Studies of Polystyrenes Using Time-of-Flight Secondary Ion Mass Spectrometry

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Time-of-Flight Secondary Ion Mass Spectra from polystyrene standards with well-defined molecular weight distribution have been obtained in the mass range m/z = 0-5,000.   Maximum yields of cationized fragments and oligomers are obtained from silver substrate covered by about one monolayer of polystyrene.   Number average molecular weights of polystyrenes and poly(2-vinylpyridine) determined from peak intensities of intact polymer molecules compare well with data from matrix-assisted laser desorption and ionization mass spectrometry (MALDI-MS) and gel permeation chromatography (GPC).   The low mass spectra (m/z = 0-200) of substituted polystyrene includes fingerprint ions characteristic of the analyzed polymer.   Repeat unit peaks and fragment ions provide information about some structually important features.

1. Introduction

The family of styrene polymers including polystyrene are used widely as packaging and insulating materials, and elucidating how thermal and radiation- induced change affect them is important.   Various mass spectrometric techniques have been imployed for characterization of styrene polymers. Field desorption [1] and laser desorption mass spectrometry [2-4] have successfully obtained fingerprint information in the low mass range and oligomer distributions for low molecular weight polymers.   Pyrolysis GC-MS [5] and quadrupole SIMS studies [6] have been limited to the fingerprint region by the limitation of the mass analyzers used.

SIMS techniques have been extensively applied to both elemental and molecular characterization of nonvolatile materials. Dynamic and static SIMS are distinguished by the primary ion dose acceptable during analysis[7].   For dynamic SIMS, the objective is to establish steady-state conditons of erosion rate and surface chemistry, and the primary ion dose retained in the near-surface region attains a stationary value.   As a consequence of its high detection sensitivity, dynamic SIMS has been successfully applied to elemental analysis in material science, as well as to trace element analysis in geological and biological sciences[9]. In contrast,   Static SIMS employs the primary ion dose density lower than 10^{13} ion/cm^2 and secondary ions produced are typically elemental, molecular, and molecular fragments from the uppermost layer of a surface[10].   High resolution Time-of-Flight SIMS has provided dramatically improved capabilities in surface chemical analysis[11]. TOF-SIMS provides good sensitivity and structural specificity for high mass ions from the top monolayers of a surface so that intact oligomers and large polymer fragments are observed.

The purpose of the present investigation was detailed analysis for the oligomers and fragment ions of polystyrenes and polymers of styrene derivatives.   Polystyrenes studied have been characterized by using TOF-MALDI-MS and GPC.   The results from these techniques allow further assessment of the information generated by TOF-SIMS

2. Experimental

Materials.   Polystyrenes, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-tert-butylstyrene), poly(4-vinylbiphenyl), and poly(vinylnaphthalene) were obtained from Aldrich Chemical Co.(Milwaukee, WI).   The source of poly(2-vinylpyridine) was Polysciences, Inc.(Warrington, PA).   The chloroform and toluene solvents were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were used as received. The structures, repeat units, and molecular weights of polystyrenes and polystyrene derivatives are shown in Table 1.   TOF-SIMS spectra of polystyrenes and polystyrene derivatives were obtained from thin polymer films cast from solutions of polymers in toluene on a silver substrate as shown in Fig.1.

TOF-SIMS Instrument.   The TOF-SIMS spectra were acquired by using a Physical Electronics model PHI 7200 TOF-SIMS/SALI instrument.   The instrument was designed for elemental and molecular ion analysis at high mass resolution, mass measurement accuracies, and detection sensitivities.   This system incorporates a pulsed Cs^+ primary ion source, and the normal impact energy of the beam on the sample surfaces was 8 keV.   The dc primary ion beam intensity at the sample was a few nanoamperes, and the operating spot size was ~50 μm in diameter.   No charge neutralization was used, since there was no

Table. 1. Structure, repeat units and molecular weights of various polystyrene studied.

Sample Name	Structure	Repeat Unit (m/z)	Molecular weights GPC(Mw)	(Mn)
polystyrene	$+CH_2CH_n$	104	794	700
polystyrene	$+CH_2CH_n$	104	2360	2180
polystyrene	$+CH_2CH_n$	104	3680	3400
poly(a-methyl styrene)	$+CH_2C_n$ CH_3	118		
poly(4-methyl styrene)	$+CH_2CH_n$ CH_3	118	72000	
poly(4-tertbutyl styrene)	$+CH_2CH_n$ $C(CH_3)_3$	160	50000	
poly(2-vinyl pyridine)	$+CH_2CH_n$	105	3300	2550
poly(4-vinyl biphenyl)	$+CH_2CH_n$	180	115000	
poly(2-vinyl naphthalene)	$+CH_2CH_n$	154		

Fig. 1 Solution casting of polymer samples

significant sample charging during the measurements. The base pressure of the chamber was 5×10^{-10} Torr, and the normal working pressure was 1×10^{-9} Torr. Secondary ions are extracted from the sample and accelerated by an ion lens operating at 3 kV into time-of-flight(TOF) mass analyzer. The TOF uses a reflectron to reduce line widths and has a total flight path of 2 m. The secondary ion beam is focused on the dual microchannel plate for ion detection. To enhance detection efficiency, especially for high masses, a postacceleration voltage of up to 13 kV is applied to the entrance of the detection unit. Positive ion mass spectra only are reported in this paper.

3. Results and Discussion

TOF-SIMS spectra of the polystyrenes studied were obtained in the mass range m/z = 0-5,000. The peaks in the spectra can be resolved into three well-defined series: oligomer, repeat unit, and fragmentation series. A segment from a typical spectrum of polystyrene in the mass range m/z = 0-500 shows metal ion peaks of Na^+, K^+, and Ag^+, and fragment ions of m/z 77, 91, 107, and 115 from aromatic ring. There are also peaks
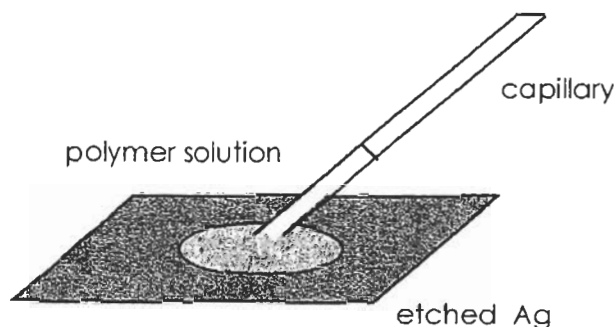
corresponding to the monomer R+Ag (R=repeat unit), the dimer 2R+Ag, and the trimer 3R+Ag, at m/z 211, 315, and 419, respectively, with decreasing intensities.

Fig.2 shows the TOF-SIMS spectra of polystyrene with different molecular weights in the high mass range ($\geq$m/z500). Oligomer peaks dominate the spectra of the low molecular weight PS-800 and PS-2500. The spacing between the oligomer peaks is 104 Da, the mass of one repeat unit. Each oligomer contains both of its original end groups: a n-butyl group (C_4H_9-) and a H-group. Fragmentation is a minor process for low molecular weight polystyrenes. For higher molecular weight PS, starting the transition from the oligomer dominating segment to the fragment dominating segment can be observed for PS-4000 in Fig.2. The oligomer distribution appears to be broader than PSs with smaller molecular weights.

It is known that polymer molecular weight distribution is a key parameter controlling polymer properties. Both number(M_n) and weight(M_w) average molecular weights can be calculated from the TOF-SIMS spectra by measuring peak intensities of cationized oligomers. M_n and M_w are defined as: $M_n = \sum N_i M_i / \sum N_i$ and $M_w = \sum N_i M_i^2 / \sum N_i M_i$ where N_i is the absolute number of counts for the oligomer ion containing i repeat units, and M_i is the molecular weight of the oligomer with i repeat units. The M_n values for polystyrenes determined by TOF-SIMS are compared to those determined by TOF-MALDI-MS and GPC in Table 2. The M_n values determined by TOF-MALDI-MS are consistently higher than values determined by TOF-SIMS for polystyrenes studied. For PS-4000, the values determined by TOF-SIMS may be shifted toward the low mass end because of decreasing ion yields of oligomers with increasing mass. Furthermore, the spectrum shows intense peaks not only from oligomers but from fragments, accurate calculation of the average molecular weights is not possible because the interference from the fragment ion peaks. Nevertheless,
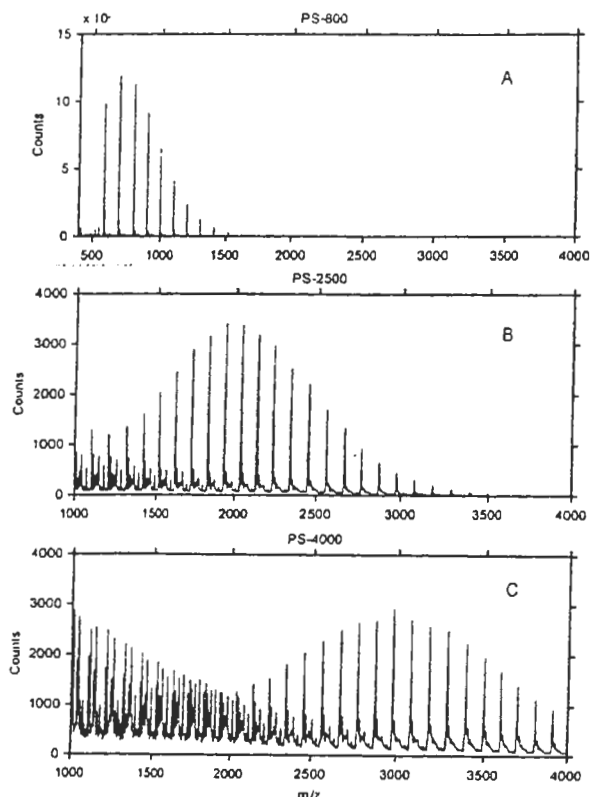
Fig. 2. TOF-SIMS Spectra of (A) PS-800 (B) PS-2500 and (C) PS-4000.

Fig. 3. TOF-SIMS Spectra of PS-4000 with raster size (A) 1 μm (B) 100 μm (C) 400 μm (D) 800 μm.

both TOF-SIMS and TOF-MALDI-MS M_n values for polystyrenes in this study agree well with those determined by GPC, given the low accuracy of GPC in the low mass range.

The effect of raster size on TOF-SIMS polymer spectra was investigated. TOF-SIMS measurements were made on the different sampling area from the identical PS-4000 polystyrene film on the silver substrate (Fig. 3) The TOF-SIMS spectrum from raster size 1μm shows more fragment ions in the low mass range than those from large raster area. Intense oligomer peaks are observed as the raster area increases while the oligomer distribution shifts in the mass range are not observed with increasing the raster size. However, in the raster size 800 μm, both of

oligomer and fragment ion intensities are decreased. In this study we used the acquisition area of 400 μm to get the TOF-SIMS spectrum.

The low-mass spectra (m/z = 0-200) of poly(α-methylstyrene), poly(4-methylstyrene), poly(4-tert-butylstyrene),poly(4-vinylbiphenyl), and poly(4-vinyl naphthalene) are shown in Fig.4. These fingerprint ions are so characteristic of the analyzed polymer that extensive information on the chemical structure can be obtained. Each spectrum shows the repeat unit peak and the fragment ion peak from the repeat unit. Fragment ions are characteristic of the backbone structure and their relative intensities indicate the stabilities of ions formed. The spectra of poly(α-methyl styrene) and poly(4-methylstyrene) containing the same repeat unit mass (R = 118 Da) constitutes a different fragment pattern of peaks that gives the information about the structure of polymer chain. Poly(α-methyl styrene) shows very intense repeat unit peak at m/z 119 (R+H) because the tertiary carbon ion of repeat unit is very stable .

Fig. 5 presents a representative spectrum of poly(2-vinylpyridine). In the mass range

Table 2. Comparison of molecular weight values determined by GPC, TOF-SIMS, and TOF-MALDI.

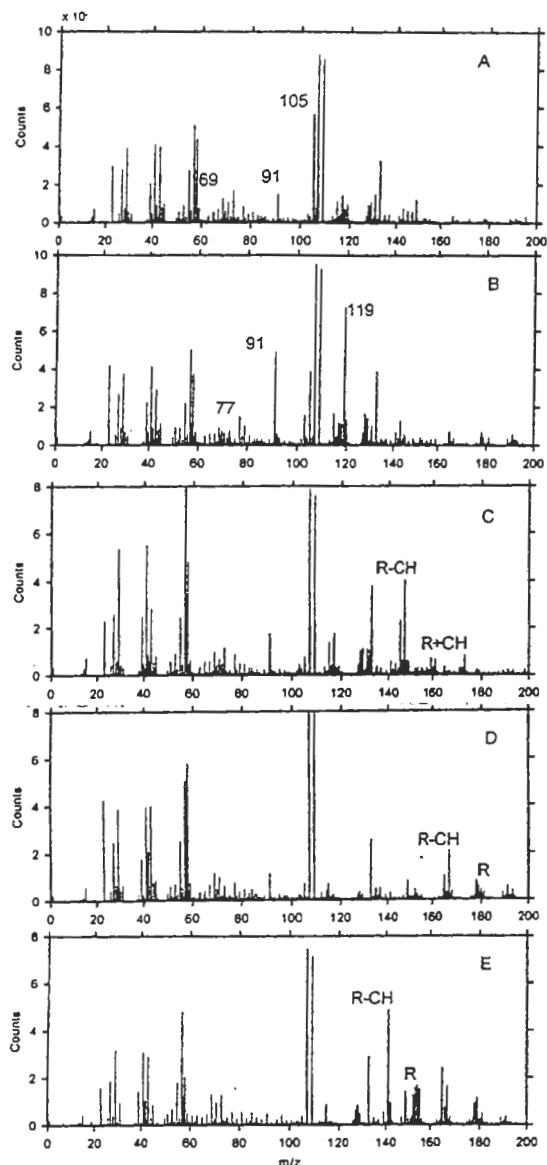| Class of Polymer	MW (U)	GPC M_n	SIMS M_n	MALDI M_n
Polystyrene	800	700	750	980
Polystyrene	2500	2180	2200	2430
polystyrene	3400	3400	3210	3499

Fig. 4. TOF-SIMS Spectra of (A) poly(4-methylstyrene) (B) poly(α-methylstyrene) (C) poly (4-tert-butylstyrene) (D) poly(4-vinyl biphenyl) (E) poly(4-vinylnaphthalene) in the mass range m/z = 0 – 200.
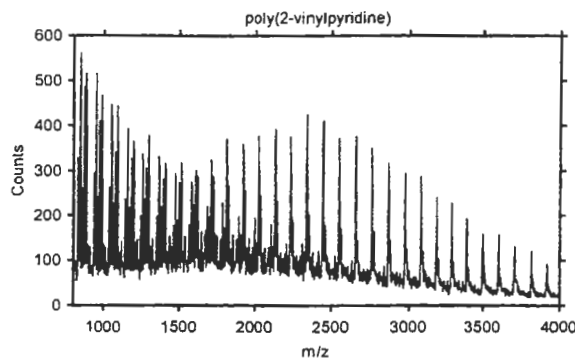

Fig. 5. TOF-SIMS spectra of poly(2-vinyl pyridine) in the mass range m/z = 800-4000.

fragments and oligomers in the mass range m/z = 0-5000 allows a reliable determination of repeat units, end groups, or oligomer distributions. The TOF-SIMS molecular weight data of polystyrenes are compared to those from TOF-MALDI-MS and GPC. There was a reasonable agreement among them. Polystyrene derivatives are well distinguished in the fingerprint region m/z = 0-200 where repeat unit and fragment ion peaks dominate.

5. References

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Reviewers' Comments

The manuscript concerns structural analysis of polystyrene molecular distribution using TOF-SIMS. Its novelty lies in the fact that the study concerns structural analysis of polystyrene derivatives as distinguished well in the fingerprint region m/z = 0-200 where repeat unit and fragment ion dominate.

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between 800 and 4000 Da Ag-cationized oligomers are detected. The spacing between the peaks Δm = 105 Da refers to the mass of one poly(2-vinylpyridine) repeat unit. The intensity distribution of the peaks reflects the oligomer distribution of the sample. Average molecular weight calculated from TOF-SIMS data is M_n=2480, which is smaller than the manufacturer's data(M_n=2550), probably due to formation of lower molecular weight oligomers from higher ones and low ion yield of high molecular weight oligomers by TOF-SIMS.

4. Conclusions

The structural analysis of polystyrene molecular weight standards have been done using TOF-SIMS. The detection of cationized