ELSEVIER

Polymer 41 (2000) 2695–2699

polymer

Polymer Communication

Influence of chain sequence structure of polymers on ToF-SIMS spectra

Jiyun Feng[a], Chi-Ming Chan[a,*], Lu-Tao Weng[b]

[a]Department of Chemical Engineering, Advanced Engineering Materials Facility, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China
[b]Materials Characterization and Preparation Facility, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China

Received 5 July 1999; received in revised form 20 August 1999; accepted 20 August 1999

Abstract

The influence of the chain sequence structure of an alternating ethylene–tetrafluoroethylene (ETFE) copolymer and poly(vinylidene fluoride) (PVDF) on both positive and negative time-of-flight secondary ion mass spectrometry (ToF-SIMS) spectra ($m/z \leq 200$) was studied. The C_1, C_2, C_3, C_4 and C_5 positive ions were found in the ETFE spectrum, while only the C_1, C_2 and C_3 positive ions were found in the PVDF spectrum. These results indicate that ETFE can be distinguished from PVDF by the presence of its characteristic C_4 and C_5 positive ions. Even though both ETFE and PVDF produce some of the same C_3 positive ions, these positive ions come from different sequence structures. The negative ToF SIMS spectra of both ETFE and PVDF are totally dominated by F^- ($m/z = 19$) because F^- is very stable, due to its largest electronegative value, and fluorine concentration in ETFE and PVDF is relatively high. These results indicate that the chain sequence structure has a significant effect on the positive ToF-SIMS spectra of ETFE and PVDF, especially in the high-mass range. However, the chain sequence structure does not have much effect on the negative spectra of ETFE and PVDF. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ethylene–tetrafluoroethylene; Poly(vinylidene fluoride); Secondary ion mass spectrometry spectra

1. Introduction

Recently, time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been widely used to study the surface of homopolymers, copolymers and polymer blends [1–17]. SIMS has much a higher sensitivity than X-ray photoelectron spectroscopy (XPS) and can provide detailed structural information of polymer surfaces that cannot be obtained by XPS. In addition, ToF-SIMS can also generate surface chemical images with high spatial resolution. With ToF-SIMS, researchers have extensively studied the effects of tacticity [4], sequence distribution [5,6], end group [7,8], branching [9], crosslinking, [10], molecular weight distribution [11–13] and molecular weight [14–16] on the surface properties of polymers. For example, Venden Eynde et al. elucidated the influence of tacticity on polymer surfaces [4]. Their results indicate that the isotacticity of PMMA and PS leads, respectively, to a decrease in and an increase in the concentration of the pendent group at the surface. Ooji et al. investigated the effects of branching and unsaturation on the fingerprint spectra of simple aliphatic hydrocarbons [9]. They found that the low-mass positive spectra reflect structural differences in the polymers. In addition, differences in branching and unsaturation lead to very distinct spectra features that show the capability of SIMS for identification of polymers.

Even though many studies have been performed, much work is still needed in this area because the fragmentation mechanisms of many polymers have not been fully understood. In general, it is well known that the SIMS fingerprint spectra ($m/z < 200$) contain fragments specific to the molecular structure of polymers These different characteristic fragments can be used to identify different polymers. The objective of this work is to test SIMS as an analytical technique for distinguishing two polymers having an identical chemical composition and a similar chain sequence structure. For example, PVDF and ETFE, which are isomers, are ideal candidates. The chain sequence structure of these two polymers is shown in Fig. 1.

2. Experimental

2.1. Materials and preparation

The ETFE used in this study is an alternating ethylene-tetrafluoroethylene copolymer supplied by Du Pont. Its

---

* Corresponding author. Tel.: +852-2358-7125; fax: +852-2358-7125.
E-mail address: kecmchan@ust.hk (C.-M. Chan)

0032-3861/00/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(99)00612-6

ETFE AABBAABBAABBAABB

PVDF ABABABABABABABAB

A = CH_2 B = CF_2

Fig. 1. Sequence structures of ETFE and PVDF.

melting point is 240°C. The PVDF is Hylar 460 available from Ausimount Co., USA. A 2 mm thick ETFE sheet was prepared by a hot press at 260°C and 16 MPa. A 2 mm thick PVDF sheet was prepared in the similar way except that the processing temperature was 200°C. To obtain a flat surface for ToF-SIMS analysis, the samples were cut by a cryo-microtome (Leica) at −100°C.

2.2. Surface characterization

ToF-SIMS measurements were performed on a Physical Electronics PHI 7200 ToF-SIMS spectrometer equipped with two ion guns (Cs^+ for high-mass resolution spectrometry and $^{69}Ga^+$ for spatially resolved imaging) and a reflection ToF analyzer. Both positive and negative high-mass resolution spectra were obtained by using an 8 kV Cs^+ ion source. The scanned area was $200 \times 200\ \mu m^2$ and the total dose for each spectrum acquisition was $< 4 \times 10^{11}$ ions/cm^2.

3. Results and discussion

3.1. Positive ToF-SIMS spectra of ETFE and PVDF

Typical positive ToF-SIMS spectra of ETFE and PVDF are shown in Figs. 2 and 3, respectively. The characteristic positive ions for both ETFE and PVDF were identified and are summarized in Table 1. As can be seen from the table, C_1, C_2, C_3, C_4 and C_5 positive ions are present in the ETFE spectrum, while only C_1, C_2, and C_3 positive ions are present in the PVDF spectrum. These results indicate that sequence structure can significantly influence the positive ToF-SIMS fingerprint spectra of ETFE and PVDF especially in the high-mass range.

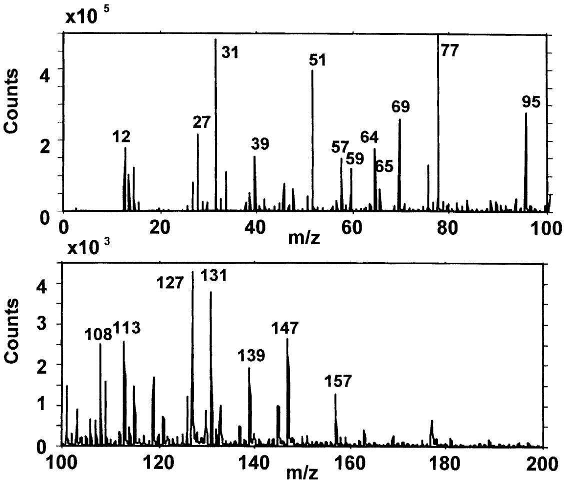

Fig. 2. Positive ToF-SIMS spectrum of ETFE.

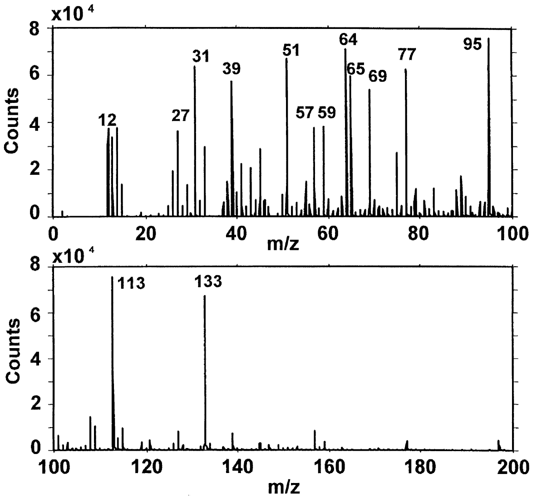

Fig. 3. Positive ToF-SIMS spectrum of PVDF.

For the C_1 positive ions, as shown in Table 1, both ETFE and PVDF generate the same characteristic positive ions, such as C^+, CF^+, CHF_2^+ and CF_3^+ with a different intensity. This result illustrates that the generation of C_1 positive ions from these two polymers is not significantly affected by the chain sequence structure, and that the fragmentation

Table 1
Characteristic positive ions of ETFE and PVDF

m/z	ETFE	PVDF
	C_1 positive ions	C_1 positive ions
12	C^+	C^+
31	CF^+	CF^+
51	CHF_2^+	CHF_2^+
69	CF_3^+	CF_3^+
	C_2 positive ions	C_2 positive ions
27	$C_2H_3^+$	$C_2H_3^+$
64	$C_2F_2H_2^+$	$C_2F_2H_2^+$
65	$C_2H_3F_2^+$	$C_2H_3F_2^+$
119	$C_2F_5^+$	
	C_3 positive ions	C_3 positive ions
39	$C_3H_3^+$	$C_3H_3^+$
57	$C_3H_2F^+$	$C_3H_2F^+$
59	$C_3H_4F^+$	$C_3H_4F^+$
77	$C_3H_3F_2^+$	$C_3H_3F_2^+$
95	$C_3H_2F_3^+$	$C_3H_2F_3^+$
113	$C_3HF_4^+$	$C_3HF_4^+$
131	$C_3F_5^+$	
133		$C_3H_2F_5^+$
	C_4 positive ion	
108	$C_4H_3F_3^+$	
127	$C_4H_3F_4^+$	
147	$C_4H_4F_5^+$	
	C_5 positive ion	
139	$C_5H_3F_4^+$	
157	$C_5H_2F_5^+$	

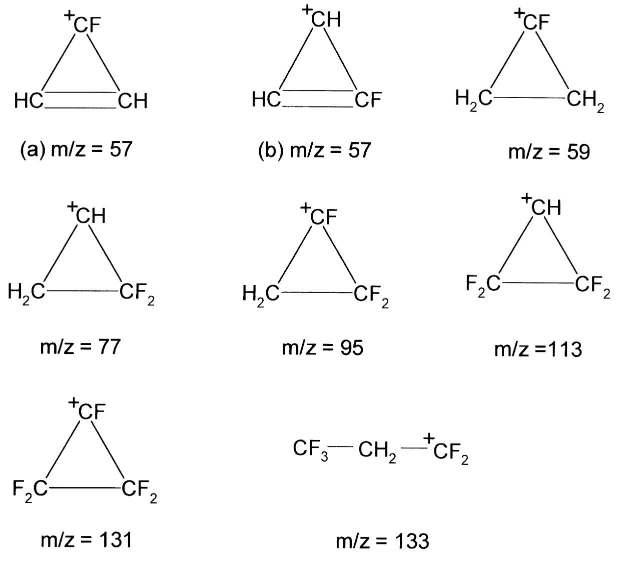

Fig. 4. Probable structures of the C_3 positive ions.

mechanisms for the C_1 positive ions are very similar. These results are also in agreement with the previously published results for polyethylene and polypropylene [2,3].

The situation is quite different for the C_2 positive ions. On the one hand, both ETFE and PVDF produce some of the same characteristic positive ions, such as $CH_2CF_2|\cdot^+$ (monomer ion for PVDF) and $CH_3–CF_2^+$. This is because both ETFE and PVDF contain the AB sequence (CH_2CF_2) in their chain structure as depicted in Fig. 1. We believe that these two characteristic positive ions come from the AB sequence. On the other hand, in addition to the two characteristic positive ions discussed above, ETFE also generates its unique characteristic positive ion $CF_3 - CF_2^+$, which is absent in the PVDF spectrum. Thus, $CF_3 - CF_2^+$ ($m/z = 119$) is a characteristic positive ion of ETFE that can be used to differentiate ETFE and PVDF. The reason for this difference is due to the fact that $CF_3 - CF_2^+$ comes from the end group ($CF_3–CF_2$) of ETFE which is only present in ETFE and not PVDF.

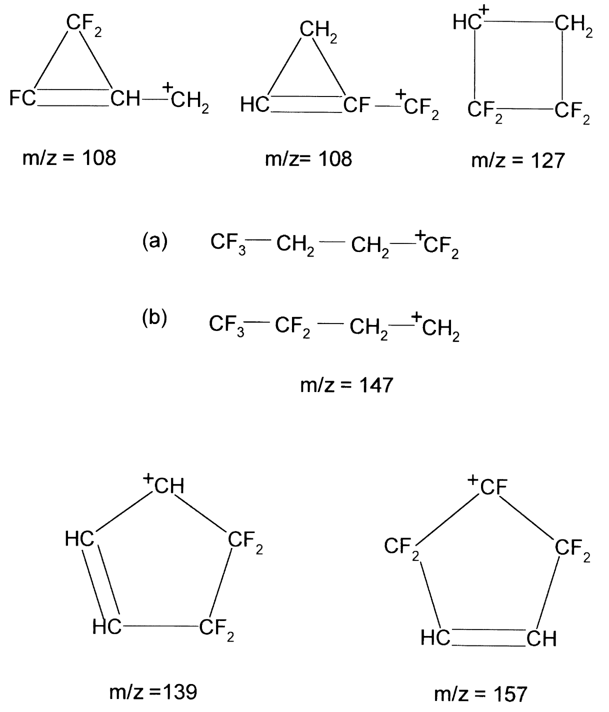

Fig. 5. Probable structures of the C_4 and C_5 positive ions.

In order to attain a deeper understanding of the effects of the sequence structure on the fragmentation mechanisms of ETFE and PVDF, it is necessary to determine the structure of these characteristic ions. Based on their chemical compositions and origins, some probable structures for the C_2 positive are displayed below:

$$CH_2CF_2|\cdot^+ \qquad m/z = 64$$

$$CH_3 - CF_2^+ \qquad m/z = 65$$

$$CF_3 - CF_2^+ \qquad m/z = 119$$

As can be seen from Table 1, the sequence structure can significantly influence the formation of the C_3 positive ions. Both ETFE and PVDF produce some of the same characteristic positive ions, such as $C_3H_2F^+$, $C_3H_4F^+$, $C_3H_3F_2^+$, $C_3H_2F_3^+$ and $C_3HF_4^+$. It should be pointed out that they come from different sequence structures. According to their chemical composition, it can be deduced that for ETFE, the positive ions such as $C_3H_2F^+$, $C_3H_4F^+$ and $C_3H_3F_2^+$ come from the AAB sequence, while $C_3H_2F_3^+$ and $C_3HF_4^+$ come from the ABB sequence. Similarly, for PVDF, the positive ions such as $C_3H_2F^+$, $C_3H_4F^+$ and $C_3H_3F_2^+$ come from the ABA sequence, while $C_3H_2F_3^+$ and $C_3HF_4^+$ come from the BAB sequence. In addition to the C_3 positive ions discussed above, both ETFE and PVDF also generate their individual characteristic positive ions. ETFE generates $C_3F_5^+$ while PVDF produces $C_3H_2F_5^+$. For ETFE, $C_3F_5^+$ comes from the ABB sequence, while for PVDF, $C_3H_2F_5^+$ comes from the BAB sequence. Obviously, these two ions can be used as the characteristic positive ions to identify these two polymers. Some probable structures for these positive ions are shown in Fig. 4. As displayed in this figure, both ions a and b can be the correct structure for $C_3H_2F^-$ ($m/z = 57$). Because fluorine has the highest electronegative value, ion b is a more stable structure.

Based on the results shown in Table 1, it is important to point out that only ETFE can produce the C_4 and C_5 positive ions. For the C_4 positive ions, $C_4H_3F_3^+$, $C_4H_3F_4^+$ (the deprotonated monomer) and $C_4H_4F_5^+$ may come, respectively, from the AABB, ABBA and BAAB sequences of ETFE. For the C_5 positive ions, $C_5H_3F_4^+$ and $C_2H_2F_5^+$ come from the ABBAA and BAABB sequences. The probable structures for some of these positive ions are shown in Fig. 5. The structures, as shown in Fig. 5, all contain $CF_x–CF_y$ which is

Table 2
The normalized intensity of some of the peaks for ETFE and PVDF. The intensity of the peaks is normalized with respect to the peak at *m/z* = 31

m/z	Normalized intensity	
	ETFE	PVDF
12	0.88	2.40
39	0.32	0.86
51	0.91	1.10
57	0.35	0.67
59	0.27	0.57
64	0.42	1.08
65	0.13	0.94
69	0.67	1.01
77	1.28	1.06
95	0.79	1.35
108	0.14	
113	0.16	2.80
119	0.12	
127	0.31	
133		2.61
139	0.14	
147	0.20	
157	0.10	

unlikely to have come from PVDF. Similar to $C_3H_2F^-$, the positive ion, $C_4H_4F_5^+$ ($m/z = 147$), also has two probable structures (a) and (b) as depicted in Fig. 5. For the same reason given above, structure (b) is a preferred structure because it is more stable.

In order to make a quantitative comparison, the intensity of the peak CF^+ at $m/z = 31$ is used as the reference and all other peak intensities are normalized with respect to this peak intensity. Table 2 shows the normalized intensity of ETFE and PVDF. As can be seen from Table 2, for ETFE, the strongest peak is at $m/z = 77$ ($C_3H_3F_2^+$), while for PVDF, the strongest peak at $m/z = 113$ ($C_3H_2F_3^+$). This shows that the sequence structure can significantly affect the intensity of the positive ions in ToF-SIMS spectra.

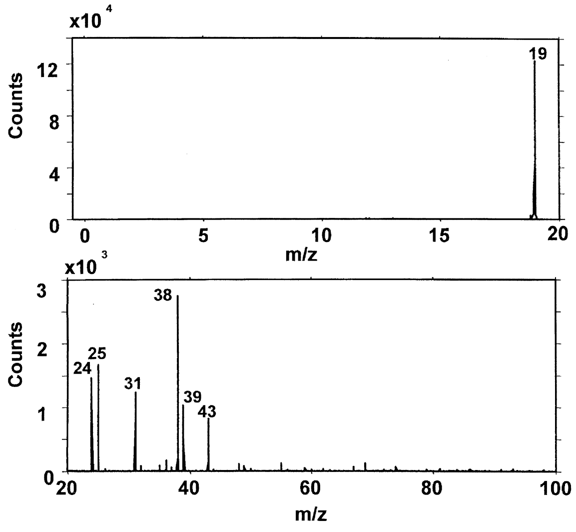

Fig. 6. Negative ToF-SIMS spectrum of ETFE.

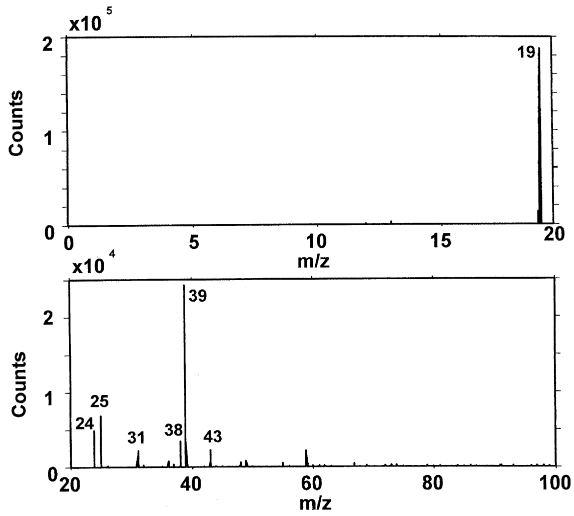

Fig. 7. Negative ToF-SIMS spectrum of PVDF.

It should be pointed out that for the positive ions having the same chemical composition, the normalized intensity of the peaks of ETFE except for the peak at *m/z* = 77, is smaller than that of the peaks of PVDF. The significant reduction in the normalized intensity of the ETFE peaks is due to the fact that C_1, C_2, C_3, C_4 and C_5 positive ions are produced by ETFE, while only C_1, C_2 and C_3 positive ions are produced by PVDF.

3.2. Negative ToF-SIMS spectra of ETFE and PVDF

Figs. 6 and 7 show the negative ToF-SIMS spectra of ETFE and PVDF, respectively. It is obvious that these two spectra are very similar. The dominant peak is at $m/z = 19$ (F^-) and many other smaller characteristic peaks are at $m/z = 24$ (C_2^-), 25(C_2H^-), 31(CF^-), 38(F_2^-), 39(F_2H^-) and 43(C_2F^-), as listed in Table 3. In addition, these two negative ToF-SIMS spectra are very similar to that of PTFE [2,3], The reason for this similarity is the presence of the F^-, which is the most stable negative ion because it has the highest electronegative value among all elements. In

Table 3
The normalized intensity of the characteristic negative ions of ETFE and PVDF

m/z	Negative ion	Normalized intensity	
		ETFE	PVDF
19	F^-	175.40	147.10
24	C_2^-	1.05	1.82
25	C_2H^-	1.12	2.51
31	CF^-	1.00	1.00
38	F_2^-	2.42	1.65
39	F_2H^-	0.77	8.82
43	CF_2^-	0.63	0.94

addition, the fluorine concentration in these three polymers is relatively high.

In order to make a quantitative comparison between the two negative ToF-SIMS spectra, we use CF^- at $m/z = 31$ as the reference peak. All other peak intensities were normalized with respect to this peak intensity. Table 3 shows the normalized intensities calculated for ETFE and PVDF. There is some difference between ETFE and PVDF in the results, as shown in Table 3. For ETFE, the normalized intensity of the peak at $m/z = 38$ is much higher than that at $m/z = 39$; while for the PVDF, the normalized intensity of the peak at $m/z = 38$ is much lower than that at $m/z = 39$. These results can be explained by the difference in the sequence structure between ETFE and PVDF, as shown in Fig. 1. A fluorine atom in the ABB sequence of ETFE has three fluorine atoms and two hydrogen atoms as its neighbors. The probability to form an F_2^- ion is thus much higher than that to form an F_2H^- ion. The fluorine atom in the ABA sequence of PVDF has only one fluorine atom and four hydrogen atoms as its neighbors. Hence, the probability to form an F_2^- ion is smaller than that to form an F_2H^- ion.

4. Conclusions

The effects of sequence structure on the SIMS fingerprint spectra of ETFE and PVDF are elucidated. Our results indicate that ETFE generates C_1, C_2, C_3, C_4 and C_5 positive ions while PVDF only produces C_1, C_2 and C_3 positive ions. These results clearly imply that sequence structure can significantly influence the positive SIMS spectra of ETFE and PVDF especially in the high-mass range ($m/z = 100 - 200$). Both ETFE and PVDF produce the same C_2 positive ions because they both contain the CH_2CF_2 sequence. Even though ETFE and PVDF also generate some of the same C_3 positive ions, these positive ions come from different sequence structures. Our results also show that ETFE can be distinguished from PVDF by the presence of its characteristic positive ions, including $C_2(C_2F_5^+)$, $C_3(C_3F_5^+)$ as well as the C_4 and C_5 positive ions.

The sequence structure does not have much effect on the negative ToF-SIMS spectra. The negative ToF-SIMS spectra of these two polymers are totally dominated by the peak at $m/z = 19$ (F^-). The only difference between the negative SIMS spectra of ETFE and PVDF is that for ETFE, the normalized intensity of the peak at $m/z = 38$ is much higher than that of the peak at $m/z = 39$, but vice versa for PVDF. Our results clearly indicate that ToF-SIMS can be used to differentiate two polymers having an identical chemical composition and a similar chain sequence structure.

Acknowledgements

This work was supported by the Hong Kong Government Research Grant Council under Grant no. HKUST 6123/97P.

References

[1] Benninghoven A. Angew Chem Int Ed 1994;33:1023.

[2] Newman JG, Carlson BA, Michael RS, Moulder JF, Holt TH. Static SIMS handbook of polymer analysis. Perkin–Elmer Corporation, 1991.

[3] Briggs D, Brown A, Vickman JC. Handbook of static secondary ion mass spectrometry (SIMS). Chichester, UK: Wiley, 1989.

[4] Venden Eynde X, Weng LT, Bertrand P. Surf Interface Anal 1997;25:41.

[5] Zhuang HZ, Gardella Jr. JA, Hercules DM. Macromolecules 1997;30:1153.

[6] Li L, Chan CM, Weng TL. Macromolecules 1997;30:3698.

[7] Affrossman S, Brertrand P, Hartshorne M, Kiff T, Leonard D, Petrick RA, Richards RW. Macromolecules 1996;29:5432.

[8] Vanden Eynde X, Bertrand P, Dubios P, Jerome R. Macromolecules 1998;31:6409.

[9] Van Ooji WJ, Brinkhuis RHG. Surf Interface Anal 1988;11:430.

[10] Lianos L, Quet C, Duc TM. Surf Interface Anal 1994;21:14.

[11] Benninghoven A. J Vac Sci Technol A 1985;3:451.

[12] Hercules DM, Bletsos IV, Benninghoven A, Griefendorf D. Polym Mater Sci Eng 1986;54:302.

[13] Bletsos IV, Hercules DM, Vanleyen D, Benninghoven A. Macromolecules 1987;20:407.

[14] Vanden Eynde X, Bertrand P, Jerome R. Macromolecules 1997;30:6407.

[15] Vanden Eynde X, Matyiszemski K, Bertrand P. Surf Interface Anal 1997;26:569.

[16] Gluska AA. Surf Interface Anal 1997;25:970.

[17] Chan CM. Polymer surface modification and characterization. New York: Hanser, 1994.