

Desorption electrospray ionization and electrosonic spray ionization for solid- and solution-phase analysis of industrial polymers

Marcela Nefliu, Andre Venter and R. Graham Cooks*

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Desorption electrospray ionization (DESI) and electrosonic spray ionization (ESSI), two new techniques, are used to measure average molecular weights and molecular weight distributions of solid-phase and solution-phase samples of the same polymers.

Mass spectrometry (MS) is a tool for polymer analysis that complements classical techniques such as gel permeation chromatography,¹ light scattering,² osmometry,³ nuclear magnetic resonance⁴ and infrared spectroscopy.⁵ MS can provide absolute, direct determinations of molecular weights for particular compounds. However, accurate average values for mixtures of polymers or oligomers require that there be no discrimination over a wide mass and concentration range with regard to efficiency of ionization, propensity for fragmentation, or mass discrimination in the course of ion transport, mass analysis and ion detection. Soft ionization techniques minimize fragmentation and are best suited to achieve these objectives; as a result in depth studies on polymers have been reported using field desorption (FD),⁶ secondary ion mass spectrometry (SIMS),⁷ matrix-assisted laser desorption/ionization (MALDI),⁸ electrospray ionization (ESI)⁹ and laser induced acoustic desorption (LIAD).¹⁰ While FD comes closest to realizing the objective of minimum fragmentation and discrimination, MALDI/TOF is more popular due to compatibility with high mass compounds and provision of simple spectra which display predominantly singly-charged ions. ESI is another method suitable for high molecular weight compounds, although this advantage comes at the expense of producing multiply-charged ions which can clutter the spectra. These MS methods have been used to characterize many classes of synthetic polymers, including nonpolar and polar compounds in the forms of homopolymers, copolymers and synthetic blends. Nevertheless, all the available methods have specific limitations and new techniques are sought to complement the existing ones.

We report the first applications of desorption electrospray ionization (DESI)¹¹ and electrosonic spray ionization (ESSI)¹² to polymer analysis. Both are new soft ionization techniques. DESI is conducted under ambient conditions by exposing the solid-phase sample to a pneumatically-assisted electrospray. Charged solvent droplets impact the solid surface and transport desorbed sample ions towards the MS inlet. ESSI, used to analyze solution-phase polymers, is a variant of ESI that uses high flow rates of nebulizing gas to produce small initial droplets which facilitate solvent evaporation. Similar spraying conditions are used for both DESI and ESSI experiments and the two techniques can be considered

complementary, the key difference being the physical state of the sample which is either in the condensed phase (DESI) or in the solution phase (ESSI).

DESI and ESSI mass spectra were recorded using a commercial Thermo Finnigan LTQ ion trap mass spectrometer with a mass/charge (m/z) range up to 2000 Th. Both experiments (Fig. 1) utilize a home-built sonic spray source described elsewhere¹³ and similar to the commercial Prosolia Inc. source. Source settings are summarized in Table 1.

The polymers tested, poly(ethylene glycol) (PEG), poly(tetramethylene glycol) (PTMG) and polyacrylamide (PAM), were supplied by Sigma-Aldrich Inc. (Milwaukee, WI).

The positive ion DESI mass spectrum of a PEG sample with a weight average molecular weight M_w of 3000 (Fig. 2a), displays five distinct charge state envelopes having approximately gaussian distributions, corresponding to multiply-charged molecular ions +2, +3, +4, +5 and +6. The +1 envelope falls outside the upper m/z range of the mass analyzer. Table 2 shows the types of ions, the calculated molecular weight distribution (MWD) and the nominal molecular weight (M_p) of each ion series, as well as the average values for the entire spectrum (Ave MWD and Ave M_p). The M_w , M_n (number average molecular weight), and the polydispersity ($D = M_w/M_n$) values presented are averages over three different spectra. Polymeric molecules are ionized by binding to one or

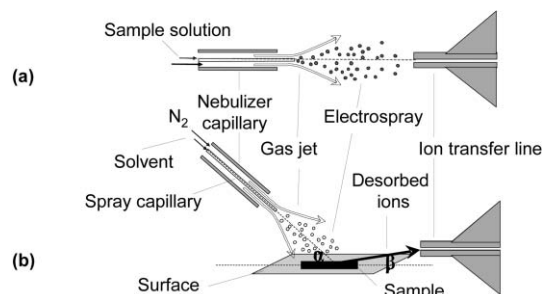


Fig. 1 Schematic of the (a) ESSI and (b) DESI experiments.

Table 1 DESI and ESSI source settings

	DESI	ESSI
Electrospray voltage ^a	5 kV	5 kV
Electrospray flow rate	5 $\mu\text{L min}^{-1}$	5 $\mu\text{L min}^{-1}$
Incident/collection angle (α/β)	50/10 degrees	N/A
MS inlet-sample distance	10 mm	N/A
Tip-sample distance	5 mm	N/A
Nebulizing gas pressure ^b	200 psi	200 psi
Tip-capillary inlet distance	N/A	30 mm
Type of surface	paper	N/A

^a Applied to the syringe needle ^b Measured at the nitrogen gas tank

Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084, USA. E-mail: cooks@purdue.edu

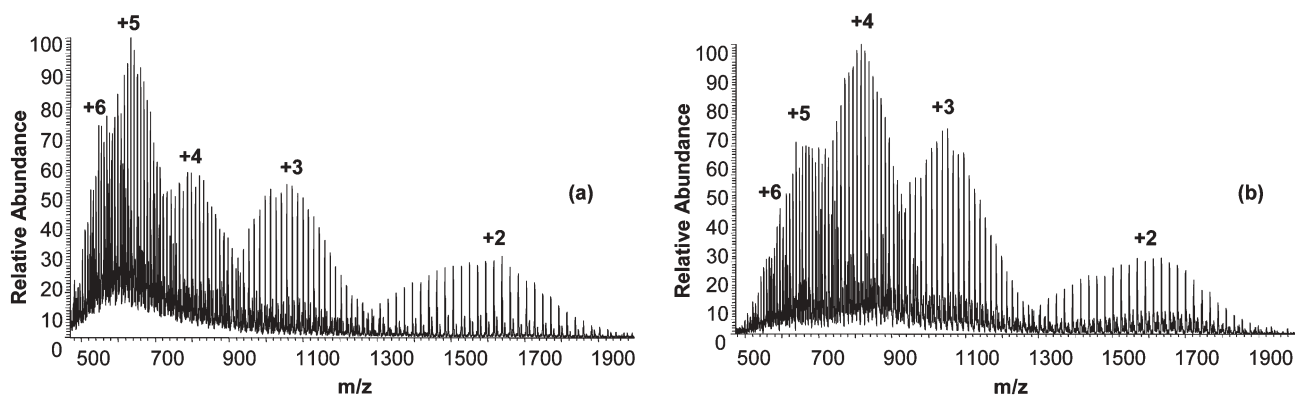


Fig. 2 Mass spectra of PEG (Mw 3000) (a) positive ion DESI mass spectrum, 0.2 μg per sample spot, spray solvent methanol : water, 1 : 1; (b) positive ion ESSI mass spectrum, sample concentration 55 $\mu\text{g ml}^{-1}$ in methanol : water, 1 : 1.

Table 2 Molecular ions produced by DESI for PEG (Mw 3000)

	+2		+3		+4	+5	+6
	$[\text{M} + 2\text{Na}]^{2+}$	$[\text{M} + \text{Na} + \text{K}]^{2+}$	$[\text{M} + 3\text{Na}]^{3+}$	$[\text{M} + 2\text{Na} + \text{K}]^{3+}$	$[\text{M} + 4\text{Na}]^{4+}$	$[\text{M} + 5\text{Na}]^{5+}$	$[\text{M} + 6\text{Na}]^{6+}$
MWD	2219–3936	2483–3716	2351–3936	2527–3716	2351–3892	2483–3848	2747–3936
Mp	3231	3055	3099	3099	3055	3055	3275
Ave MWD (RSD)	2452 (6.9%)–3854 (2.6%) (32 repeat units)						
Ave Mp (RSD)	3124 (2.9%)						
Mn (RSD)/Mw (RSD)/D	3105 (0.60%)/3146 (0.56%)/1.013						

more adventitious ions Na^+ , K^+ , NH_4^+ and H^+ . Adducts with solvent molecules may also occur. Generally, for each charge state, more than one ion series is observed *e.g.* $[\text{M}+2\text{Na}]^{2+}$, $[\text{M}+\text{Na}+\text{K}]^{2+}$ *etc.* The Mw value of 3146 calculated from the DESI mass spectrum is in good agreement with the expected value of 3000.

The positive ion ESSI mass spectrum (Fig. 2b) of the same polymer shows five multiple-charge-state envelopes ranging again from +2 to +6. While in the DESI mass spectrum Na^+ adducts are the most abundant, in the ESSI NH_4^+ adducts predominate for each charge state. Collection of Na^+ from the paper substrate readily explains the cations seen in the DESI spectrum. Calculated Mn, Mw, MWD, Mp and D values compare favourably with the values reported by the manufacturer and also with the DESI experiments (Table 3). The calculated polydispersity index in both cases is lower than expected for this polymer, a result not unexpected for ESI-related techniques.¹⁴ The overall data demonstrate that the two types of ion sources generate comparable results starting from two different physical states of the same material. Both DESI and ESSI mass spectra closely resemble previously acquired ESI mass spectra for PEG (Mn 3500)⁹, in spectral appearance, ion types and in the multiply-charged envelopes seen.

As mentioned, the reliability of measured molecular weights and molecular weight distributions can be negatively influenced by

mass discrimination. Previous studies¹⁵ suggest possible discrimination against ions of higher molecular weight due to decreased ionization efficiency. Changes in cone potential in the atmospheric interface could also affect the relative intensities of the ions.¹⁶ Moreover, shifts of the higher charge state distributions towards higher mass/charge values are possible as large molecules accommodate multiple charges better than smaller ones.¹⁷ These as well as other factors may influence molecular weight accuracy in ESI-MS. Nevertheless, for low polydispersity polymers, all such inaccuracies are likely to be small. Based on our results, we expect similar quality for DESI-MS and ESSI-MS data. Note that the raised baseline in both spectra in Fig. 2 is not a sign of fragmentation, but is due to loss of resolution due to the increased number of possible types of ionic clusters for charges +4 and higher. Moreover, the small relative standard deviation values for Mp and MWD among all ion series for both the DESI and ESSI experiments, indicates a negligible degree of fragmentation (it is unlikely that clusters with different ions and different number of charges will fragment similarly). Various other polymer studies using ESI sources¹⁶ found no fragmentation at the same cone voltage (65 V) as used here.

Other polymers, both hydrophilic and hydrophobic, were also investigated, including PTMG and PAM. Hydrophobic polymers

Table 3 Molecular ions produced by ESSI for PEG (Mw 3000)

	+2		+3		+4	+5	+6
	$[\text{M} + 2\text{NH}_4]^{2+}$	$[\text{M} + \text{NH}_4 + \text{K}]^{2+}$	$[\text{M} + 3\text{NH}_4]^{3+}$	$[\text{M} + 2\text{NH}_4 + \text{K}]^{3+}$	$[\text{M} + 4\text{NH}_4]^{4+}$	$[\text{M} + 5\text{NH}_4]^{5+}$	$[\text{M} + 6\text{NH}_4]^{6+}$
MWD	2307–3936	2483–3716	2439–4024	2615–3628	2351–3980	2571–3716	2747–3848
Mp	3099	3055	3099	3099	3188	3099	3408
Ave MWD (RSD)	2502 (6.2%)–3835 (4.0%) (30 repeat units)						
Ave Mp (RSD)	3150 (3.8%)						
Mn (RSD)/Mw (RSD)/D	3172 (0.20%)/3209 (0.28%)/1.012						

are difficult analytes for DESI and ESSI, as they are for ESI.¹⁸ For ESSI they require dissolution systems (usually mixtures of polar and non-polar solvents) which produce no discrimination among different molecular weight oligomers and which also supply the ionization agents. In DESI, the same restrictions are imposed on the spray solvent which must aid in desorption of the sample molecules from the surface and in their ionization. Moreover, the tendency towards multiple-charging decreases in low-polarity solvents, thus limiting the accessible mass range and perhaps increasing the likelihood of discrimination in the ionization of oligomers. Our results for this kind of polymer reflect these drawbacks. The positive ion DESI mass spectrum of PTMG (Fig. 3) shows three ion series corresponding to $[M+Na]^+$, $[M+Na+NH_4]^{2+}$ and $[M+2Na+NH_4]^{3+}$. The spray solvent used was methanol : water, 1 : 1. The calculated Mn for this polymer was 1412, much smaller than the corresponding value reported by the manufacturer, of 2900. Nevertheless, the MWD and the Mp values calculated for each charge state agree fairly well, a clear indication that accurate results should be possible when an appropriate spray solvent is used. The hydrophilic polymer, PAM, also generated a skewed distribution of oligomer peaks. PAM (Mn 1500), was analyzed in both the positive and negative modes. Negative ion DESI and ESSI mass spectra (Fig. 4) feature singly-charged ions of the type $[M-H]^{-1}$, both yielding an average molecular weight of approximately 500.

Besides the preparation of representative samples for DESI and ESSI experiments, identifying suitable solid surfaces for the DESI experiments is important but much easier to achieve. Different types of surfaces were tested, including paper, Teflon and glass, with no noticeable differences in the ion types and molecular weight distributions. From Teflon or glass however, the sample was depleted faster as the spray physically removes polymer from the surface. The sensitivity of both DESI and ESSI increases with

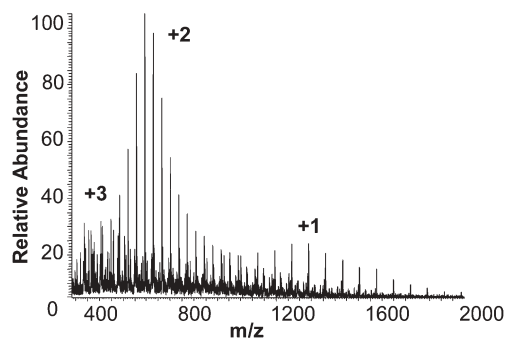


Fig. 3 DESI mass spectrum of PTMG (Mn 2900).

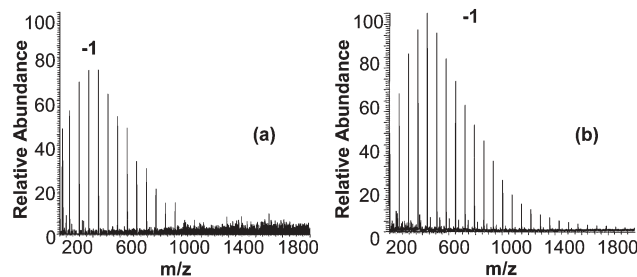


Fig. 4 Negative ion mass spectra of PAM (Mn 1500): (a) DESI mass spectrum; (b) ESSI mass spectrum.

increasing ionization efficiency and decreases with an increase in the number of ion series generated. Our data are focused on low molecular weight polymers due to the limitations of the mass analyzer used but this does not represent an intrinsic limitation of the ionization technique. A practical issue when working with polymers is sample carry-over. Polymer molecules (especially PEG) deposit in the MS inlet capillary and are released over time during the analysis of subsequent samples. Thus, there has to be a compromise between the analysis time and concentrations used and the degree of instrument contamination which can be tolerated.

In conclusion, we have demonstrated that DESI and ESSI can provide average molecular weights and molecular weight distributions for some industrial polymers. The results generated by the two techniques for PEG (Mw = 3000) in solid and solution states, are in good agreement, proving them complementary with regard to the physical state of the sample. The results are also in agreement with the Mw values reported by the manufacturer, revealing DESI as a technique with potential value for polymer analysis. Our study also indicates, however, that the same limitations experienced with ESI analysis of polymers might be observed for ESSI and DESI with regard to both the kind and the size of polymers that can be accurately characterized. Problems such as reduced multiple charging in low-polarity solvents, overlapping peaks and discrimination among different molecular weight oligomers have to be considered when higher molecular weight polymers are investigated.

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