Macromolecules

Volume 34, Number 15 July 17, 2001

Communications to the Editor

Influence of Triad Sequences on the Secondary Ion Emission in Random Copolymers

X. Vanden Eynde,*,†,§ K. Reihs,‡ and P. Bertrand†

Université catholique de Louvain, Unité PCPM, Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium, and Bayer AG, Central Research, D-51369 Leverkusen, Germany

Received August 10, 2000
Revised Manuscript Received March 5, 2001

Introduction. Secondary ion mass spectrometry (SIMS) is well-known as a powerful technique for polymer surface characterization and nicely complements X-ray photoelectron spectroscopy (XPS).[2−4] With optimized equipment of SIMS using high mass resolution and imaging modes, molecular differentiation and localization are quite straightforward. By contrast, quantification is still difficult due to the complex secondary ion emission processes. Indeed, the polymer fragmentation/ion emission processes are altered by the intra- and intermolecular environment, called the matrix effect.[5,6]

A few copolymers have been intensively studied by SIMS.[7−20] The content of constituents in copolymers can be easily determined by semiempirical calibration based on intensity ratios. Such intensity ratios can include peak intensities of atomic or molecular fragments. The effect of the copolymer sequence on fragment ion intensities in SIMS has already been observed for different molecular fragments[5,18] and atomic ions.[17] In some cases, fragments comprising different repeat units are observed, and their peak intensities can be directly related to the copolymer sequences.[15] Our results obtained on styrene-*r*-methyl methacrylate copolymers (S-*r*-M) synthesized by bulk radical polymerization are presented in a companion paper.[1] At these bulklike surfaces, we observed that, for some fragments, the peak intensities are higher than those observed for the pure polymers. These observations indicate that the arrangement of the copolymer units along the chain influences the secondary ion emission. Most notably, the $C_7H_7^+$ fragment formation seems to be promoted by the copolymer intramolecular arrangement compared to either PS or PMMA.

In the companion paper, the effect was only discussed qualitatively and the presented curves were obtained by data smoothing.[1] Since the S-*r*-M samples were synthesized under the same conditions, the reactivity ratios are kept constant, and therefore the copolymer internal arrangements (diads, triads, etc.) can be established assuming a statistical distribution (Bernouillian model) or by a detailed analysis of the polymerization process (terminal model). The aim of this communication is to relate the secondary ion peak intensities to the copolymer repeat unit sequences, thus quantifying the corresponding intramolecular matrix effect.

Table 1. Experimental Conditions Used during the Copolymerization and Copolymer Bulk Charaterization

ID code	reaction time (min)	styrene mole fraction in the feed (mol %)	styrene mole fraction in the copolymer (mol %)	
			NMR	elemental analysis
copo-70	15	79	71	70
copo-60	15	58	58	62
copo-46	30	35	45	47
copo-40	30	25	38	41

[a] General conditions: bulk, AIBN (0.67 mol %), 80 °C.

Experimental Setup. *Polymer Materials and Film Preparation.* Free-radical copolymerizations of styrene and methyl methacrylate were carried out in bulk at 80 °C using azobis(isobutyronitrile) (AIBN) as the initiator. Exact experimental conditions are provided in Table 1. The final polymer was obtained by precipitation in methanol at room temperature, filtered, and dried in an oven under vacuum. Exact copolymer compositions

† Université catholique de Louvain.
‡ Bayer AG.
§ New address: CRM, rue E. Solvay 11, B-4000 Liège, Belgium.
* To whom the correspondence should be addressed. E-mail vdeneynde@rdmetal.ulg.ac.be.

10.1021/ma0014113 CCC: $20.00
Published on Web 06/21/2001

were determined by elemental analysis (Microanalysis Laboratory, University of Massachusetts) and quantitative ^{1}H NMR spectroscopy (Bruker 300 MHz, $CDCl_3$). Copolymerization kinetic parameters were computed using Prism software (2.0 Power PC Macintosh version) from GraphPad Software Inc. We obtained $r_1 = 0.44 \pm 0.04$ and $r_2 = 0.25 \pm 0.03$ for styrene (index 1) and methyl methacrylate (index 2) with a correlation coefficient $R^2 = 0.9986$. These numbers compare favorably to values obtained from the literature.

Each polymer was dissolved in benzene at 30 mg/mL concentration (HPLC grade solvent from Union Chimique Belge, Belgium). A drop of this solution was spin-coated onto a polished silicon wafer (Wacker), yielding a film thickness of approximately 150 nm. The deposited films were then washed with *n*-hexane (Merck) in order to remove any residual contamination by poly(dimethylsiloxane) (PDMS) and were immediately dried in air. No further treatment was applied prior to the analysis. Film depositions were made in a clean room environment directly before analysis.

Static SIMS measurements were carried out at UCL, Louvain-la-Neuve, using a PHI-Evans TFS-4000 MMI time-of-flight spectrometer using a $^{69}Ga^+$ (15 keV) liquid metal ion source. Secondary ions were accelerated to 3 keV before being 270° deflected by three electrostatic hemispherical analyzers (TRIFT).[4] Before entering the detector, the ions are accelerated to 6 keV in order to enhance the detection efficiency (especially at high m/z). A 880 pA dc primary ion beam is pulsed at 11 kHz repetition rate with a pulse width of 23 ns (finally bunched down to 4 ns to increase mass resolution) and rastered over a $130 \times 130\ \mu m^2$ surface area. All spectra were acquired with a fluence $\approx 10^{12}$ ions cm^{-2}, ensuring static conditions. A mass resolution $m/\Delta m$ of $\approx$4000 measured at $m/z = 28$ on a Si wafer was achieved. No charge neutralization was needed.

SIMS Data Treatments. All spectra processing was performed with Cadence 2.0 software from PHI-Evans. For each peak x contributing to the spectrum z, the absolute intensity $Y_{x,z}$ was measured and, as much as possible, a unique ion composition X was assigned. Four spectra per polarity were acquired for each sample. Absolute intensity standard deviations for characteristic peaks were about ±10%.

Modelization. We have previously shown by XPS that the studied polymers present bulklike surfaces.[1] This implies that the polymer sequence formation probabilities can be directly used to characterize the polymer sequence content at the surface. Details of the SIMS data are presented in the companion paper. In summary, three different types of dependencies of fragment ion intensities on the copolymer composition have been observed: one linear and two nonlinear dependencies. The linear dependency is observed for atomic or small ions (for examples: O^-, OH^-, CHO^-, etc.) and molecular ions such as $C_5H_9O_2^+$. Some hydrocarbon fragments (such as $C_4H_3^+$, $C_7H_7^+$, $C_8H_7^+$, etc.) exhibit higher peak intensities in the copolymer spectra compared to the linear combination of the pure polymer spectra. This has been qualitatively attributed to a fragmentation promotion due to the copolymer sequence. Other characteristic peak intensities are lower in the copolymer spectra compared to the linear combination of the pure polymer spectra. This has also been qualitatively attributed to alternance between styrene and methyl methacrylate repeat units inside the macromolecular chain.

To quantitatively relate the peak intensities to the copolymer composition, different levels of structural contributions are considered: monads, diads, triads, and so on. If monads, i.e., the repeat units themselves, were the relevant structures for secondary ion emission, a linear dependency would be observed. For diads, an intensity maximum (or minimum) at the 50/50 composition is expected.[11] Only higher level structures such as triads can account for nonlinear dependencies that are observed for most fragment ions in S-*r*-M copolymers. Therefore, we quantitatively investigate an ion emission model based on triad sequences of repeat units S and M as follows:

We assume that the secondary ion yield of pure SSS and MMM triads can be approximated by the average absolute peak intensities of the pure polymer spectra, $\bar{Y}^{PS}_{(X)}$ or $\bar{Y}^{PMMA}_{(X)}$ in eq 1a. Moreover, when in a triad the M (S) unit is adjacent to one S (M) unit, the formation probability of X is multiplied by a factor $\alpha_{(x)}$ or $\beta_{(x)}$ compared to the emission probability from the pure polymers (eqs 1b and 1c). Consequently, a S (M) unit next neighbored to two M (S) units will change the X peak intensity by a factor $\alpha^2_{(x)}$ or $\beta^2_{(x)}$ (eq 1d).

$$y^{SSS}_{(X)} = \bar{Y}^{PS}_{(X)} \qquad y^{MMM}_{(X)} = \bar{Y}^{PMMA}_{(X)} \tag{1a}$$

$$y^{SSM}_{(X)} = \alpha_{(X)}\bar{Y}^{PS}_{(X)} \qquad y^{MMS}_{(X)} = \beta_{(X)}\bar{Y}^{PMMA}_{(X)} \tag{1b}$$

$$y^{MSS}_{(X)} = \alpha_{(X)}\bar{Y}^{PS}_{(X)} \qquad y^{SMM}_{(X)} = \beta_{(X)}\bar{Y}^{PMMA}_{(X)} \tag{1c}$$

$$y^{MSM}_{(X)} = \alpha^2_{(X)}\bar{Y}^{PS}_{(X)} \qquad y^{SMS}_{(X)} = \beta^2_{(X)}\bar{Y}^{PMMA}_{(X)} \tag{1d}$$

where $\bar{Y}^m_{(X)}$ is the average peak intensity of an ion X in the m sample SIMS spectra (m = PS or PMMA).

In a binary copolymer, each ijk sequence has a given probability of occurrence (P_{ijk}), which is related to the polymerization process and the internal macromolecular arrangements. The relative proportion of an ijk triad with i, j, k equal to S or M is defined by P_{ijk}. There is a closure relationship for P_{ijk}: The ion yield of a secondary

$$\sum_{i,j,k} P_{ijk} = 1 \tag{2}$$

ion X ($Y_{(X)}$) is composed of the ion yield from the M and S precursors in all their environments. Finally, $Y_{(X)}$ can be written as the sum of yields of all triads contributing to the signal:

$$Y_{(X)} = \sum_{i,j,k} P_{ijk} y^{ijk}_{(X)} \tag{3}$$

Finally, the relative concentration of the different triads must be determined. Two models are applied to determine the probabilities P_{ijk}: (a) the Bernouillian statistical and the (b) terminal model.

(a) *Bernouillian Statistical Model.* In the Bernouillian statistical model, the probability for a sequence to contain a S unit is related to the S content in the whole polymer chain, n. The last parameter is approximated by the average S content from NMR measurements, which is an average over many different macromolecules (Table 1). The value $(1 - n)$ for M is related to the probability of occurrence, and then the triad content can be determined by simple Bernouillian statistics (Table 2).

Table 2. Bernouillian and Terminal Relationship To Determine the Sequence Probabilities

	ijk	Bernouillian model	terminal model
1	SSS	n^3	$F_1 p_{11}^2$
2	MSS	$(1-n)n^2$	$F_2 p_{21} p_{11}$
	SSM	$(1-n)n^2$	$F_1 p_{11} p_{12}$
3	MSM	$(1-n)^2 n$	$F_2 p_{21} p_{12}$
4	SMM	$(1-n)^2 n$	$F_1 p_{12} p_{22}$
	MMS	$(1-n)^2 n$	$F_2 p_{22} p_{21}$
5	SMS	$(1-n)n^2$	$F_1 p_{12} p_{21}$
6	MMM	$(1-n)^3$	$F_2 p_{22}^2$

For the Bernouillian statistical model (Table 2), the peak intensity can be written using eq 3 as

$$Y_{(X)} = \bar{Y}^{PS}_{(X)} n[n^2 + 2(1-n)n\alpha_{(X)} + (1-n)^2\alpha^2_{(X)}] + \bar{Y}^{PMMA}_{(X)}(1-n)[(1-n)^2 + 2(1-n)n\beta_{(X)} + n^2\beta^2_{(X)}] \quad (4)$$

(b) Terminal Model. In contrast to the previous model, the terminal model takes into account the effect of the polymerization process on the copolymer sequence. The probability that a styrene monomer is attached to a growing end varies with the type of radical, namely, styrene or methyl methacrylate. Based on the calculated reactivity ratio, the probability of a monomer *k* to react with the radical l (p_{lk}) is given by[21]

$$\text{for styrene radicals:} \quad p_{11} = \frac{r_1}{r_1 + \frac{F_2}{F_1}} \qquad p_{12} = 1 - p_{11} \quad (5a)$$

$$\text{for methyl methacrylate radicals:} \quad p_{22} = \frac{r_2}{r_2 + \frac{F_1}{F_2}} \qquad p_{21} = 1 - p_{22} \quad (5b)$$

where F_1 and F_2 are the styrene and methyl methacrylate feed ratios, respectively (Table 1).

The triad sequence probabilities based on the terminal model are defined in Table 2 and follow the definitions of Rempp.[21] Finally, the X peak intensity is related to the copolymer sequence by eq 3 and becomes

$$Y_{(X)} = \bar{Y}^{PS}_{(X)}[F_1(p_{11}^2 + \alpha_{(X)}p_{11}p_{12}) + F_2(\alpha_{(X)}p_{21}p_{11} + \alpha^2_{(X)}p_{21}p_{12})] + \bar{Y}^{PMMA}_{(X)}[F_1(\beta_{(X)}p_{12}p_{22} + \beta^2_{(X)}p_{12}p_{21}) + F_2(p_{22}^2 + \beta_{(X)}p_{22}p_{21})] \quad (6)$$

The penultimate effect on the styrene−methyl methacrylate copolymerization is not included in the model because it is rather limited.[22] Thus, our copolymer sequence determination is restricted to the terminal model only. In addition, the effects of the termination reactions are neglected.

Results. In Table 3, the probabilities of each triad are listed for both models. The P_{ijk} vary significantly between the two models. The terminal model gives systematically higher P_{SMS} and P_{MSM} values than the Bernouillian model. All the other P_{ijk} values are smaller for the terminal model because of the closure relationship given in eq 2. The high values for the mixed species indicate that these two monomers lead to copolymer with mainly alternate arrangements. The copolymer content can be also determined from the terminal model, and for copo-70, -60, -46 and -40, it leads to 0.733, 0.577, 0.431, and 0.359% styrene, respectively, which are close to those measured in the bulk (Table 1).

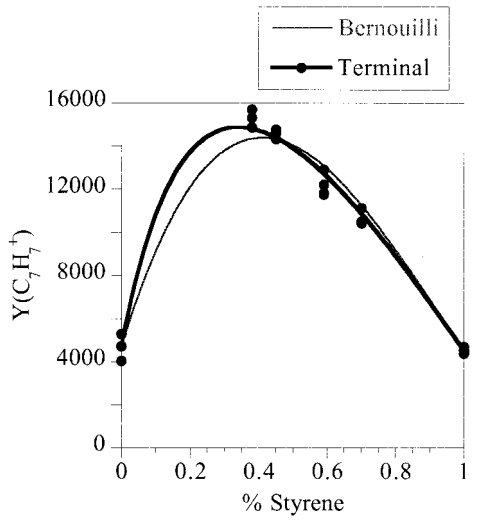

Figure 1. $C_7H_7^+$ at $m/z = 91$ as a function of the bulk styrene content fitted with the Bernouillian and terminal model.

Table 3. Copolymer Sequence Content As Determined by the Bernouillian and the Terminal Models

	SSS	SSM	SMM	SMS	MSM	MMS	MSS	MMM
				Bernouillian				
PS	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
copo-70	0.343	0.147	0.063	0.147	0.063	0.063	0.147	0.027
copo-60	0.238	0.146	0.090	0.146	0.090	0.090	0.146	0.055
copo-46	0.104	0.117	0.132	0.117	0.132	0.132	0.117	0.149
copo-40	0.069	0.099	0.143	0.099	0.143	0.143	0.099	0.205
PMMA	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000
				Terminal				
PS	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
copo-70	0.307	0.185	0.019	0.279	0.074	0.012	0.123	0.001
copo-60	0.083	0.136	0.055	0.305	0.221	0.055	0.134	0.010
copo-46	0.013	0.054	0.090	0.193	0.359	0.141	0.085	0.065
copo-40	0.004	0.028	0.093	0.125	0.374	0.184	0.055	0.138
PMMA	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000

Once the P_{ijk} are known, the correlation with the SIMS data can be tested. The $\alpha_{(x)}$ or $\beta_{(x)}$ parameters are adjusted in order to fit the experimental data by eq 4 or eq 6. For the M (S) characteristic peaks, $\alpha_{(x)}$ ($\beta_{(x)}$) is fixed to one and $\beta_{(x)}$ ($\alpha_{(x)}$) is adjusted to fit the experimental data. Following this procedure, for each curve, only one parameter is adjusted.

In Figure 1, $Y(C_7H_7^+)$ at $m/z = 91$ is plotted as a function of the bulk copolymer content, and the variations are fitted by eq 4 and eq 6 with $\beta = 1$. As already discussed, the $C_7H_7^+$ peak intensity is higher for copolymers than for pure polymers. The $C_7H_7^+$ fragment formation is promoted in the S-*r*-M copolymers compared to both pure polymers.[1] The maximum seems to appear at about 30% styrene. The curve obtained with the terminal model fits the data closer than the Bernouillian relationship. Since the Bernouillian model seems to underestimate the MSM or SSM triads, the better agreement of the terminal model with the data could be attributed to this particular type of molecular arrangement. The enhancement coefficients $\alpha_{C_7H_7^+}$ are for the Bernouillian model $\alpha_{C_7H_7^+} = 3.76$ (with $R^2 = 0.986$) and for the terminal model $\alpha_{C_7H_7^+} = 2.63$ (with $R^2 = 0.996$).

The less precise fit of the Bernouillian model can be understood in terms of its statistical polymer sequence which is notably different from the sequence from the

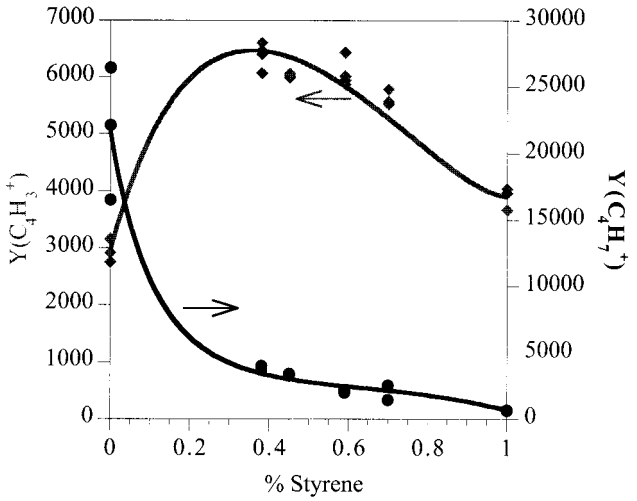

Figure 2. $C_4H_3^+$ and $C_4H_7^+$ at $m/z = 51$ and 55 as a function of the bulk styrene content fitted with the terminal model.

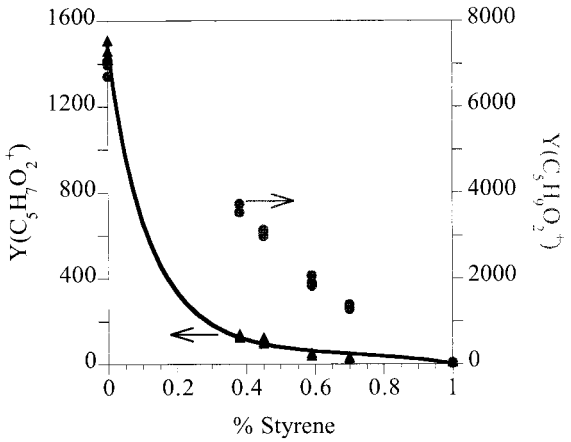

Figure 3. $[M - H]^+$ and $[M + H]^+$ at $m/z = 99$ and 101 as a function of the bulk styrene content fitted with the terminal model.

terminal model that seems to be more realistic. On the other hand, these differences indicate the strong link between the intramolecular polymer sequence and SIMS peak intensities. Differences from a statistical sequence can be easily detected by SIMS. In the following considerations, only the terminal model will be used.

In Figure 2, the $C_4H_3^+$ and $C_4H_7^+$ peak intensities at $m/z = 51$ and 55, respectively, are plotted as a function of the bulk styrene content. $C_4H_3^+$ is much more characteristic of styrene than methyl methacrylate and exhibits a behavior similar to $C_7H_7^+$ (Figure 1). The $C_4H_7^+$ peak intensities for the copolymers are lower than expected for the linear combination of the pure polymer peak intensities, which indicates that its formation is unfavored in the copolymers.[1] This fragment has been related to the PMMA hydrocarbon backbone.[19] With $\alpha = 1.7$ and $\beta = 1$, the $C_4H_3^+$ data are well described by eq 6 ($R^2 = 0.98$). Similarly with $\alpha = 1$ and $\beta = 0.364$, the $C_4H_7^+$ data are also well described by eq 6 ($R^2 = 0.975$).

In Figure 3, the $[M + H]^+$ and $[M - H]^+$ peak intensities are plotted as a function of the styrene content. The $[M - H]^+$ peak intensity decreases strongly with the styrene content in the copolymers. Such behavior is well described by eq 6. By contrast, $[M + H]^+$ exhibits a linear behavior, which cannot be accurately followed by the Bernouillian and terminal model.

Table 4. α and β Parameters for Different Positive Characteristic Fragments (Terminal Model)

formulas	*m/z*	α (std)[a]	*β* (std)	R^2
$C_4H_3^+$	51	1.703 (0.0142)	1	0.980 35
$C_4H_4^+$	52	1.983 (0.119)	0.572 (0.107)	0.985 58
$C_4H_5^+$	53	1	0.509 (0.019)	0.994 75
$C_4H_6^+$	54	1	0.374 (0.042)	0.983 85
$C_4H_7^+$	55	1	0.364 (0.053)	0.975 03
$C_4H_8^+$	56	1	0.372 (0.063)	0.964 55
$C_4H_9^+$	57	1	0.439 (0.068)	0.947 1
$C_5H_3^+$	63	1.812 (0.0169)	1	0.980 76
$C_5H_4^+$	64	1.717 (0.0154)	1	0.977 52
$C_5H_5^+$	65	2.211 (0.145)	0.367 (0.100)	0.997 41
$C_5H_6^+$	66	1	0.410 (0.013)	0.998 23
$C_5H_7^+$	67	1	0.303 (0.036)	0.990 87
$C_5H_8^+$	68	1	0.292 (0.060)	0.975 91
$C_5H_9^+$	69	1	0.278 (0.090)	0.950 63
$C_6H_3^+$	75	1.652 (0.029)	1	0.909 54
$C_6H_4^+$	76	1.915 (0.021)	1	0.974 65
$C_6H_5^+$	77	1.570 (0.037)	1	0.962 72
$C_6H_6^+$	78	1.903 (0.046)	1	0.949 85
$C_6H_7^+$	79	1	0.456 (0.023)	0.993 01
$C_6H_8^+$	80	1	0.264 (0.032)	0.993 99
$C_6H_9^+$	81	1	0.224 (0.049)	0.987 92
$C_7H_5^+$	89	1.838 (0.021)	1	0.971 23
$C_7H_6^+$	90	2.034 (0.015)	1	0.988 38
$C_7H_7^+$	91	2.634 (0.013)	1	0.996 01
$C_7H_8^+$	92	2.404 (0.031)	1	0.977 55
$C_7H_9^+$	93	1	0.228 (0.031)	0.995 17
$C_7H_{10}^+$	94	1	0.120 (0.048)	0.992 89
$C_7H_{11}^+$	95	1	0.121 (0.076)	0.982 21
$C_5H_7O_2^+$	99	1	0.154 (0.011)	0.999 53
$C_5H_8O_2^+$	100	1	0.125 (0.017)	0.999 07
$C_5H_9O_2^+$	101			

[a] Standard deviation.

When the data are close to linearity, this model does not give good approximation. Two reasons can be given. The first one is that the influence of the matrix effect is negligible. The other explanation would be that different mechanisms or fragmentation pathways come into play, leading to the formation of fragments that are almost similarly promoted/inhibited whatever the adjacent functionalities.

In Table 4, the different α and *β* values are listed for series of peaks. When α or *β* values are above (below) one, there is a clear fragment formation promotion (inhibition). In summary, the hydrocarbon fragments characteristic of the methyl methacrylate units exhibit inhibition values. By contrast, α values for the styrene unit peaks are above one. The $C_7H_7^+$ and $C_5H_5^+$ have the most significant α values. This correlated promotion between these fragments could be attributed to $C_7H_7^+$ dissociation into $C_5H_5^+$.[2] Up to now, these values are preliminary; it would be necessary to increase the number of samples in order to sample the concentration range completely.

Such peak intensity modelization demonstrates the close links between the molecular structure and the secondary emission. The quantification of the matrix effect defined by the α or *β* parameter is then possible with random copolymers with known sequence compositions or synthesis conditions. If, for the same bulk proportion, there is clear variation in the SIMS signals influenced by the local arrangement, it would indicate a change in the copolymer sequence distribution. In summary, the matrix effect in SIMS polymer analysis has always to be related to the local inter- or intramolecular arrangements. Such determination should be very useful in the future to evaluate the sequence content at polymer surfaces.

Unfortunately, for the moment, it is impossible to check which of the SSM or MSM has the most influence on the fragmentation process. Moreover, for very large fragments from tetrad or longer sequences, the model should be expanded.[19]

Conclusion. On the basis of our previous SIMS measurements and the proposed model, it can be concluded that the SIMS fingerprint fragments are sensitive to the copolymer sequence and particularly to the triads in the case of St-*r*-MMA. With the terminal model, the extent of matrix effects has been determined quantitatively.

The same random copolymer synthesized by different methods or with different synthesis parameters leads to different intramolecular copolymer arrangements. With such a series of polymer reference samples, it would be possible to calibrate the SIMS signals and afterward to establish the triad content at St-*r*-MMA surfaces. It should be possible to expand this approach to other copolymers such as polyamino acids, peptides,[23] or even nucleic acids.

To complete this study, other measurements of tagged or selectively deuterated copolymers and other well-defined copolymer structures should give new important insights into the understanding of the influence of the copolymer arrangements in SIMS.

Acknowledgment. The financial support from the "Fonds National de la Recherche Scientifique (FNRS)-Loterie Nationale" (Belgium) and from the "Région Wallonne" (Belgium) for the acquisition of the ToF-SIMS spectrometer is gratefully acknowledged. This work is sponsored in part by the Belgian Interuniversity Attraction Pole Program (PAI-IUAP P4/10) on "Reduced Dimensionality Systems".

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MA0014113