , and  $C_4H_9^+$  at  $m/z = 29$ , 43, and 57,  $I(F_{29})$ ,  $I(F_{43})$ , and  $I(F_{57})$ , of the BA and 6FBA polymers. The positive ion intensities of the rigid segments were examined using the characteristic ions such as  $C_9H_{11}O^+$  and  $C_{14}H_{13}O^+$  at  $m/z = 135$  and 213,  $I(R_{135})$  and  $I(R_{213})$ , of the BA polymers. The characteristic positive ions such as  $C_9F_6H_5O^+$  and  $C_{14}F_3H_{10}O_2^+$  at  $m/z = 243$  and 267,  $I(R_{243})$  and  $I(R_{267})$ , of the 6FBA polymers were used. As an example, the ion ratios of the BA polymers  $I(F_{57})/I(R_{135})$  ( $C_4H_9^+/C_9H_{11}O^+$ ) and  $I(F_{57})/I(R_{213})$  ( $C_4H_9^+/C_{14}H_{13}O^+$ ) are plotted vs  $n$ , as shown in Figure 3a. The ion ratios,  $I(F_{57})/I(R_{135})$  and  $I(F_{57})/I(R_{213})$ , increase monotonically with  $n$ , as shown in Figure 3a. It is obvious that the ratios do not increase linearly with  $n$ . However, the ion ratios,  $I(F_{57})/I(R_{135})$  and  $I(F_{57})/I(R_{213})$ , increase fairly linearly with  $n_s$  as shown in Figure 3b. The ion ratios of 6FBA polymers,  $I(F_{57})/I(R_{243})$  ( $C_4H_9^+/C_9F_6H_5O^+$ ) and  $I(F_{57})/I(R_{267})$  ( $C_4H_9^+/C_{14}F_3H_{10}O_2^+$ ), increase linearly with  $n_s$ , as shown in Figure 4. The other ion ratios,  $I(F_{29})/I(R_j)$  and  $I(F_{43})/I(R_j)$ , show similar results. These results further reflect the fact that these ion ratios are directly related to the surface concentration of the flexible segments and can be used in quantitative analysis of these polymers.

Negative ions in ToF-SIMS mass spectra of most polymers have been ignored due to the fact that the intensity of negative ion fragments above 30 amu is often too weak to be used accurately in quantitative analysis. However, negative ion ToF-SIMS spectra of the 6FBA polymers can be used because of their high intensity. In particular, negative ions, such as  $O^-$ ,  $F^-$ ,  $CF^-$ ,  $CF_3^-$ ,  $C_3F_3^-$ ,  $C_9F_5H_4O^-$ , and  $C_{14}F_3H_8O_2^-$  at  $m/z = 16$ , 19, 31, 69, 93, 243, and 265, are unique to the rigid segment of the 6FBA polymers. The aliphatic ion,  $CH_2^-$  at  $m/z = 14$ , is unique to the flexible aliphatic segments.



**Figure 4.** Positive ion intensity ratios of  $I(F_{57})/I(R_{243})$  and  $I(F_{57})/I(R_{267})$  of the 6FBA polymers as a function of  $n_s$ .



**Figure 5.** Negative ion intensity ratios of the 6FBA polymers: (a)  $I(F_{14})/I(R_j)$ ,  $j = 16, 31,$  and  $69$ ; (b)  $I(F_{14})/I(R_j)$ ,  $j = 93, 223,$  and  $265$ .

Therefore, it is worth showing that these negative ions can also be used in quantitative analysis. The negative ion ratios  $\text{CH}_2^-/\text{O}^-$ ,  $\text{CH}_2^-/\text{CF}^-$ ,  $\text{CH}_2^-/\text{CF}_3^-$ ,  $\text{CH}_2^-/\text{C}_3\text{F}_3^-$ ,  $\text{CH}_2^-/\text{C}_9\text{F}_5\text{H}_4\text{O}^-$ , and  $\text{CH}_2^-/\text{C}_{14}\text{F}_3\text{H}_8\text{O}_2^-$  are used. All these ion ratios increase linearly with  $n_s$ , as shown in Figure 5a,b.

### Conclusions

XPS and ToF-SIMS analyses of BA and 6FBA polymers with a well-defined segment length have revealed the details of the polymer surfaces. Both positive and negative SIMS spectra, combined with the XPS calibration, can be used in quantitative analysis of the BA and 6FBA polymers. It is the first time that the influence of the segment length of one of the components on the surface chemical composition is quantitatively determined. The flexible aliphatic segments can segregate

on the surface of the BA polymers only when the length of the flexible segment is above a certain value ( $n > 14$  and the length  $> 17 \text{ \AA}$ ). There is no significant difference between  $n_s$  and  $n$  for  $n$  ranging from 4 to 18 for the 6FBA polymers determined by XPS and ToF-SIMS. Therefore, the surface segregation may occur at different lengths even for polymers with a similar structure.

**Acknowledgment.** This work was supported by the Hong Kong Government Research Grand Council under Grant HKUST 9123/97P.

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MA991445E