
Time-Lag Focusing and Cation Attachment in the Analysis of Synthetic Polymers by Matrix-Assisted Laser Desorption/Ionization–Time-of-Flight–Mass Spectrometry

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Ultraviolet matrix-assisted laser desorption/ionization–mass spectrometry has been employed with time-lag focusing to explore its utility for the characterization of synthetic polymers with broad distributions. Mixtures of five polymer standards with narrow molecular weight distributions were analyzed. The spectra were found to be broadly those expected for three different types of polymer systems—poly(styrene), poly(methyl methacrylate), and poly(ethylene glycol)—when equimass mixtures were used. Large changes in the apparent molecular weight distribution of poly(ethylene terephthalate) were observed when the cation was varied. The shift in the envelope was found to be related to the size and the ability of the oligomers to solvate the cation. © 1997 American Society for Mass Spectrometry (*J Am Soc Mass Spectrom* 1997, 8, 132–139)

The introduction of matrix-assisted laser desorption/ionization (MALDI) [1, 2] has greatly extended the mass range amenable to direct analysis by means of mass spectrometry. This approach has been of great utility in the biological area where the sensitivity and ease of use of the technique have made a major impact [2]. Initial attempts to extend the experimental approach to the characterization of synthetic polymers gave promising results on narrow molecular weight dispersion homopolymer standards [3–18], but general applicability to polymer systems containing varying end groups [19–21], copolymers [22, 23], and wide molecular weight dispersions [24–30] has proven more difficult. More systematic experiments are required to establish the current limitations and possible future development of the use of MALDI in the characterization of polymer formulations.

The development of the time-lag focusing method, first shown by Wiley and McLaren in 1955 [31] and

applied to matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF) by Spengler and Cotter [32], has increased the resolution and signal-to-noise ratio that is attainable in time-of-flight (TOF) analyzers by means of matrix-assisted laser desorption/ionization–mass spectrometry (MALDI-MS). The technique has recently been applied to the characterization of synthetic polymers [19, 20, 33, 34].

The issue of the collection of quantitative data over wide mass ranges (1–30 ku) is addressed by using a range of polymer systems. In addition, the issue of characterization of polymers with different end groups is addressed. The effects of the cationization adduct on the molecular weight distributions that are observed in the UV-MALDI spectra also have been explored.

Experimental

Mass Spectrometry

The time-lag focusing UV-MALDI data were obtained by using a TofSpec E (Micromass, Manchester, UK) TOF mass spectrometer, operated in linear mode at an

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accelerating voltage of 25 kV. A hybrid microchannel plate-electron multiplier detector was used and was sampled at 500 MHz. A VSL-337i nitrogen laser (Laser Science Inc., Newton, MA) was employed, operating at 337 nm with a pulse width of 4 ns and a maximum energy output of 180 mJ.

UV-MALDI spectra were also obtained by means of the ToFSpec TOF mass spectrometer (Micromass) operated in linear mode with an accelerating potential of 25 kV. The instrument is similar in design to the ToFSpec E but has a shorter path length. Approximately 100 laser shots were employed to obtain the mass spectra under control of the OPUS data system.

Calibration for analysis of polymer samples by MALDI-MS may be carried out in a number of ways. In the simplest case an external two point calibration is used, often with unrelated compounds. External calibration by using related compound classes with similar experimental parameters gives more accurate data [35], particularly if a multipoint calibration is employed. The most accurate results are obtained by using an internal calibration compound [36], but given that polymer samples are often complex mixtures, this can be experimentally difficult. Montaudo et al. [37, 38] successfully used a self-calibration method for polymer samples. For the data shown here an external multipoint calibration was employed, giving a mass accuracy of approximately 0.03%. The same class of polymer was used as that for the experiments. For example, poly(methyl methacrylate) (PMMA) samples were the calibration compounds for MALDI-MS analysis of the same type of polymer system. Average molecular weight data (M_n , M_w , and polydispersity) was generated by using the Poly software (Micromass).

Sample Preparation

Mixtures. All polymer standards were purchased from Polymer Laboratories (Church Stretton, UK), except poly(styrene) E, which was from Aldrich Chemical Co. (Gillingham, UK), and were used without further purification. Dithranol (1,8-dihydroxy-9[10H]-anthracenone) and 1,1,1,3,3,3-hexa-fluoro-*iso*-propanol (HFIP) were purchased from Sigma Chemical Co. (St. Louis, MO). Silver tri-fluoroacetate was from Aldrich Chemical Co., sodium iodide from BDH Ltd. (Poole, UK), analytical grade acetone from Fisher Scientific (Loughborough, UK), and analytical grade tetrahydrofuran from Fisons Scientific Equipment (Loughborough, UK).

The most probable mass or peak average molecular weight (M_p) and polydispersity values of the polymers, which are estimated by the manufacturer by using gel permeation chromatography, are 2010 and 1.10 for PMMA A, 5270 and 1.06 for PMMA B, 10,300 and 1.06 for PMMA C, 20,200 and 1.06 for PMMA D, 1700 and 1.06 for poly(styrene) A, 3250 and 1.04 for

poly(styrene) B, 7000 and 1.04 for poly(styrene) C, 11,600 and 1.03 for poly(styrene) D, 1470 and 1.05 for poly(ethylene glycol) (PEG) A, 4100 and 1.05 for PEG B, 7100 and 1.03 for PEG C, 12,600 and 1.04 for PEG D, and 22,800 and 1.06 for PEG E. The mean molecular weight generated by viscometry, also estimated by the manufacturer, is 24,150 for poly(styrene) E. The structure of the end groups of poly(ethylene terephthalate) (PET) A, PET B and PET extracts 1-6 were determined by nuclear magnetic resonance spectroscopy (data not shown). Average mass data were not available for these polymers.

All solutions were prepared at a concentration of 10 mg mL⁻¹. The samples, matrix (dithranol), and salt (silver tri-fluoroacetate) were separately dissolved in tetrahydrofuran for analysis of mixtures of poly(styrene)s. A ratio of 50:[5:5:5:5]:2 matrix solution to sample solution to salt solution (v/v) was employed and approximately 0.5 μ L of this mixture was deposited on the sample disk. Each separate component of poly(styrene) was made up with an equal weight of sample. A layer of sodium iodide (from approximately 0.5 μ L of a solution in acetone) was applied to the target in both the PEG and PMMA cases. These samples and corresponding matrix (dithranol) were separately dissolved in HFIP. The ratios used were 10:[1:1:1:1] and 10:[1:1:1:1] matrix solution to sample solution (v/v), respectively, and approximately 0.5 μ L of these mixtures was applied to the sample stage. Equal weights of each of the components were used, as for the mixture of polystyrene standards.

Single components. The alkali metal salt was again applied to the sample disk before deposition of the sample and matrix for analysis of PMMA, PEG, and PET. The alkali metal salts were dissolved in acetone (LiI, NaI, KI) or water (RbI, CsI). The separate matrix and sample solutions, each at a concentration of 10 mg mL⁻¹, were mixed in a 10:1 ratio (v/v) prior to deposition on the sample stage.

The optimization of the sample preparation conditions was found to be very important for the generation of spectra that are representative of the analyte. The conditions described in the preceding text were found to provide consistent results for many classes of polymer. The only difference is the mechanism of cationization. Sodium salts were added (a layer of sodium iodide added initially before the sample and matrix were deposited on the sample stage) to obtain spectra from polymers containing oxygen atoms, such as PEG, PMMA, and PET, whereas silver salts were required for hydrocarbon polymers such as poly(styrene) and poly(butadiene) [15]. The use of HFIP as the solvent has been found to be particularly useful for many polymer systems analyzed in this laboratory. Furthermore, the use of dithranol as a matrix is also important [15] because the crystals that form on the sample disk are small, therefore aiding the generation of a homogeneous surface.

Results and Discussion

Matrix-Assisted Laser Desorption/Ionization–Time-of-Flight–Mass Spectrometry of Poly(ethylene Terephthalate)

Varying time process analysis. PET is a polymer that has recently been shown to be amenable to analysis by means of MALDI-MS [39, 40] and is currently used for applications such as films and bottles. The spectra obtained from a series of PET samples, extracted by means of a drain from a semitechnical reactor vessel at varying time intervals (extracts 1–6 were sampled in chronological order), are displayed in Figure 1. These data indicate the progress of the polymerization process in terms of an increase in average molecular weight and polydispersity. This is also demonstrated by the average molecular weight data that are shown in Table 1. An expansion over a narrower mass range, for the final time aliquot (extract 6), is displayed in Figure 2 and illustrates more clearly the variation in end group structure of the polymer. The major series of oligomers has a mass consistent with the expected bis-hydroxy-ended polymers (1), which were observed at m/z $192n + 85$, where 192 is the mass of the repeat unit and 85 is the mass of the end groups and the cation (Na^+). Adduct ions of acid-ended oligomers (2) were seen at mass-to-charge ratios that were 44 u lower and di-glycol-containing oligomers (3) at mass-

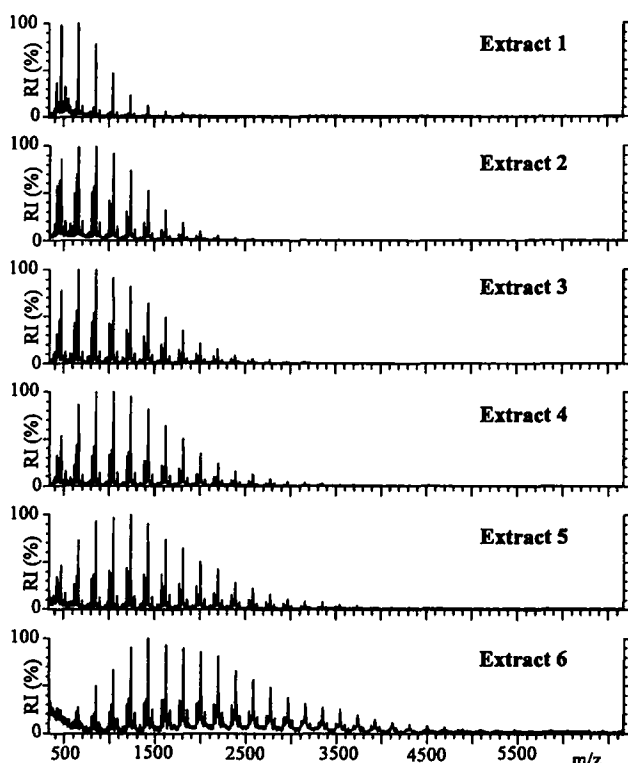


Figure 1. UV-MALDI spectra of PET samples (extracts 1–6) obtained from a semitechnical reactor vessel at varying time intervals (TofSpec instrument).

to-charge ratios that were 44 u higher than that of the bis-hydroxy-ended polymer. In addition, $[\text{M} + \text{H}]^+$ ions of the bis-hydroxy-ended species were also observed in the spectra.

Variation of cation. In the course of this study it was observed that with sodium and potassium salts that are indigenous in the matrix (dithranol), a shift in the M_m —most abundant oligomer species as measured by mass spectrometry [30]—value to higher molecular weight was observed for the $[\text{M} + \text{K}]^+$ over the $[\text{M} + \text{Na}]^+$ adducts in the MALDI-MS spectra. The effect of ionization by addition of lithium, sodium, potassium, rubidium, and cesium salts was therefore also investigated. The resulting spectra are displayed in Figure 3 for PET A and it can be deduced from these data that the effect of increase in cation size is progressive, with the M_m value being observed to shift to higher molecular weight in descending the alkali metal series. The shift in M_m was approximately 1900 u when the cation was changed from Li^+ to Cs^+ . Measurements of the peak areas have also indicated the same behavior for the series of lower intensity. A large shift in the M_n and M_w values to higher molecular weight is also observed when the metal salt is varied from lithium to cesium (Table 1). The polydispersity values obtained, however, get progressively lower as the size of the cation is increased. Peaks are also observed in the spectra of PET A when the matrix is doped rubidium and cesium iodide, which have mass-to-charge ratios consistent with that of adducts of polymer with sodium ions. The origin of the Na^+ ions may be the matrix, because sodium salts are indigenous in dithranol.

To establish whether the effects observed for linear PET (PET A) with alkali metal cations were associated in any way with cation attachment to the end groups of the oligomers, an equivalent set of experiments was performed for a sample of a cyclic polymer. A sample containing a mixture of cyclic oligomers ranging from trimer to approximately decamer—PET B—was obtained and analyzed by means of MALDI-MS with cation attachment again by means of alkali metal ions.

It can be observed from the resulting spectra (Figure 4) that the same successive shift of distribution to a higher M_m value occurs with an increase in size of the cation. The extent of this change in molecular weight is approximately 1000 u in the most extreme case between lithium and cesium (Table 1). This shift, although very significant, is less than that occurring for PET A. This is possibly because of the lower degree of polymerization of PET B. The trend in M_n , M_w , and polydispersity values is comparable, however, to that seen for PET A (Table 1).

A series of peaks in addition to the major component is also observed in the spectra of the cyclic polymer (4), which is 44 u higher than the major species. This minor series of ions has mass-to-charge ratios that are consistent with the incorporation of an extra glycol unit into the ring (5).

Table 1. Calculated average molecular weight values for PET, PEG A, PMMA A, and equimass mixtures of polymers^a

	Most abundant oligomer species (M_m)	Number average molecular weight (M_n)	Weight average molecular weight (M_w)	Polydispersity (M_w/M_n)
<i>PET — Varying Time Process Analysis^b</i>				
Extract 1	600	685	851	1.24
Extract 2	700	931	1152	1.24
Extract 3	750	1072	1367	1.28
Extract 4	950	1268	1537	1.21
Extract 5	1200	1405	1752	1.25
Extract 6	1450	2072	2455	1.19
<i>PET A — Variation of Cation^b</i>				
[M + Li] ⁺	800	1843	2363	1.28
[M + Na] ⁺	1350	1915	2411	1.26
[M + K] ⁺	1850	2093	2606	1.24
[M + Rb] ⁺	2250	2380	2919	1.23
[M + Cs] ⁺	2700	2637	3146	1.19
<i>PET B — Variation of Cation^b</i>				
[M + Li] ⁺	900	797	1038	1.3
[M + Na] ⁺	1250	1284	1526	1.11
[M + K] ⁺	1650	1452	1579	1.09
[M + Rb] ⁺	1750	1512	1596	1.06
[M + Cs] ⁺	1850	1618	1692	1.05
<i>PEG A — Variation of Cation</i>				
[M + Li] ⁺	1400	1459	1496	1.03
[M + Na] ⁺	1420	1429	1467	1.03
[M + K] ⁺	1430	1461	1497	1.03
[M + Rb] ⁺	1500	1490	1528	1.03
[M + Cs] ⁺	1530	1466	1507	1.03
<i>PMMA A — Variation of Cation</i>				
[M + Li] ⁺	1670	1748	1891	1.08
[M + Na] ⁺	1710	1830	1963	1.07
[M + K] ⁺	1760	1949	2085	1.07
[M + Rb] ⁺	1840	1934	2073	1.07
[M + Cs] ⁺	1870	1928	2067	1.07
<i>Equimass Mixtures of Polymers</i>				
Poly(styrene)s A, B, C, D, & E	1550	3788	6872	1.81
Poly(ethylene glycol)s A, B, C, D, & E	1350	3946	8039	2.04
Poly(methyl methacrylate)s A, B, C, & D	1600	3361	5807	1.73

^a M_n , M_w , and polydispersity values calculated from UV-MALDI spectra from the peak areas.^bFrom the most intense series in the spectra.

The most important observation from this study is that PET behaves very differently from PEG and PMMA [41, 42], where a relatively small or no change in the M_m value is observed when the metal cation is varied. This is indicated by the data in Table 1 for PEG A and PMMA A samples, which have M_m values similar to that of the PET samples. Alkali metal salts were again added to aid ionization by means of lithium, sodium, potassium, rubidium, and cesium ions.

The proposed explanation for the reported findings is that the ability of an oligomer of PET to solvate the cation is dependent on the molecular weight of the sample and the size of the cation. The most stable conformation for the adduct of an oligomer with an

alkali metal cation would involve that cation being totally encased by the polymer chain. This was shown to be the most stable conformation for PEG oligomers of low molecular weight, by means of ion chromatography and molecular modeling, when cationized by attachment of sodium ions [43]. It is predicted that a PET oligomer would be more rigid than either a PMMA or PEG oligomer, of similar molecular weight, in the gas phase. This would be expected as a consequence of the phenyl rings in the structure of PET, and hence the most favorable interactions with the metal cation would occur for higher molecular weight species than for PEG and PMMA, which have more flexible chains. A larger cation would therefore provide a more favorable

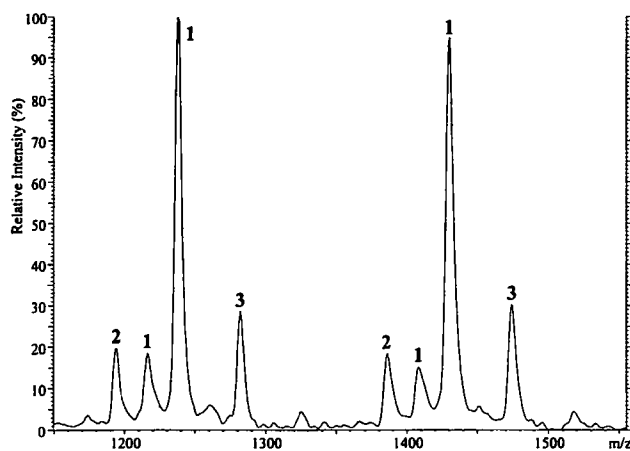
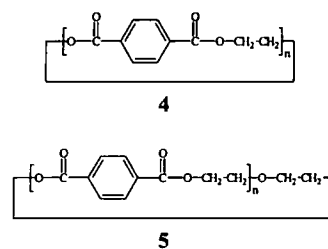
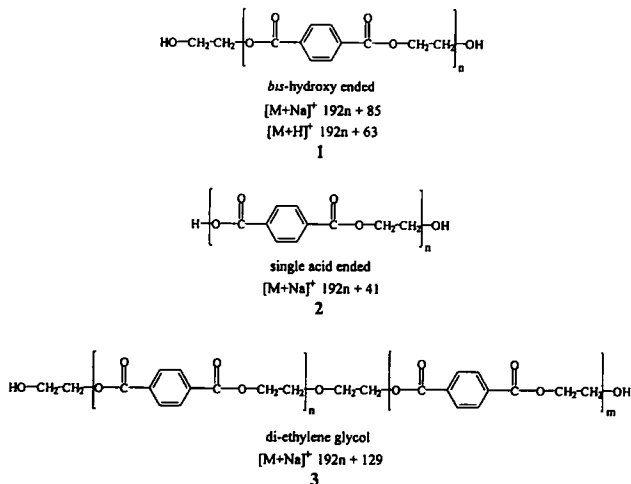


Figure 2. An expansion of the UV-MALDI spectrum of the final aliquot of PET (extract 6) from the reactor vessel (TofSpec instrument).

site for interaction with oligomers of higher molecular weights during ionization of PET. Cesium ions would be expected to interact more favorably with PET oligomers of greater molecular weight, and hence the distribution that is observed in the spectra is shifted to higher mass-to-charge ratios. Lithium ions interact favorably with oligomers of lower, as well as those of higher, molecular weights and the envelope of peaks in the spectra is therefore seen to have a higher intensity at lower mass-to-charge ratios than for that with attachment of cesium ions. This is also indicated by the drop in the polydispersity values for these samples when the cation is changed from Li^+ to Cs^+ . The distributions observed in the spectra of PET A and B are expected to be more representative of the sample with attachment of smaller cations, such as Li^+ . With a more flexible structure such as that of PEG and PMMA, changing the cation would hence be expected to be less of an issue across the molecular weight spread, because oligomers of lower molecular weight would have more mobility to encompass the larger cations.



Extended Mass Range Data

Mixtures of standards have been studied to explore the utility of MALDI in the study of polymer systems of wide mass distributions. The spectra of a mixture of narrow distribution poly(styrene) standards A, B, C, D, and E have been obtained. Figure 5 shows a spectrum of an equimass mixture of all five components together. If the distributions for each of the components were similar, the ratio of M_m intensities would be expected to be approximately 15:7:4:2:1. The higher molecular weight components have a broader distribution in practice and this reduces their expected contribution, but the results are broadly those expected.

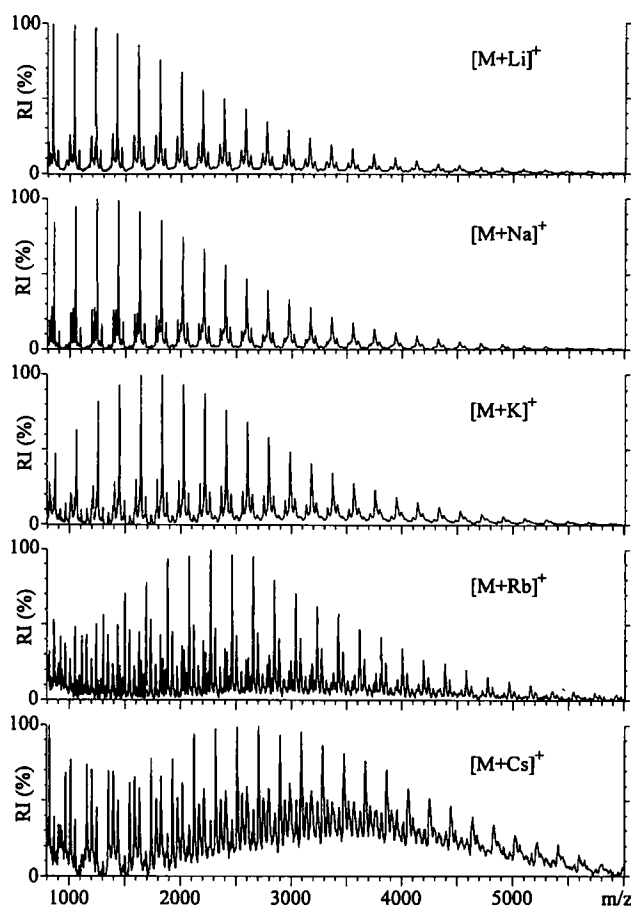


Figure 3. UV-MALDI spectra of PET A with addition of different alkali metal salts (TofSpec instrument).

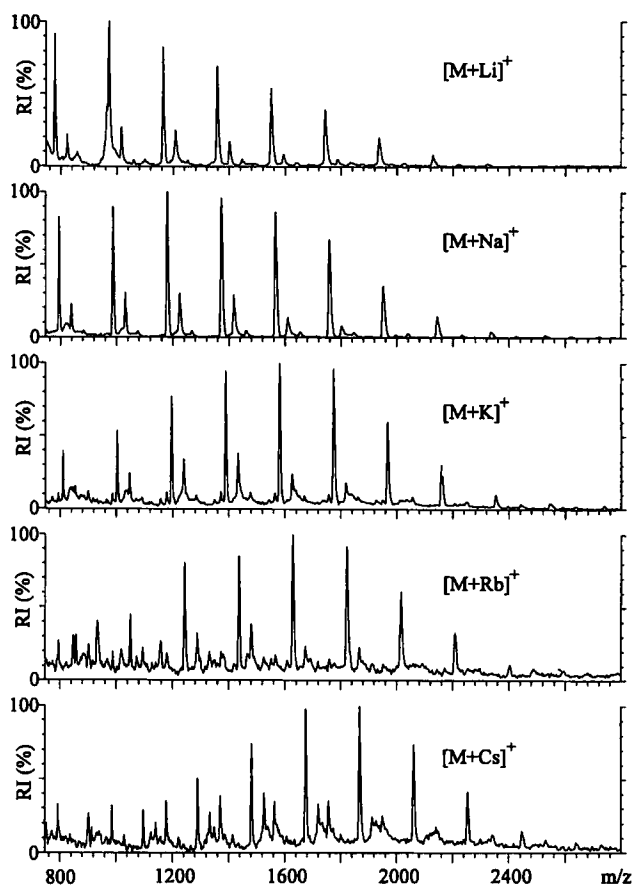


Figure 4. UV-MALDI spectra of PET B with addition of different alkali metal salts (TofSpec instrument).

Similar experiments have been performed to compare results with other polymer systems, namely, PEG and PMMA polymers. For experiments with PEG, standards PEG A, B, C, D, and E were employed whilst standards PMMA A, B, C, and D were used for PMMA.

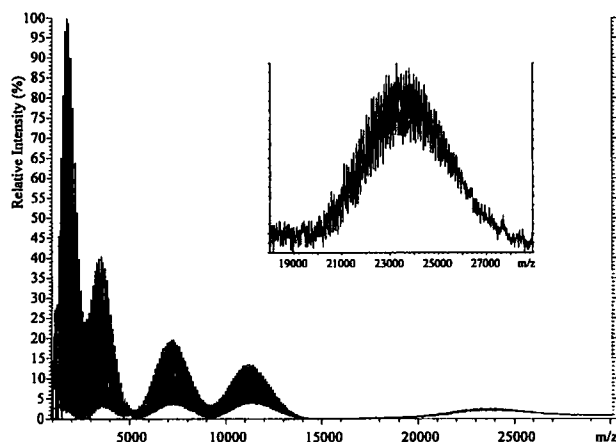


Figure 5. UV-MALDI spectrum of an equimass mixture of poly(styrene)s A, B, C, D, and E (high mass-to-charge ratio expanded) obtained with time-lag focusing (TofSpec E instrument).

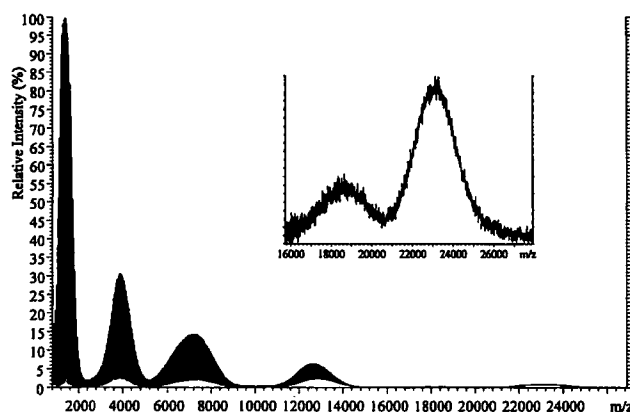


Figure 6. UV-MALDI spectrum of an equimass mixture of poly(ethylene glycol)s A, B, C, D, and E (high mass-to-charge ratio expanded) obtained with time-lag focusing (TofSpec E instrument).

Figures 6 and 7 show that the MALDI spectra of the equimass mixtures of PEG and PMMA samples, respectively. The high mass-to-charge ratio regions of the spectra are expanded and it may be observed that PEG E has a bimodal distribution. This was confirmed by analysis of this sample as a single component. Furthermore, doubly charged ion peaks ($[M + 2Na]^{2+}$) were observed for the PEG oligomers of higher molecular weight that contributed to the signal in the region of m/z 10,000. Doubly charged ion peaks were not observed in the spectra of the mixtures of poly(styrene)s and poly(methyl methacrylate)s.

The mass range covered by these samples covers the range 1–30 ku. Although each of the components is a polymer with a narrow dispersion, together they cover a significant mass range. The instrument was set up by optimizing the response for the heaviest component present and then checking that the lowest mass

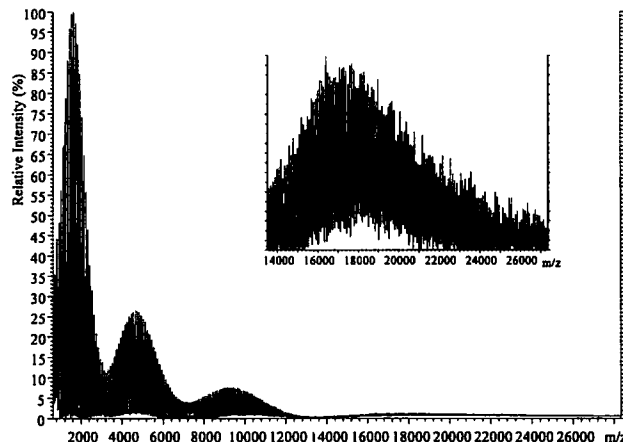


Figure 7. UV-MALDI spectrum of an equimass mixture of poly(methyl methacrylate)s A, B, C, and D (high mass-to-charge ratio expanded) obtained with time-lag focusing (TofSpec E instrument).

component was observed under the same conditions. The mass spectrum of the mixture was then acquired. The relative intensities of the M_m values for each of the separate components is in reasonable agreement with what would be calculated from the relative number of molecules present for mixtures of poly(styrene), PEG, and PMMA. These data show that, for a restricted number of components covering a reasonable mass range, MALDI-MS gives good qualitative and quantitative results. This shows, among other things, that the mass dependence of the detector [11], when using time-lag focusing, does not pose a significant practical difficulty over this mass range. The sample preparation for these concentrations allows the relative number of molecules at the M_m to be determined. The fact that the data are similar for three quite chemically different polymers with different cation interactions indicates that these variables are not, in themselves, causing difficulties with these sample systems.

It was noticed that spectra representative of the analyte were not generated when an equimolar mixture of the same samples was analyzed by means of time-lag focusing MALDI-MS. Ion peaks of lower mass-to-charge ratio were observed at higher signal-to-noise ratios than expected. The expected mass envelope, however, was seen in spectra of an equimolar mixture of poly(styrene) standards over a narrower mass-to-charge ratio range [33]. It has previously been shown that the data generated by means of MALDI-MS give M_p values that are lower than that observed by gel permeation chromatography (GPC) [30]. This is, in part, a consequence of the method of displaying the data and the increased sensitivity of the detector used for GPC at higher mass. There are a number of possible sources for the problems in analyzing polymer samples of high polydispersity directly. These could include sample preparation issues, source design aspects, and detector performance. Representative results may be obtained, however, for samples of high polydispersity by combining GPC with MALDI-MS [26-28].

Conclusions

It has been shown that MALDI-MS data from synthetic polymers are not always representative of the sample if the cation is varied. This is highlighted by the spectra from PET A and PET B when the cation was changed from Li^+ to Cs^+ .

The observed distributions in time-lag focusing MALDI-MS spectra of equimass mixtures of poly(styrene), poly(ethylene glycol), and poly(methyl methacrylate) standards are very similar to those expected. These data indicate that for the analysis of synthetic polymers by means of MALDI-MS the dynamic range is increased when time-lag focusing is used instead of prompt extraction. The spectra obtained from equimolar mixtures of the same polymers, however, were not representative of the sample. This is

a phenomenon that has been seen by other workers for polymers with broad distributions [24-30].

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