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International Journal of Mass Spectrometry 202 (2000) 241–250

International Journal of Mass Spectrometry

A comparison of electrospray versus nanoelectrospray ionization Fourier transform mass spectrometry for the analysis of synthetic poly(dimethylsiloxane)/poly(ethylene glycol) oligomer blends

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Received 15 November 1999; accepted 5 May 2000

Abstract

The transfer efficiency of synthetic oligomer ions in monocomponent systems of polymer mixtures from solution phase to gas phase is examined here for electrospray ionization (ESI) and nanoelectrospray (nanoES) ionization. For poly(dimethylsiloxane) (PDMS), one sees a significant bias in favor of methyl-terminated (ME) PDMS versus 2-methylpropyl-terminated (MP) PDMS in ESI. This ionization dependence (even for two very similar polymers differing only in end-group functionality) would be problematic for quantification efforts of polymers within blends by ESI. It is known that the surface tension of droplets containing polymer blends and solutions is strongly dependent on molecular weight of the polymer and on potential surface activity of the end groups, which occurs primarily via differential adsorption and depletion at the surface. This theory can be used to describe the solution to gas phase bias for PDMS ions with different end groups. For oligomers of similar mass but very different polarity, such as PDMS and poly(ethylene glycol) (PEG), this preferential bias is even more notable, as the PDMS ion signal is nearly completely attenuated relative to the PEG ion signal in ESI mass spectra when drying gas is applied. This bias against PDMS may be due to thermal denaturation and loss of the lone charge or conformational effects. However, both the drying gas flow rate and the ESI skimmer potential influences the degree of this bias. In the absence of drying gas, the PDMS ion signal in the PEG/PDMS mixtures is readily observable. Furthermore, the PEG signal scales with drying gas flow rates, which is consistent with the notion that higher surface tension hydrophilic PEG becomes more efficiently desolvated and ionized with increasing collisions with drying gas molecules. The observation that nanoES (which uses no drying gas) has far less solution-to-gas-phase transfer bias is indicative of the critical role that heat of vaporization of the solvent plays in ion formation for polymers of very different polarities and surface tensions. (Int J Mass Spectrom 202 (2000) 241–250) © 2000 Elsevier Science B.V.

Keywords: Polymers; Electrospray ionization; Nanospray; Fourier transform mass spectrometry

1. Introduction

The coupling of electrospray ionization sources with Fourier transform mass spectrometry (ESI-FTMS) toward oligomer analysis is gaining attention as a method for characterizing synthetic oligomer structure [1–8]. This is due to the ability of ESI-FTMS to rapidly provide detailed information concerning molecular weight distributions, repeat unit and end group sequences, degrees of oligomerization and evidence for co-oligomers, impurities, or structural modifications due to the high mass accuracy, tandem mass spectrometry and broadband detection of FTMS [1, 3–8]. However, we have recently

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PII S1387-3806(00)00248-7

observed unequal detection efficiencies in the analysis of well-defined polymer and oligomer mixtures. Taken to its extreme, under a particular set of conditions, it is even possible for a particular polymer component in a complex mixture to be completely undetected in cases where the same oligomer is routinely detected in a single solute system at the same concentration. Such an effect is attributed to preferential transfer of the analyte from solution to the gas phase where ESI-compatible solutes enjoy higher efficiency.

An ideal analytical method allows one to rapidly identify all relevant components in real, complex mixtures without extensive sample preparation and with minimal sample quantities. When mindful of such considerations, nano-electrospray (nanoES) [9, 10] is far less prone to interference from the presence of salts and buffers than its conventional ESI counterpart, while requiring sample levels down to the attomole level [11, 12]. In nanoES, the nanometer regime droplets formed in close proximity to the mass spectrometer inlet result in an ionization efficiency enhancement over conventional ESI, reducing artifacts arising from differential liquid-to-gas transfer rates [9]. This feature is particularly germane to the reliable analysis of complex, real-world mixtures that may possess analytes over a wide range of chemical and physical properties.

The performance features of ESI and nanoES toward the analysis of binary and ternary polymer systems are evaluated here with a commercial external source Fourier transform mass spectrometer. These studies focus on poly(ethylene glycol) (PEG) and poly(dimethylsiloxane) (PDMS) systems because of their importance in the bioconjugation and biomaterials fields as well as membrane, coating and implant technologies (e.g., contact eye lenses) [13–16]. Furthermore, they represent prototypical polymer extremes of polarity and surface tension. Polarity in a polymer (X^P) may be defined relative to the cohesive energy density (ΔE) and the Hildebrand solubility parameter (δ) according to Eq. 1 [17]:

$$X^P = \left(\frac{\Delta E^P}{\Delta E}\right) = \left(\frac{\delta^P}{\delta}\right) \qquad (1)$$

where ΔE^P and δ^P are the polar components of the energy density and solubility parameter, respectively. Typical X^P values for PEG (as diol end groups) range from 0.165–0.284, whereas that of PDMS is 0.042 [17]. Surface tension for PEG (diol end groups) is considerably higher (>42 dyne/cm) than that of PDMS (~20 dyne/cm) [17, 18].

2. Experimental

2.1. Instrumentation

All experiments were performed on a Bruker (Billerica, MA) BioApex 30es Fourier transform mass spectrometer, equipped with Analytica of Branford (Branford, CT) ESI and NanoES sources. During ESI operation, a Cole-Palmer (Vernon Hills, IL) Series 74900 syringe pump was used to continuously infuse a sample solution at a rate of 60 μl h^{-1}. A potential between −2.5 kV and −3.5 kV (relative to the grounded needle) was applied to the metal-capped glass capillary. Nitrogen (N_2) countercurrent drying gas was used to desolvate droplets produced by the ESI source. The flow and temperature of N_2 drying gas was variable for these experiments and therefore is specified where appropriate.

Gold-coated borosilicate nanospray emitters with ~4 μm i.d. were obtained from New Objective (Cambridge, MA). These emitters were inserted into the nanoES source assembly and placed approximately 0.5–3.0 mm from the orifice of the metal-capped glass capillary. The onset of nanospray was initiated with an applied potential of −600 V to −2 kV (relative to the grounded emitter) at the metal-capped glass capillary.

Ions, formed from either source, were electrostatically injected into the Infinity cell [19] (2.0 V trapping potential) using the patented Sidekick method [20]. Frequency-sweep excitation from *m/z* 400 to 2500 was applied at an amplitude of ~44–63 $V_{p\text{-}p}$. Detection was in direct mode (500 kHz Nyquist bandwidth) from time domain data sets of 128K (10 acquisitions per experiment). The data sets were apodized with a Gaussian function, Fourier trans-formed and displayed in magnitude mode using XMASS 4.0.2 on a Silicon Graphics (Mountain View, CA) RPC 4600 INDY data station. In calculating the index values, the spectral magnitude of the most abundant isotope peak was determined by XMASS; the peak heights from each individual oligomer were then summed. This tacitly assumes that each isotopic distribution is symmetrical about the most abundant mass, which is an obvious oversimplification. Nonetheless, if the same isotope peak is used for each oligomer independent of the mass spectrum collected, this serves as a useful benchmark in comparing absolute ion intensities.

2.2. Sample preparation

The following materials were used in these experiments: 1250 Da nominal mass methyl terminated PDMS (ME-PDMS), 2000 Da nominal mass 2-methylpropyl terminated PDMS (MP-PDMS) and 1000 Da nominal mass PEG (Sigma Chemical Co., St. Louis, MO), methanol (HPLC grade, Mallinckrodt, Paris, KY), 2-propanol (Fisher Scientific, Fairlawn, NJ) and sodium hydroxide pellets (99.99% semiconductor grade, Aldrich Chemical Co., Inc., Milwaukee, WI). All PDMS and PEG samples were prepared as 20 μM solutions in a solvent system composed of methanol: isopropanol:10 mM NaOH (49:49:2, v/v/v), and all ions were observed as their sodium adducts $(M+Na)^+$ at this Na^+/polymer molar ratio (10:1), which was maintained in all the experiments described. All reagents were used as received and without further purification.

3. Results and discussion

3.1. Analysis of PDMS/PEG oligomer blends via ESI-FTMS

As desolvation occurs during ESI, there is competition among the analytes present initially within the charged droplets for transfer to the gas phase. Thus, desolvation becomes increasingly biased in favor of particular analyte(s) as the physicochemical properties of the analytes within the condensed phase become more dissimilar. This selectivity, although useful in some applications, poses a very real limitation on the use of ESI-FTMS for the analysis of ill-defined oligomer mixtures containing species possessing diverse solution properties. Figure 1 provides ESI-FTMS mass spectra of 20 μM 2-methylpropyl terminated PDMS (MP-PDMS, 2000 Da nominal mass) and 20 μM methyl terminated PDMS (ME-PDMS, 1250 Da nominal mass), respectively, under identical experimental conditions. By summing the *n*-mer peak intensities for each oligomer distribution, one obtains a (MP-PDMS / ME-PDMS) normalized total ion intensity ratio (0.57) which serves as a useful benchmark for comparison to results for binary mixtures. That is, in the absence of any liquid to gas preferential transfer during the ESI process, one expects, within experimental error, the same index value of 0.57. The resulting ESI-FTMS spectrum for an equimolar mixture of the two oligomers (under the same conditions as for Figure 1) is shown in Figure 2. The two isotopically resolved MP-PDMS and ME-PDMS distributions are denoted in the inset as (●) and (□), respectively. The resulting binary mixture total ion intensity ratio (MP-PDMS / ME-PDMS) of 0.26 indicates a pronounced liquid-to-gas-phase bias favoring ME-PDMS transfer to the gas phase. What accounts for this bias?

It is instructive to bear in mind some fundamentals of surface tension as they apply to droplet dynamics. The surface tension of polymer blends, melts and solutions is a strong function of molecular weight and the potential surface activity of the chain termini. The molecular weight dependence of surface tension for a polymer (γ) is traditionally described by one of two equations [18]:

$$\gamma^{\frac{1}{4}} = \gamma_{\infty}^{\frac{1}{4}} - \frac{k_1}{M_n} \tag{2a}$$

$$\gamma = \gamma_{\infty} - \frac{k_2}{M_n^{\frac{2}{3}}} \tag{2b}$$

where M_n is the number average molecular weight, γ is the surface tension at infinite molecular weight and

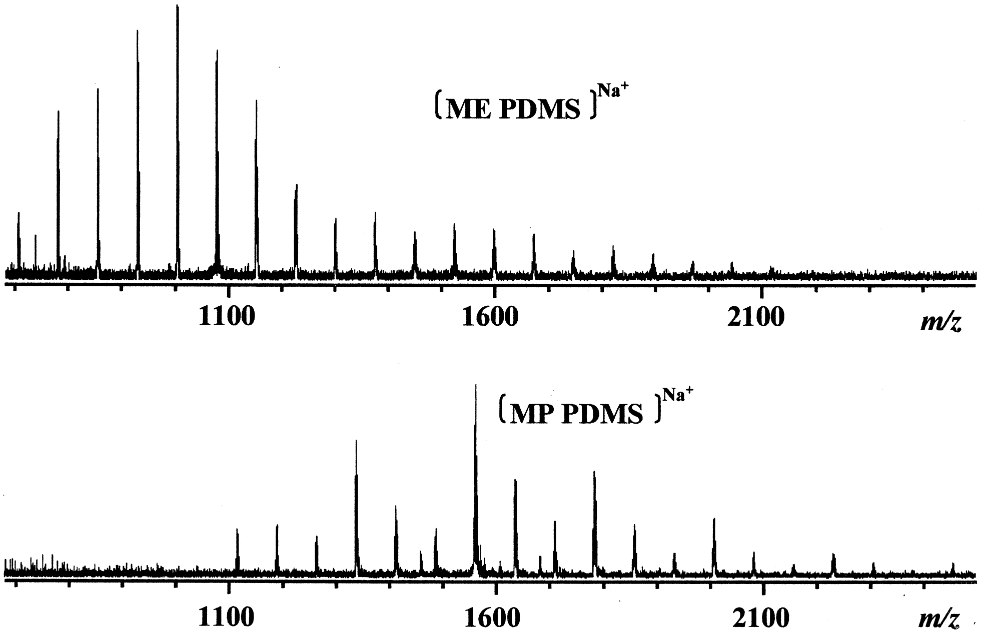

Fig. 1. ESI-FT mass spectra of (lower) 20 μM, 2000 Da nominal mass MP-PDMS and (upper) 20 μM, 1250 Da nominal mass ME-PDMS analyzed under identical experimental conditions.

k_1 and k_2 are semi-empirical parameters that depend on end-group type. If the end groups and repeat unit have a similar composition, Eq. (2a,b) scales with molecular weight. However, when the end groups possess a different composition than the repeat unit in the polymer chain, segregation effects for the polymer at the surface may be emphasized. The constant k_2 in Eq. (2b) relates the surface energy at infinite molecular weight (γ_∞) with end-group surface energy (γ_e) according to Eq. (3):

$$k_2 = (\gamma_\infty - \gamma_e)(2m_r)^{\frac{2}{3}} \tag{3}$$

where m_r is the repeat unit molecular weight. This segregation effect, which occurs primarily via preferential adsorption or depletion at the surface, was recently demonstrated by Jalbert and coworkers for an end-functionalized PDMS series [21]. Enrichment of ME-PDMS at the surface is predicted based on the lower surface energy of the methyl end groups versus the dimethylsiloxane repeat unit [21]. The surface enrichment of the lower energy component correlates with the surface tension, which, according to Tate's law, ultimately determines the drop size that can be supported [22]. The ESI-FT mass spectra in Figs. 1 and 2 suggest an enrichment of ME-PDMS relative to MP-PDMS at the droplet surface during ESI of the binary mixture. Because the end groups are chemically both low energy, the major difference accounting for their differential solution to gas phase transfer may involve surface tension, which does depend on MW. Here, the MP-PDMS is slightly less than twice the MW of the ME-PDMS. The increased surface tension of MP-PDMS, when mixed directly with ME-PDMS, could inhibit its transfer into the gas phase. This immediately suggests that, if quantification of polymer blends is going to be achieved by ESI-MS, each of the polymers in the blend will need to have similar surface tensions. In addition, the heat of vaporization of a liquid is also a function of drop size, a matter further complicated by the use of hot gas drying streams [22].

In light of these issues, preferential transfer to the gas phase (and subsequent detection by mass spectrometry) is expected to become an even more serious

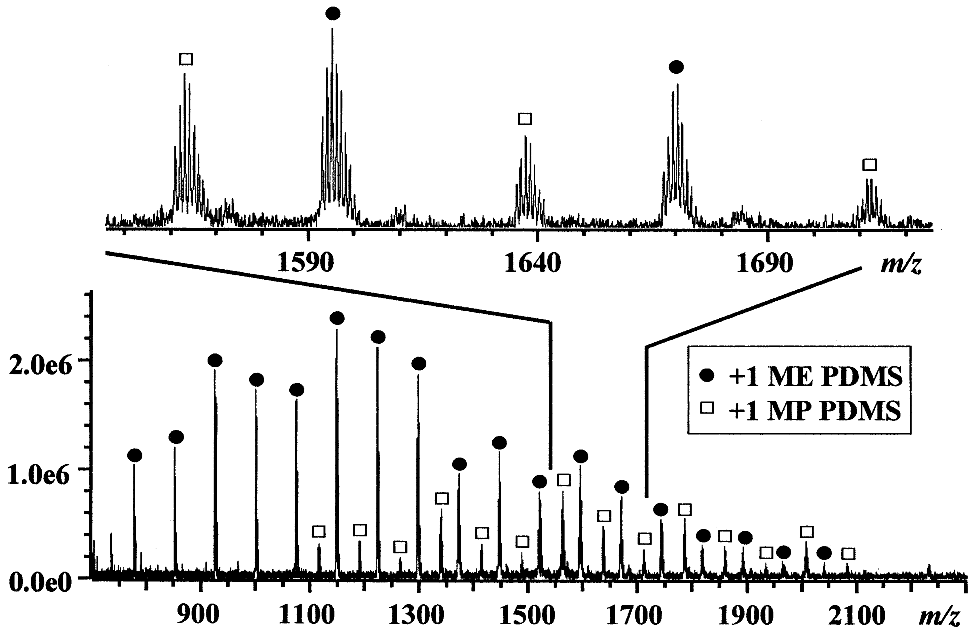

Fig. 2. ESI-FT mass spectrum of an equimolar mixture of 2000 Da nominal mass MP-PDMS and 1250 Da nominal mass ME-PDMS. The inset shows isotopically resolved MP-PDMS and ME-PDMS *n*-mers.

problem for ESI of binary mixtures of oligomers with vastly different physicochemical properties, such as PEG and PDMS. These polymers reside at the extremes of polarity and surface tension as noted in the Introduction. This effect is illustrated in the bottom panel of Figure 3 which presents an ESI-FTMS mass spectrum for an equimolar mixture of 1000 Da PEG and 1200 Da ME-PDMS. Although both +1 and +2 charge state distributions are apparent for PEG (denoted by ▲ and Δ, respectively), the ion signal from ME-PDMS is highly attenuated in this spectrum. The applied potentials within the ESI source can be modulated to differentially focus analyte charge states, giving rise to the common practice of potential sweeping in order to tune specific ions of interest. The top panel of Figure 3 illustrates an ESI-FTMS mass spectrum where the applied potentials were systematically varied to optimize ME-PDMS oligomer signal. However, from the inset it is clear that despite such iterative tuning, the ME-PDMS distribution appears only modestly above the baseline noise, and PEG is preferentially detected.

A key experimental variable that exerts a profound influence on condensed phase droplet desolvation is the drying gas flow rate. Figure 4 illustrates how nitrogen drying gas flow alters the appearance of the ESI-FTMS mass spectrum for an equimolar 1000 Da PEG/1200 Da ME-PDMS mixture. For the spectrum in the top panel (1 L/s flow rate, 250°C), the +2 and +1 charge state distributions of PEG are prominent, while the ME-PDMS oligomers are almost totally attenuated. However, in the spectrum in the bottom panel (no drying gas), ME-PDMS *n*-mers enjoy relatively high ion intensity, while the +2 and +1 PEG distributions experience somewhat diminished ion intensity. Since the time-averaged ion intensity is proportional to the total number of ions detected, it is clear that decreased drying gas flow rate favors the transfer of ME-PDMS analyte from the condensed phase droplets to the gas phase for detection. Since the drying gas actually involves two experimental variables (i.e., flow rate and temperature), it is possible that differential ion transfer is influenced by some combination of these variables. Although we make no attempts to ascertain their relative contributions here, the general effect of drying gas flow is rapid desol-

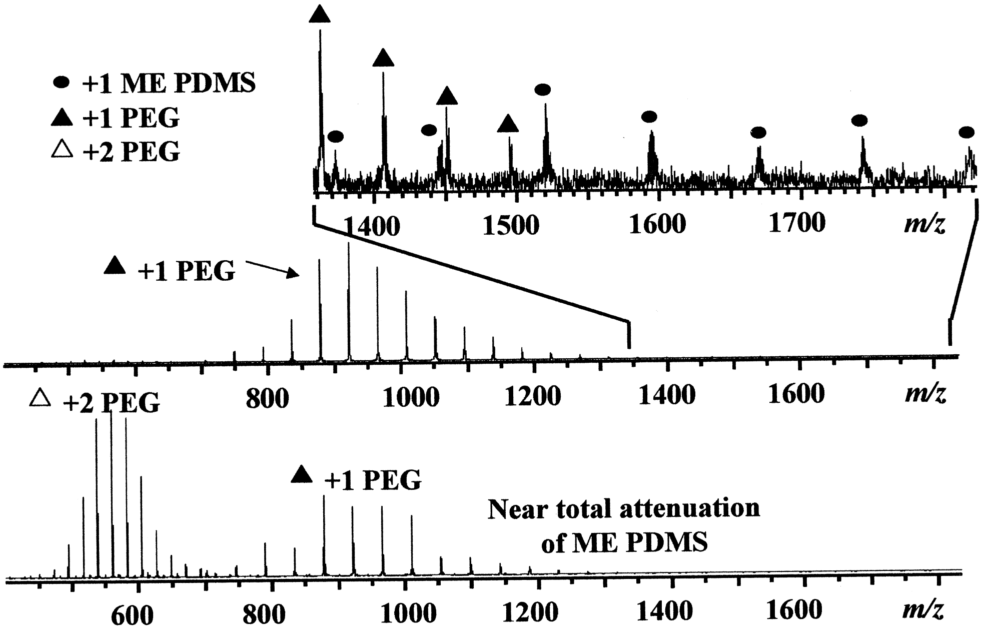

Fig. 3. ESI-FT mass spectra of an equimolar mixture of 1000 Da nominal mass PEG and 1250 Da nominal mass ME-PDMS. The bottom panel was obtained under experimental conditions that favor the high-charge state. The top panel was obtained under experimental conditions that favor low-charge state. The inset in the top panel shows the isotopically resolved *n*-mer peaks from the +1 charge state distributions of PEG and ME-PDMS.

vation of the ESI-generated droplets. Oligomers of PEG, which are notoriously hydrophilic, tend to be solvated within the bulk of the liquid droplets. On the other hand, ME-PDMS molecules are expected to diffuse spontaneously from the bulk and partition to the surface based on the predictions of Jalbert et al. [21]. The surface tension of PEG is almost twice that of PDMS (~42 dyne/cm vs. ~20 dyne/cm) [17, 18]. Thus, the ion signal from the higher surface tension and more favorably solvated PEG is expected to scale with the drying gas flow rate. This is, in fact, what is observed as gas flow is applied (1 L/s) during the ESI process (Figure 4).

Rather unexpectedly, however, the gas flow (and thermal energy) also results in an apparent quenching of the PDMS ion signal. Since all other conditions remain static, some combination of gas flow and heat must account for the attenuation of PDMS *n*-mers observed in the upper panel of Figure 4. In general, multiply charged PDMS *n*-mers are rarely observed [6, 7] unless they contain easily protonated end groups (e.g., free amines) [7]. As is common for polymers lacking such ionizable end groups, all PDMS oligomers reported here use Na^+ as a charging agent. PDMS oligomers may exist in any one of a number of conformations [23], and as such one hypothesis is that Na^+ adduction occurs via solvation within discrete, coiled PDMS chains. We postulate that thermal denaturation during assisted desolvation results in random coil PDMS oligomer chains lacking in Na^+ binding sites. Of course, since these unfolded species cannot support an extrinsic charge, *they remain neutral and therefore go undetected in the mass spectrum.* For PEG, which can be successfully multiply cationized, thermal effects resulting in a loss of a single Na^+ to produce neutral oligomers undetectable by mass spectrometry would not be as significant as for singly charged PDMS, since some proportion of the PEG ion population exists in the multiply charged state. Also, one might wonder if solubility differences between PEG and PDMS in methanol-isopropanol might account for the differences in observed behavior. However, the Hildebrand solubility parameters for PEG (20.2 ± 0.2 $MPa^{1/2}$) and PDMS (19.4

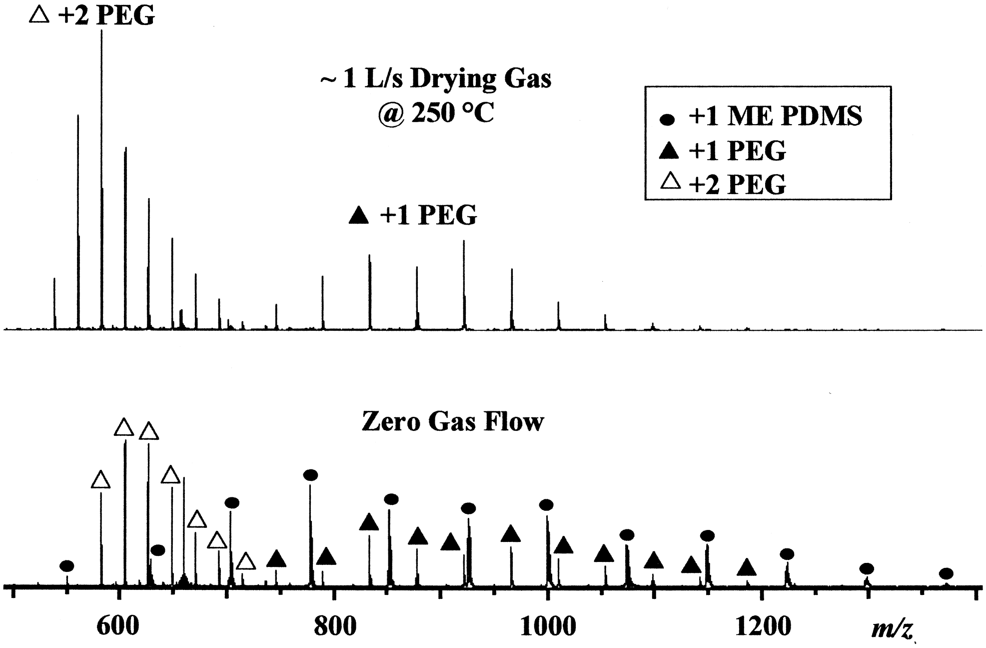

Fig. 4. ESI-FT mass spectra of an equimolar mixture of 1000 Da nominal mass PEG and 1250 Da nominal mass ME-PDMS. The bottom panel was obtained with no drying gas. The top panel was obtained with a drying gas flow rate of ~1 L/s and a temperature of 250°C.

MPa$^{1/2}$) [24] are similar in strong H-bonding solvents like alcohols, suggesting that there should not be significant solubility differences for these polymers in methanol-isopropanol.

Conformational effects of the oligomer chains may also be relevant. Bowers and coworkers have shown that ion chromatography (or ion mobility mass spectrometry) shows considerable promise in the investigation of synthetic polymer tertiary structures [25—27]. These authors have demonstrated that for PEG, the polymer will completely envelop the metal cation, which coordinates to several oxygen atoms [25, 26], resulting in a compact structure. As described by Lenk et al., conformational structures proposed for PDMS range from the highly extended (and open) *cis-trans* caterpillar-like conformation (cross section 52 Å^2) to the highly compact Damaschun helix conformation (96 Å^2) [23]. It is possible that thermal denaturation of compact PEG structures, resulting in loss of cation-charging agents, is more difficult than it is for PDMS, especially if the PDMS is in an open conformation, due to the high degree of coordination observed for alkali ions with PEG [25, 26].

In the final stages of ESI desolvation, a skimmer electrode assists in the removal of residual solvent clustered about the analyte. By increasing the potential applied to this electrode, ions are coarsely energy selected in the ESI source. Figure 5 illustrates ESI-FTMS mass spectra from an equimolar mixture of PEG and ME-PDMS analyzed under constant conditions save the applied skimmer electrode potential. Initial experimental conditions [Figure 5(bottom)] were chosen such that PDMS *n*-mers were observed in the mass spectrum. In accordance with the above results for hot drying gas, as the skimmer electrode potential is increased (thermal energy), PDMS *n*-mers decrease in intensity to near baseline values, while PEG *n*-mers with two charge state distributions begin to evolve in the mass spectra, possibly as a result of greater desolvation.

3.2. Analysis of PDMS/PEG oligomer blends via nanoES-FTMS

Less bias in solution to gas phase transfer is expected for diverse analytes from the relatively small

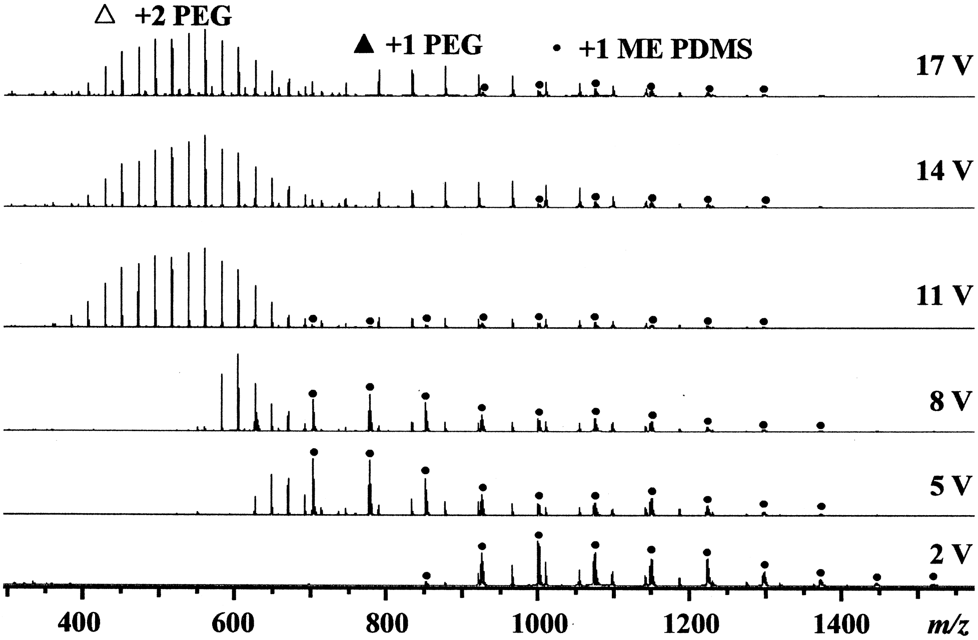

Fig. 5. ESI-FT mass spectra of an equimolar mixture of 1000 Da nominal mass PEG and 1250 Da nominal mass ME-PDMS obtained under the same experimental conditions save the applied skimmer potential. As skimmer potential is increased, ME-PDMS *n*-mers become attenuated while PEG *n*-mers appear in the mass spectrum.

diameter droplets (nanometer regime) formed from a nanoES source due to a lower volume of solvent and a larger number of analyte molecules existing at the surface of the droplet. Figure 6 provides nanoES-FTMS mass spectra of 20 μM ME PDMS (1250 Da nominal mass) and 20 μM PEG (1000 Da nominal mass), respectively, under identical experimental conditions. By summing the *n*-mer peak intensities for each oligomer distribution in the PDMS and PEG spectra, one obtains a (ME-PDMS / PEG) normalized total ion intensity ratio of 0.29. Once again this serves as a useful benchmark for comparison with results for binary mixtures of ME-PDMS and PEG. The nanoES-FTMS spectrum for an equimolar mixture of the two oligomers (under the same conditions as for Figure 6) is shown in Figure 7. The isotopically resolved ME-PDMS and +1 charge state PEG distributions are denoted in the inset as (●) and (▲), respectively. The resulting binary mixture total ion intensity ratio (ME-PDMS/PEG) is 0.32. This is indicative of minimal bias in the liquid-to-gas phase transfer. This result is consistent with our hypothesis that the reduced volume and effectively increased concentration of the analyte ions on the droplet's surface permit a more uniform transfer efficiency to the gas phase independent of the analyte's polarity or surface tension. Surely this is (at least in part) because analytes in the nanometer-sized droplets produced by nanoES are more efficiently desolvated than the droplets produced by normal ESI and is strongly suggestive of the role of heat of vaporization of the solvent (which depends on drop size).

4. Conclusions

There is a difference in ion transfer efficiency in ESI for synthetic oligomer ions in mono-component compared to the same oligomer incorporated into a binary synthetic oligomer mixture. This may result from a combination of differences in polymer surface tension, the heat of vaporization of a liquid (a function of drop size), or conformational effects. However, under careful control of desolvation conditions, we

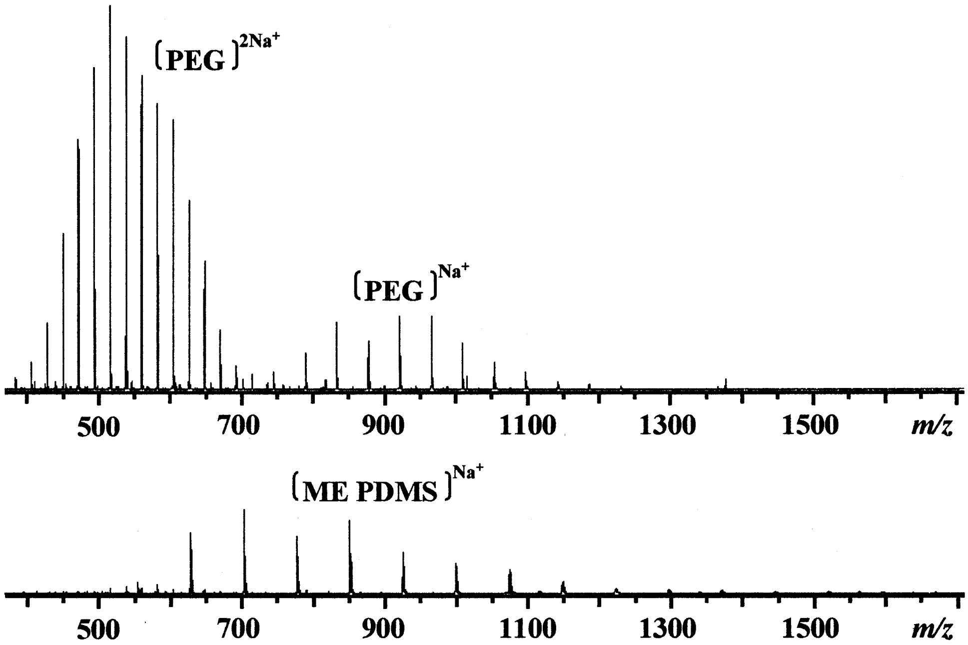

Fig. 6. NanoES-FT mass spectra of (lower) 20 μM, 1250 Da nominal mass ME-PDMS and (upper) 20 μM, 1000 Da nominal mass PEG analyzed under identical experimental conditions.

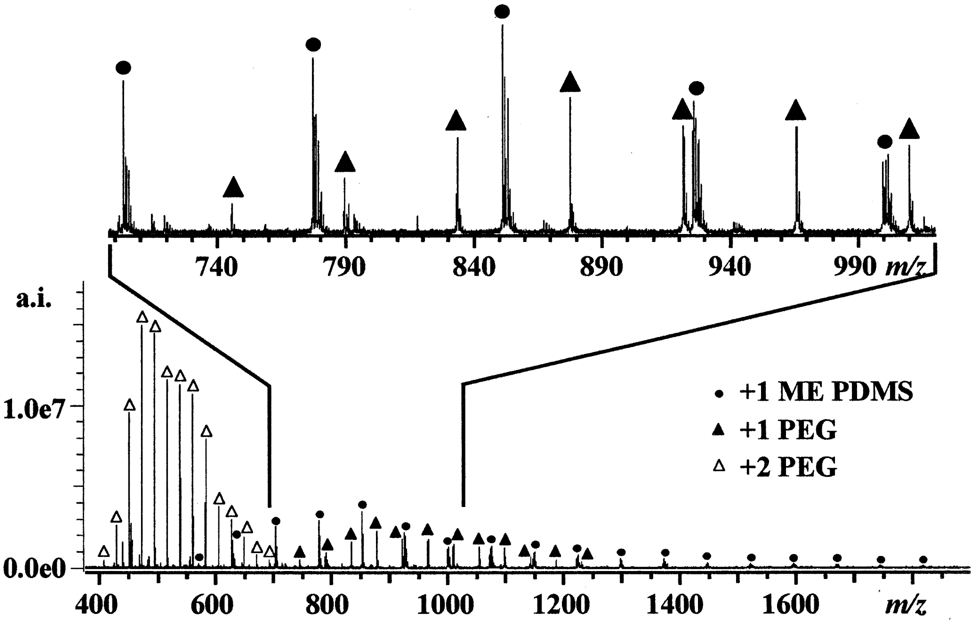

Fig. 7. Nano-FT mass spectrum of an equimolar mixture of 1250 Da nominal mass ME-PDMS and 1000 Da nominal mass PEG. The inset shows isotopically resolved ME-PDMS and PEG *n*-mers.

demonstrate that ESI can be used as an ionization source to qualitatively analyze oligomer mixtures containing species possessing diverse properties (e.g., polarity or surface tension). We observe here that nanoES introduces far less bias stemming from selective ion transfer to the gas phase compared with conventional ESI, suggesting that heat of vaporization of the solvent (which depends on droplet size) plays a critical role in reducing such bias in nanoES. In this regard, nanoES might be considered the ionization method of choice for the analysis of complex oligomer mixtures and may prove especially useful for quantitation experiments.

Acknowledgements

The authors would like to thank Todd M. Alonzo, Anthony R. Dolan, Sarah A. Lorenz and Thomas P. White for helpful discussions. Financial support from the American Society for Mass Spectrometry Research Award (sponsored by the Exxon Education Foundation), the Center for Biotechnology Innovative Technology Grants Program at the State University of New York at Stony Brook and the State University of New York at Buffalo is gratefully acknowledged.

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