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Characterisation of synthetic polymer systems

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Abstract

Mass spectrometry has been used in the study of synthetic polymer systems since the 1960s. The application has been, for the most part, limited to the characterisation of polymer additive systems and polymers that had either been chemically or thermally degraded. The advent of newer ionisation approaches, coupled with the development of analyser technology, has led to the reappraisal of mass spectrometry for this work. Molecular weight distributions have been obtained and information on end groups and chemical variation with molecular weight has been measured. Polymer microstructure has been probed with information obtained on partial and, in some cases, complete sequence for oligomeric systems. Fundamental work to support these developments is needed and is being carried out. Information on gas-phase polymer conformations has been obtained and an important link with calculation established. The future of the approach, particularly when used in conjunction with other complimentary chromatographic and spectroscopic techniques, looks promising. (Int J Mass Spectrom 200 (2000) 261–276)

Keywords: Review; Synthetic polymer; Mass spectrometry

1. Introduction

The introduction of matrix-assisted laser desorption/ionisation (MALDI) [1,2] and electrospray ionisation (ESI) [3], coupled with the use of time-of-flight (TOF) and Fourier transform ion cyclotron resonance (FTICR) analysers has revolutionised the utility of mass spectrometry. This increased capability has mainly been focussed in the biosciences where the greatly increased mass range, sensitivity and resolution has made mass spectrometry an integral part of many important research areas. The field of polymer science did not appreciate the importance of these developments until recently and is only now starting to take advantage of the information that can be obtained. There is still significant work to do to fully exploit these new opportunities, but exciting results have already been obtained, and the future potential is significant. Here, we will highlight the measurement challenge, show the progress already made and speculate on potential future developments.

Synthetic polymers form an integral part of everyday life. They range from high-volume commodity products such as polypropylene and polyethylene, the ubiquitous polyesters such as nylon and poly(ethylene terephthalate) (PET) to low tonnage, specialty products such as poly(ether ether ketone) (PEEK) and carbon fibre reinforced resins. In addition to these well known, established, systems, however, there are thousands of specialised products, which are specially

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synthesised for a particular task. These range from electronic applications (such as circuit board adhesives) to medical areas (such as drug release and tissue replacement). These systems tend to be more chemically complex and would benefit most from generation of additional structural information.

Synthetic polymers, unlike naturally occurring biopolymers (which are predominately monodisperse), are mixtures with a distribution of molecular size, molecular structure and shape. The details of these distributions taken together with the chemical and physical history of the material and any additives present determine the properties of the polymer. Paul Flory expressed this concept, together with many other important ideas, in 1953 [4]. He stated that "Polymers are composed of covalent structures many times greater in extent than those occurring in simple compounds and this feature alone accounts for the characteristic properties that set them apart from other forms of matter. Appropriate means need to be used to elucidate their macromolecular structure and relationships established to express the dependence of the physical and chemical properties on the structures so evaluated." It is the use of mass spectrometry to study the macromolecular structures of synthetic polymers that we are concerned with here. A number of reviews of the use of mass spectrometry in polymer studies have been written [5–9]. These focus, in general, on the applications prior to recent advances.

2. Polymer formulations

In addition to the synthetic polymer itself, which consists of hundreds of separate molecules (even for the simplest system), a polymer formulation contains many additional components. These range from components that reflect the synthetic and processing history of the system, such as catalyst residues, partially reacted monomers and oligomers and residual solvents, to components deliberately added to enhance the required properties of the system. Table 1 shows a list of some of the common additive types used.

A wide variety of chemical types, some of them complex mixtures, may be utilised within each of these classes at concentrations ranging from PPM to percent levels. One of the major contributions of mass spectrometry in polymer science has been the characterisation and quantification of these additives [10–12]. Application of the newer ionisation techniques and analysers has led to improvements in the information that can obtained about additive systems [13-16] but most work is still based on chemical extraction, chromatographic separation and mass spectrometric detection.

Table 1
Classes of polymer additives

Antiblocking agents	Antifoaming agents
Radiation stabilisers	Heat stabilisers
Antifogging agents	Antimicrobial agents
Antioxidants	Antistatic agents
Blowing agents	Colouring agents
Coupling agents	Curing agents
Fillers	Flame retardants
Foaming agents	Impact modifiers
Low profile materials	Lubricants
Mold release agents	Odorants/fragrances
Plasticizers	Preservatives
Reinforcements	Slip agents
Flow enhancers	Thickening agents

3. Indirect measurements

The majority of mass spectrometric studies of polymer systems required optional extraction of the additives from the polymer followed by a chemical [17] or thermal degradation of the polymer itself, prior to the recent innovations in instrumentation.

Thermal studies encompass:

1. Evolved gas analysis (EGA) [18], where the polymer is melted releasing trapped volatiles, which are then characterised.
2. Thermal degradation [19], in which the onset of decomposition of the polymer system under various conditions is studied.
3. Pyrolysis [20,21], where the polymer system itself is extensively degraded to give structural information.

These studies have supplied much important information

but are, by necessity, indirect measurements. Structural information must be inferred from the results.

4. Direct measurements

4.1. Field desorption

For many years the only ionisation method capable of generating data directly from synthetic polymers was field desorption (FD) [22]. This approach, coupled with magnetic sector analysers, was shown to give useful data, particularly for nonpolar systems, from polymers with average molecular weights of up to approximately 15 kDa [23,24]. The field desorption experiment is challenging, with experimental times of 1–2 h not uncommon. Difficulties with thermally labile polymers have been experienced when thermal degradation occurs before desorption. This approach still has much to recommend it for nonpolar systems of low molecular weight [25]. The advent of new instruments that couple field ionisation and field desorption with TOF analysers may lead to an increase of interest in this method.

4.2. Matrix-assisted laser desorption/ionisation (MALDI)

MALDI requires co-crystallisation of sample and matrix molecules. Although this is relatively straightforward in protein and peptide studies, the nature of synthetic polymer systems makes it difficult to achieve the correct balance of solvent, salt, matrix and sample. Different sample preparations are often needed, in practice, for different polymer types and indeed for different molecular weight ranges within a polymer type. MALDI-TOF has great advantages for the characterisation of polymer systems, because the spectra obtained are often simple. The spectra consist predominately of peaks from cationised, singly charged molecule ions with little, if any fragmentation. It has been shown that MALDI gives good agreement with polymer standards with a polydispersity {weight average molecular weight (M_w) divided by number average molecular weight (M_n)} [26] of approximately less than 1.2 [27]. Poor agreement with standards of known value is obtained for broader distributions. A number of suggestions have been made to explain this difficulty. The main issues are shown in Table 2 [28–44].

Table 2
Some issues in the use of MALDI to characterise synthetic polymers

Source parameters	Laserpower[28–33]
Detector design [32,34–39]	Cation (Type, concentration, physical position [40–42]
Postacceleration value	Sample preparation [43]
Data processing/acquisition settings [44]	Solvent/matrix/sample (Type, ratios) [9]
Dynamic range limitations	Delayed extraction parameters
Laser wavelength	Analyser performance [36]

Each of these factors has been shown to contribute to the measured molecular weight distribution in certain cases. There appears to be no single parameter that will solve the problem at the current time, and MALDI is limited, for quantitative use, to the study of low-polydispersity systems. The combination of wide mass range (typically 500–500,000 Da), high dynamic range requirement (0.01–100%) and a large number of components present in a system of broad polydispersity has been too great an experimental challenge. This has not been a major limitation since fractionation of a broad polydispersity polymer system into a number of low polydispersity fractions is an established procedure [45].

Figure 1 shows a MALDI-TOF spectrum of a narrow polydispersity polystyrene sample with M_n approximately equal to 12,500. Also shown is a FD spectrum of a similar polystyrene polymer. The MALDI spectrum consists of peaks from silver attachment ions, and the FD spectrum consists of peaks from radical cations. The similarity of these two spectra, generated using different ionisation methods, different analyser systems and different detection systems, gives confidence in the utility of the approach. The FD spectrum takes 1–2 h of careful experimentation to obtain, in contrast to the 1–2 min for the MALDI data. Early MALDI spectra were obtained on instruments with a resolution of only a few hundred, but developments in analyser and source design, particularly the introduction of delayed ex-

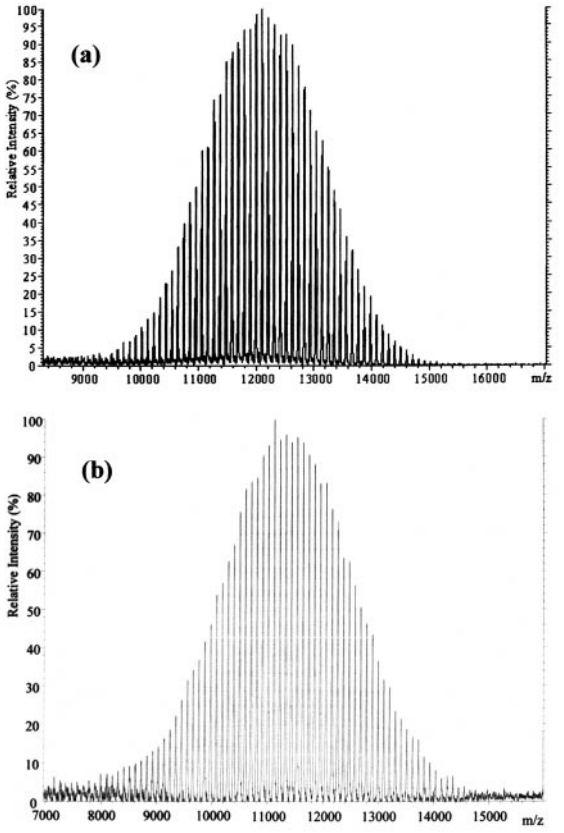


Fig. 1. (a) FD-MS and (b) MALDI-TOF spectra of a narrow polydispersity poly(styrene) sample with an average molecular weight of approximately 12.5 kDa.

traction methods [46,47], has led to resolutions (FWHH) of 10,000 to 20,000. Data from narrow distribution polymers, with average molecular weights of up to 1.5 million Da, have been obtained, although, at this mass range, no structural information can be determined [48]. The improved instrument performance has also led to better mass measurement accuracy. Early spectra were within a mass accuracy of 1 Da, at best, whereas now figures of 10–20 PPM are common. These measurements enable indirect information regarding total end-group mass to be inferred from the MALDI spectrum [49–52]. The mass of the cation, together with an integral number of monomer masses, is subtracted for a particular oligomer. The residual mass corresponds to the sum of the masses from the two end groups of the polymer.

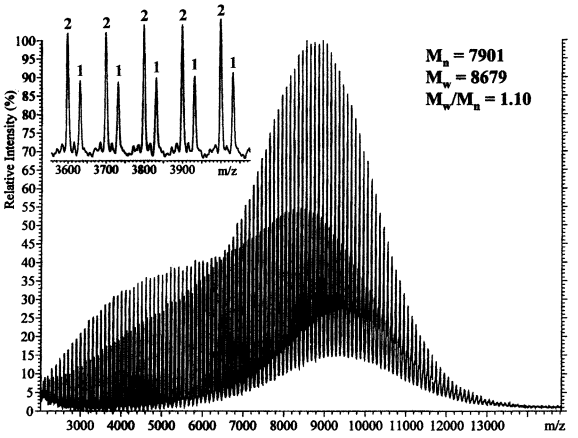
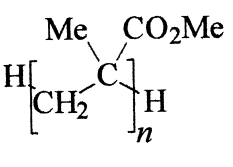


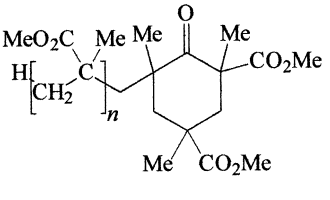
Fig. 2. MALDI-TOF spectrum of a poly(methyl methacrylate) (PMMA) sample [that was generated by means of group transfer polymerisation (GTP)], indicating that species with two modes of termination are present.

Fig. 2 shows a MALDI-TOF spectrum of a low-polydispersity poly(methyl methacrylate) with two main, differing, terminating end groups. These correspond to a conventional terminating group and a cyclic group formed via a backbiting mechanism. The MALDI spectrum enables the concentration of these end groups to be correlated with increasing molecular weight. This is an important measurement and difficult to carry out by other methods.

MALDI-TOF has also been used successfully in the study of copolymer systems [53–56]. The number of peaks observed generally increases dramatically for spectra from copolymers, and, at higher masses, specific oligomeric information may be lost from overlap. The copolymer composition can be measured against molecular weight where the oligomers can be identified. Figure 3 shows an example of a MALDI-TOF spectrum from a block copolymer system of methyl methacrylate and butyl methacrylate. The



Scheme 1.



Scheme 2.

spectrum is complex, but the resolution is good enough to enable each of the oligomeric peaks to be identified without confusion. This enables the distribution of methyl methacrylate units and butyl methacrylate units in the copolymer to be established. These distributions are shown in Figure 4. Important assumptions can then be made in polymer chemistry, such as the random coupling hypothesis, and be directly verified for the first time [54]. These MALDI spectra of copolymers can also be used to compare the distributions obtained with those predicted from polymer theory. This link between experimental measurement and theoretical prediction is an area in which MALDI has made an important contribution. Developments are required in processing software to analyse the raw MALDI data and make these measurements easier to interpret.

4.3 Electrospray ionisation (ESI)

Although ESI has had a major impact in the characterisation of biopolymers, its use in the study of synthetic polymers has been more restricted. This is largely due to the formation of multiply charged species. This phenomenon has been a major advantage with monodisperse proteins, enabling analyser systems with relatively low molecular weight ranges to be employed. Synthetic polymers, as we have seen, are very much more complex, and multiple charging can lead to spectra that are very difficult to interpret. The use of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry coupled with ESI has proven of significant utility. The very high resolution afforded by the FTICR enables the complex charge states to be unambiguously assigned and the spectra deconvoluted. ESI-FTICR approaches have been used to study molecular weight distribution [57,58], end groups [52,59,60] and chemical composition [58,61–63]. An alternative approach is to couple ESI with an orthogonal TOF (oa-TOF) analyser [64] and attempt to study the singly charged species at a higher mass-to-charge ratio. This can give interesting results for systems in which there is no significant overlap between the various charge states and for which singly charged species can readily be formed. Figure 5 shows ESI-oa-TOF spectra (LCT, Micromass UK

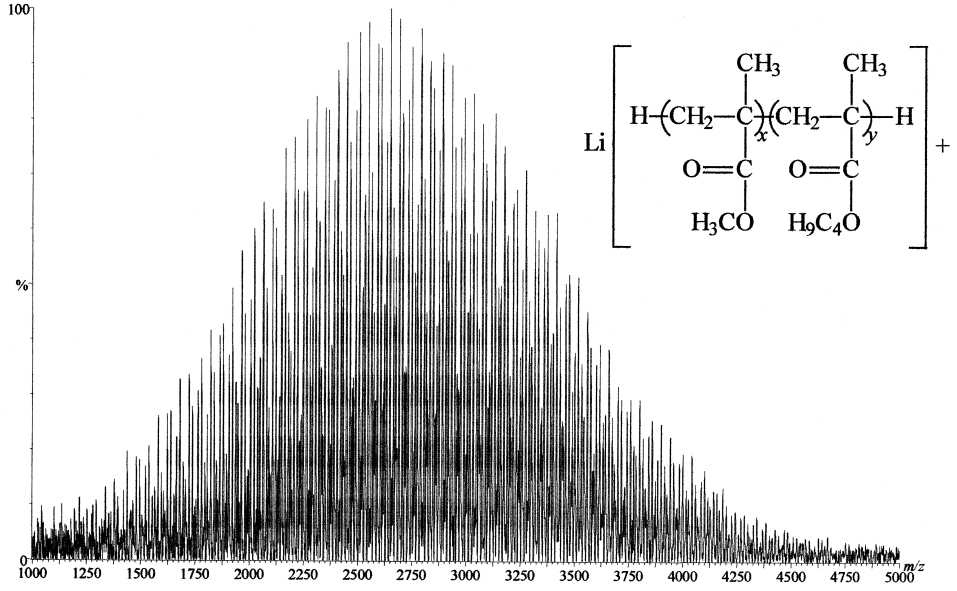
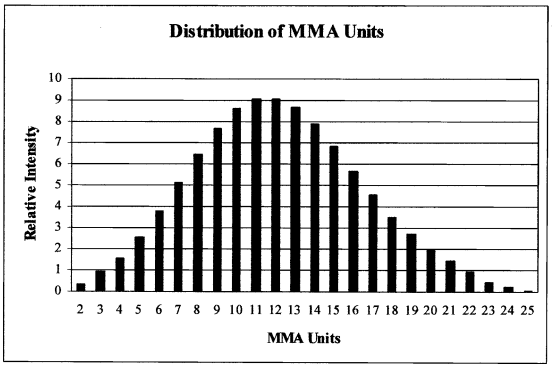


Fig. 3. MALDI-TOF spectrum of a block methyl methacrylate/butyl methacrylate (MMA/BMA) copolymer that was generated by means of group transfer polymerisation (GTP).



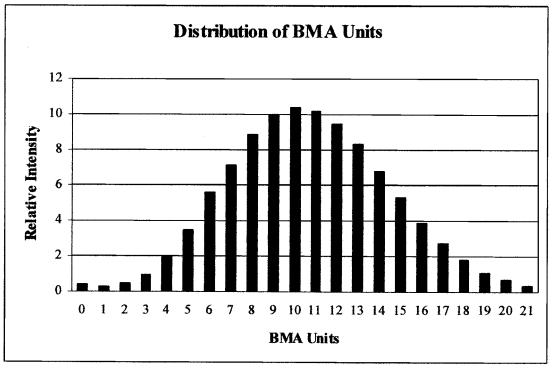


Fig. 4. Number distributions of methyl methacrylate (MMA) and butyl methacrylate (BMA), calculated from the MALDI-TOF data from a block MMA/BMA copolymer (MALDI-TOF spectrum shown in Fig. 3).

Ltd.) of polystyrene with a M_n (gel permeation chromatography, GPC) of 9850. Various cation salts have been used and the doping cation in each spectrum is shown. These distributions give results that are in reasonable agreement with expectations, and the approach has promise for some applications, particularly for qualitative studies. Figure 6 shows a comparison of ESI-oa-TOF and MALDI data for polystyrene of M_n 7000. The cation for both ESI and MALDI was silver. Both the singly (6300) and doubly charged (6310) distributions from the ESI spectra give M_n data that are lower than that obtained from MALDI-TOF (6670), although further work to optimise sample preparation (including cation type and concentration) may improve this agreement. In a recent interesting development, MALDI has been used to characterise polymer systems that have been subjected to partial thermal degradation. This is used to study the mechanisms of thermal degradation, but can also provide useful structural information about the polymer systems which could not be obtained directly [65–67].

5. Chromatographic links

As we have seen, MALDI has difficulty in obtaining quantitative data for polymers with polydispersity values of greater than approximately 1.2. ESI can give complex spectra that require specialised analysers and software to deconvolute the data obtained. A solution to these problems could potentially be reached by performing prefractionation of the polymer system using an appropriate chromatographic approach. MALDI has been linked with capillary electrophoresis (CE) and liquid chromatography (LC) although most results are in the biosciences [68]. ESI is routinely linked with both CE and LC. The most appropriate chromatographic technique for synthetic polymers is undoubtedly size exclusion chromatography (SEC) [also named gel permeation chromatography (GPC)]. In this technique, which was first applied to synthetic polymers in the 1960s, a dilute solution of polymer is passed through a column packed with a rigid gel with a range of pores whose sizes are comparable with the dimensions of the molecules. Small molecules penetrate the gel and are retarded relative to larger ones, which elute first. True quantitative GPC requires no chemical interaction between polymer and gel surface. The relationship between elution volume and molecular weight can be expressed as a calibration curve. Calibration is performed by using standards of a similar chemical nature to the synthetic polymer being studied or by using a universal calibration which plots log ($[\eta]$ M) versus elution volume (where η is the limiting viscosity number and M the molecular weight). Efforts have been made in GPC to overcome calibration difficulties by using two detectors simultaneously, one sensitive to the concentration of the polymer and independent of molecular weight and one measuring molecular weight independent of concentration. Laser

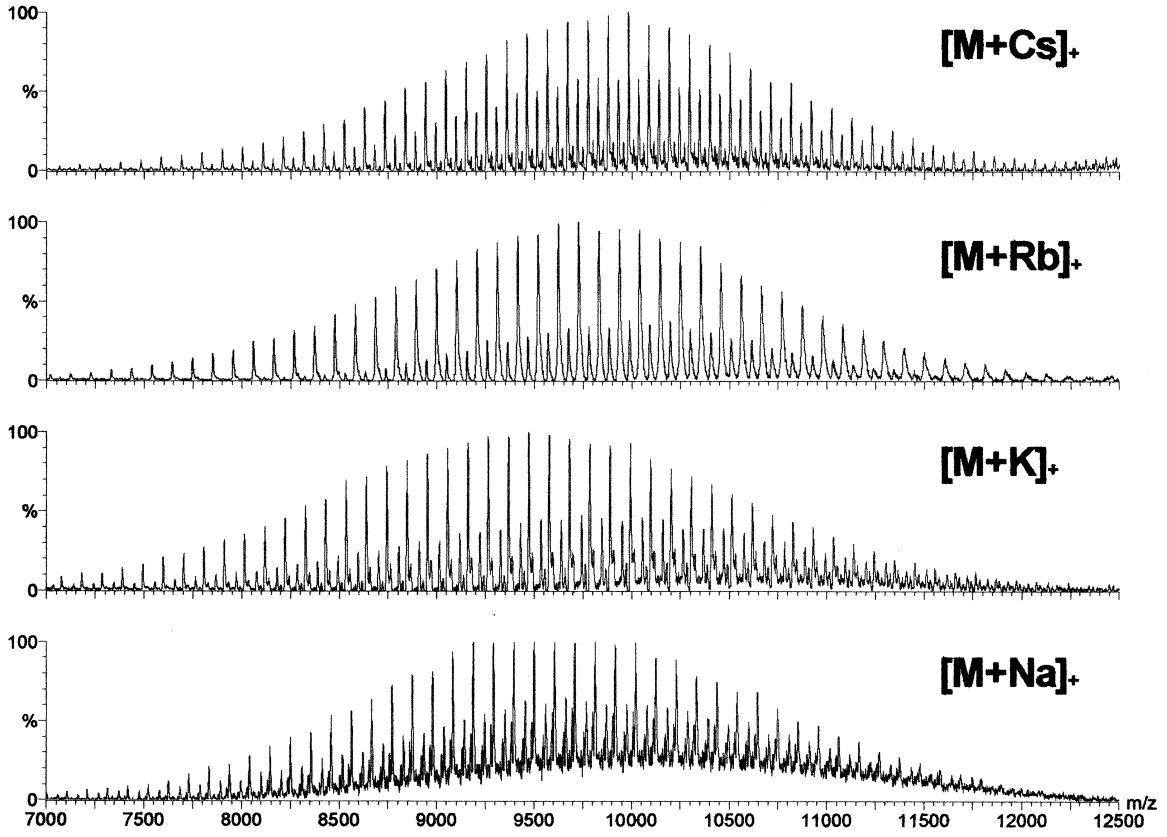


Fig. 5. Electrospray spectra obtained in an orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer from poly(styrene) 9850, using alkali metal cations for ionisation.

light scattering (LLS) and on-line viscometry are commonly used, often in combination with differential refractive index detection (termed triple detection) [69]. GPC has become the dominant method for the characterisation of molecular weight distributions in synthetic polymers. It is the only simple method that gives molecular weight distributions as well as averages for polymers of broad polydispersity. It has evolved into a very sophisticated method. GPC requires excellent flow stability and a combination of sophisticated detectors to achieve its full potential. It can have difficulty with copolymer systems where there is no simple relationship between viscosity and molecular weight. It can (in skilled hands), however, give information on polymer branching and can detect small amounts of high molecular weight polymer. Attempts have been made, in recent years, to extend the compositional information obtained from GPC by using composition-sensitive detectors such as IR or UV [70]. Furthermore, the link between GPC and MALDI is a particularly attractive proposition.

Early comparisons between GPC and MALDI results were confused by the different way that data are displayed [71]. MALDI plots number fraction against molecular weight, whereas GPC generates information that is usually displayed as weight fraction against log mass. The most probable values shown by each method (such as M_p for GPC) would therefore be expected to be different. GPC can be used as a method to prepare polymer samples of narrow polydispersity from a polymer of wider polydispersity. MALDI can then provide an effective method of mea-

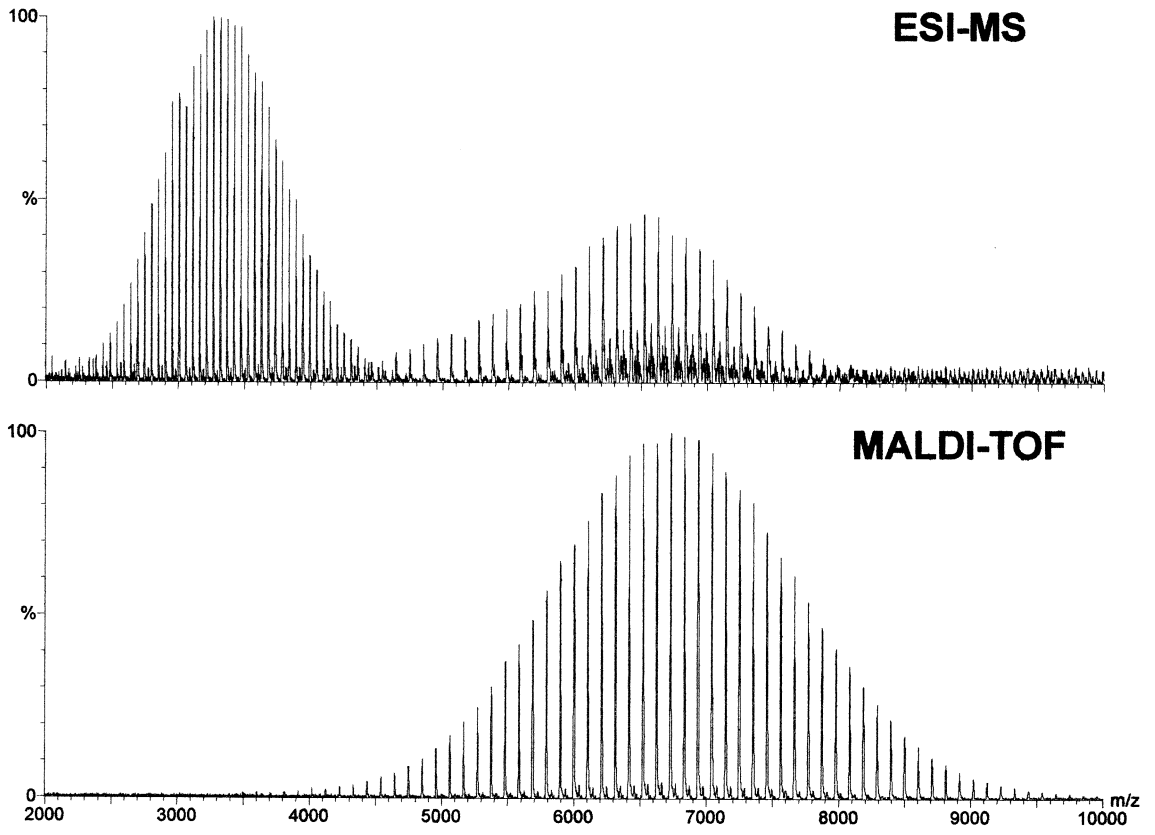


Fig. 6. Electrospray (obtained in an oa-TOF mass spectrometer) and MALDI-TOF spectra obtained from poly(styrene) 7000, using silver ions as the cationisation agent.

suring molecular weight, and these values can be used to generate reference points on the GPC calibration graph [log (*M*) versus elution volume]. This is an effective symbiotic relationship with MALDI providing calibration data for GPC and GPC overcoming the difficulties that MALDI experiences with high polydipersity. This approach has been elegantly demonstrated in a number of recent papers [72–77]. These off-line methods, although successful, are time consuming and effort has gone into automating the process [45,78,79]. The future development of this area should lead to a wider use of MALDI among polymer chemists.

ESI, after GPC separation, has also been used in combination with FTICR [80,81] or oa-TOF detectors [82]. ESI has the advantage that on-line coupling is straightforward, but the presence of multiple charged peaks can make the data difficult to use for calibration purposes.

6. Polymer microstructure

A complete understanding of polymer structure needs to include the following:

- Atomic connectivity.
- Stereochemistry of subunits.
  - Individually.
  - With respect to each other.
  - With respect to other units.

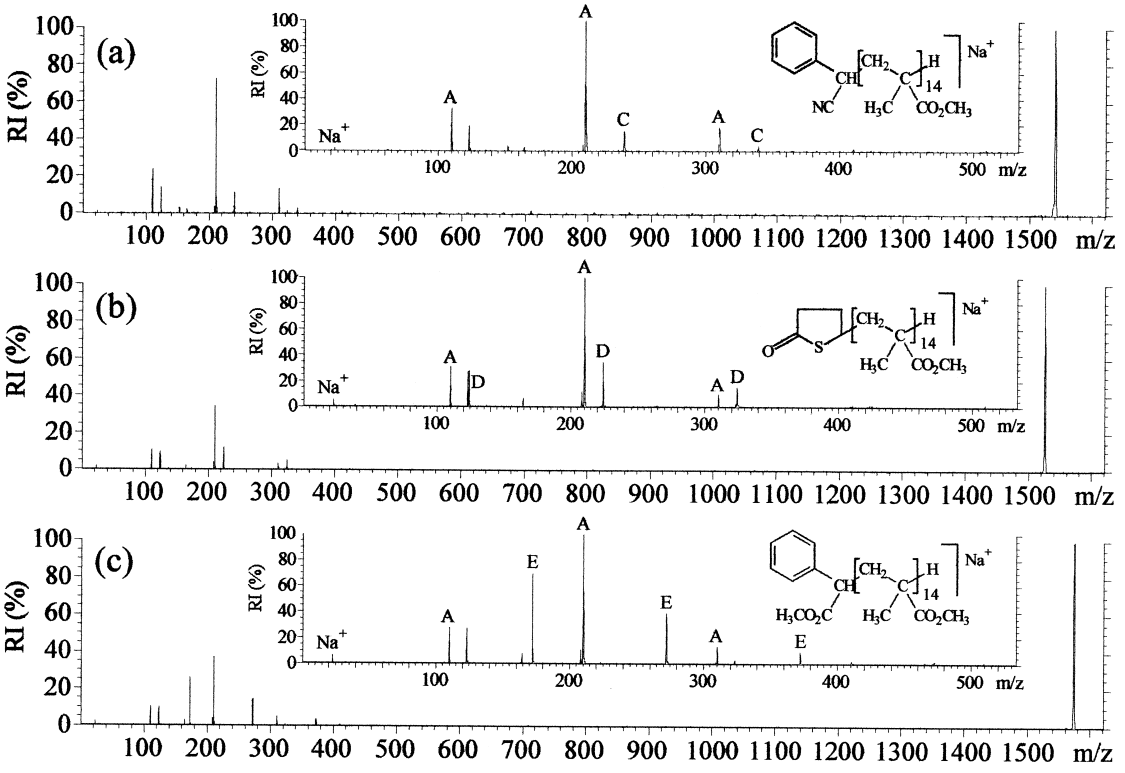


Fig. 7. MALDI-CID spectra from PMMA samples with different initiating end groups (see text for description of fragmentation), obtained in a hybrid sector-oa-TOF mass spectrometer. The A, C, D and E series of peaks allow information on the masses of the end groups to be inferred.

- Sequences and distributions of subunits.
- Distribution, configuration and arrangement of chain lengths.
  - Within one chain.
  - With respect to other chains.
- Arrangement of different domains of the material.
  - With respect to each other.
  - With respect to other components of the material.

This is clearly a large and multidimensional problem, which cannot be studied by one technique alone. A subset of these issues, which involves aspects of the molecular structure of linear chain polymers, is often referred to as polymer microstructure. Mass spectrometry has been shown to be able to contribute significantly to this area. The ability of mass spectrometry to select an ion of known mass-to-charge ratio, coupled with the fact that the MALDI spectra of synthetic polymers show little fragmentation, enable single oligomers to be selected for further study. Fragments from a selected oligomeric cationised species can be formed in three ways in a conventional MALDI-TOF instrument:

Fragmentation can occur in the ion-source region at high laser fluences. This is referred to as prompt fragmentation.

Fast metastable fragmentation can occur during the delay time before extraction (100–1200 ns) in delayed extraction sources. This is termed in-source decay [83]. In-source decay increases with laser energy, at a fixed delay time, due to a greater number of collisions in the expanding plume. Prompt and in-source decay fragmentation yield fragment ions in the mass spectra obtained from both the linear and reflectron detector.

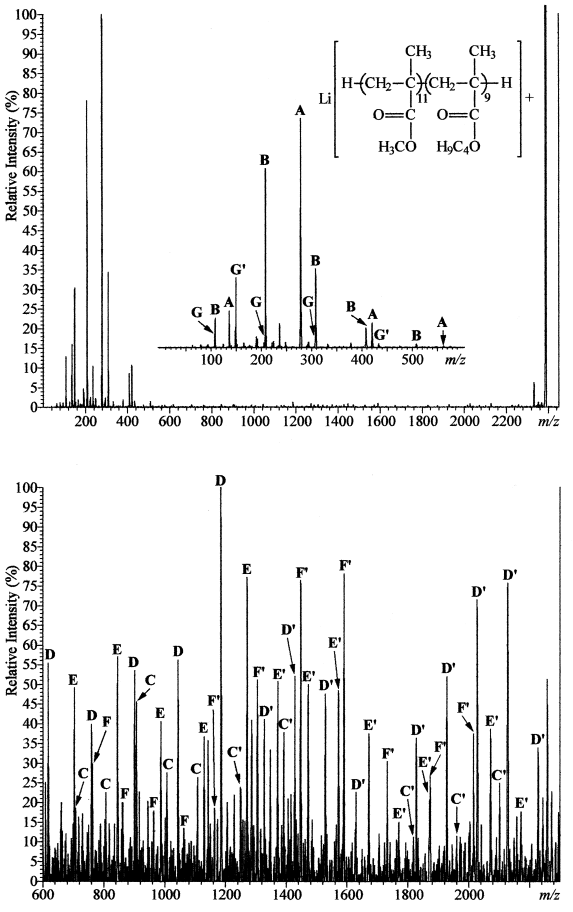


Fig. 8. MALDI-CID spectrum of a block methyl methacrylate/butyl methacrylate (MMA/BMA) copolymer that was generated by means of group transfer polymerisation (GTP), obtained in a hybrid sector-oa-TOF mass spectrometer. Full spectrum (top) with expansion of *m/z* 0–600 and partial spectrum (bottom) of *m/z* 600–2300. A description of the fragmentation is in the text.

Metastable fragmentation can occur in the field-free region (post source decay, PSD). This occurs on the 10 μs time scale and yields ions in the mass spectrum obtained from the reflectron detector only. A PSD product ion spectrum can be obtained with a precursor ion selector in the field-free region and by scanning the reflectron voltage [9]. A collision cell can be placed in the field-free region, giving access to high-energy PSD collision-induced dissociation (CID) spectra.

These methods have been used successfully in peptide characterisation but have not been used extensively for synthetic polymers, possibly because of the increased complexity of the mixtures involved coupled with the experimental challenges of the experiments.

Product ion spectra, from selected ions generated by MALDI, may be obtained by using tandem mass spectrometry (MS/MS) instrumentation. A coupled magnetic sector-oa-TOF combination has been used successfully to study a number of polymer systems [84–88]. High-energy CID at 800 eV using xenon as a target gas is employed. Figure 7 shows the results obtained for a series of poly(methyl methacrylate) (PMMA) oligomers made with different initiators. The fragment series labelled *A* in each spectrum originates from the terminal end of the molecule, with retention of cation, and the series labelled *C*, *D* and *E* originate from the initiator end of the molecule, again with retention of cation. The features seen in these data, such as fragmentation observable from both ends of the molecule with retention of cation and peaks at lower mass-to-charge ratios being the most intense, are common for a number of polymer systems. The product ion spectra from the MALDI precursors, obtained by this approach, show a number of advantages over data obtained using a MALDI-TOF instrument alone. These include improved precursor and product ion resolution, better signal-to-noise ratio and greatly improved reproducibility. The results obtained from these experiments enable, in many cases, the individual masses of the end groups of the polymer systems to be obtained.

This approach has been recently applied to a block copolymer system of methyl methacrylate (MMA) and butylmethacrylate (BMA). The MALDI-TOF spectrum is shown in Figure 3. Figure 8 shows the MALDI-CID spectrum of the selected cationised oligomer with *m/z* 2387. This spectrum enables the masses of the initiating and terminating ends of the polymer to be established, as we have already seen from data obtained from homopolymers. The less intense peaks in the higher *m/z* region (*m/z* 600–2200) can also be interpreted. These peaks correspond mainly to rearrangements that can be assigned to both sides of the polymer chain. The complete sequence of the block copolymer chain

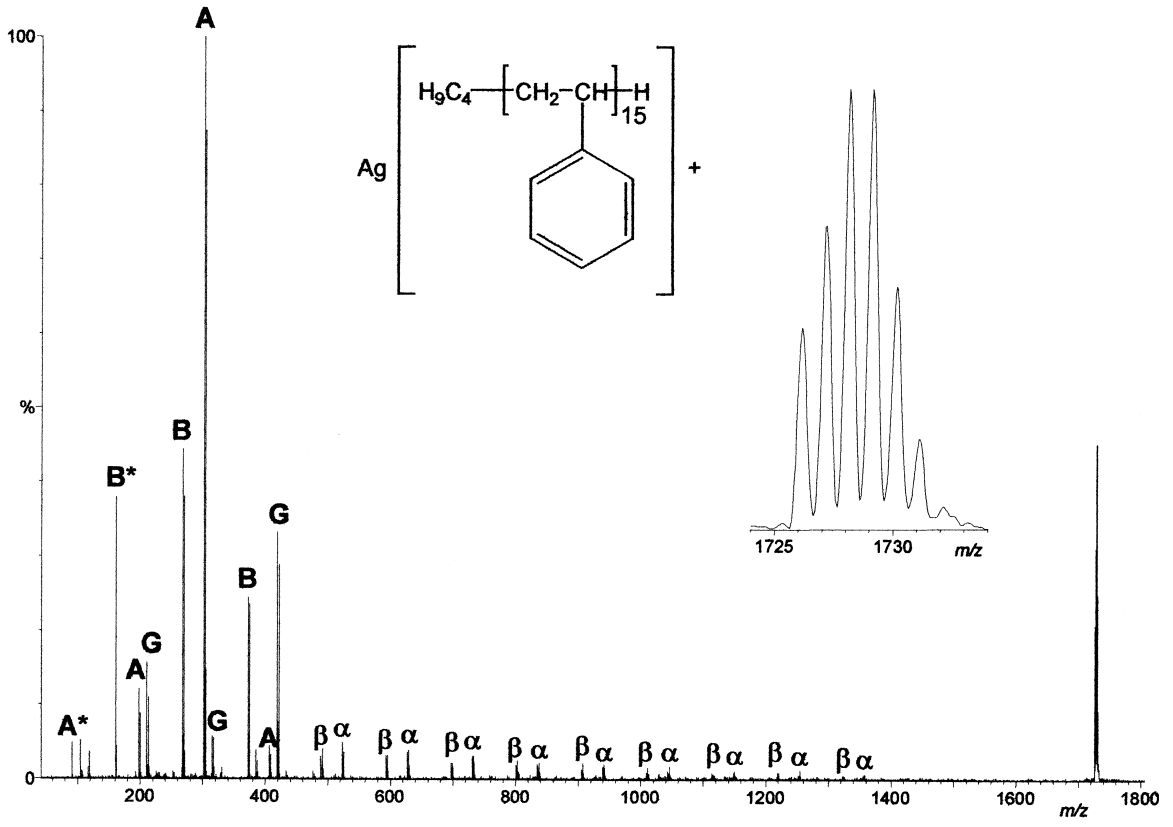


Fig. 9. MALDI-CID spectrum of the 15-mer of a poly(styrene standard), obtained in a hybrid quadrupole-oa-TOF mass spectrometer. The fragmentation pattern (namely the A and B series) enables end group information to be inferred.

can be confirmed in this case. This result, together with other MALDI-MS/MS studies of random and block copolymers, indicate that significant structural information can be obtained.

A barrier to the wider use of this approach has been the requirement for specialised instrumentation, which is not widely available. The combination of a quadrupole analyser with an orthogonal TOF has proven of great utility for structural studies in the biosciences [89–91]. The collision regime in this instrument is low energy, with multiple collision conditions being employed. Recently, this design of instrument has been fitted with a MALDI source [92,93]. Figure 9 shows the MALDI-CID product ion spectrum of the silver cationised 15-mer of polystyrene. This was obtained in a modified Q-TOF instrument (Micromass UK Ltd.). Although low-energy collision conditions were used for the CID experiment (150 eV with argon as collision gas), the spectrum shows significant similarities to that obtained at higher collision energies (800 eV with xenon as collision gas) using a magnetic-oa-TOF hybrid instrument. End-group information is readily deduced from the data. The wider availability of this type of instrumentation should result in many more MALDI-CID experiments being carried out on synthetic polymer systems.

This approach has also been used to study cation attachment in various polymer systems [94]. Figure 10 shows the product ion spectra of the MALDI produced cationised 30-mers of PMMA. The spectra

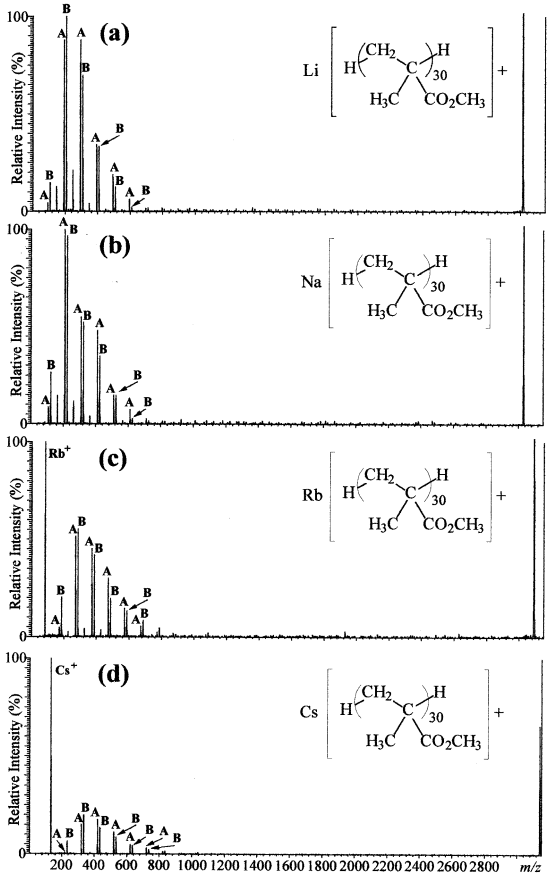


Fig. 10. MALDI-CID spectra of the 30-mer of poly(methyl methacrylate) (PMMA) with ionisation by addition of varying alkali metal salts, obtained in a hybrid sector-oa-TOF mass spectrometer. The A and B series of peaks allow information on the masses of the end groups to be inferred.

show that the lithium cationised species does not tend to fragment to form a lithium ion (Li^+) whereas the caesium cationised species readily leads to the generation of a caesium ion (Cs^+). This is related to the binding energy of the cation. The rest of the spectra are very similar with fragments formed from both initiation and terminating ends of the oligomer (with retention of cation). These, and other, studies lead to the suggestion that mass discrimination due to cation effects are more pronounced with low-molecular-weight rigid polymer systems such as poly(ethylene terephthalate) [40] and less important with higher molecular weight mobile polymer systems.

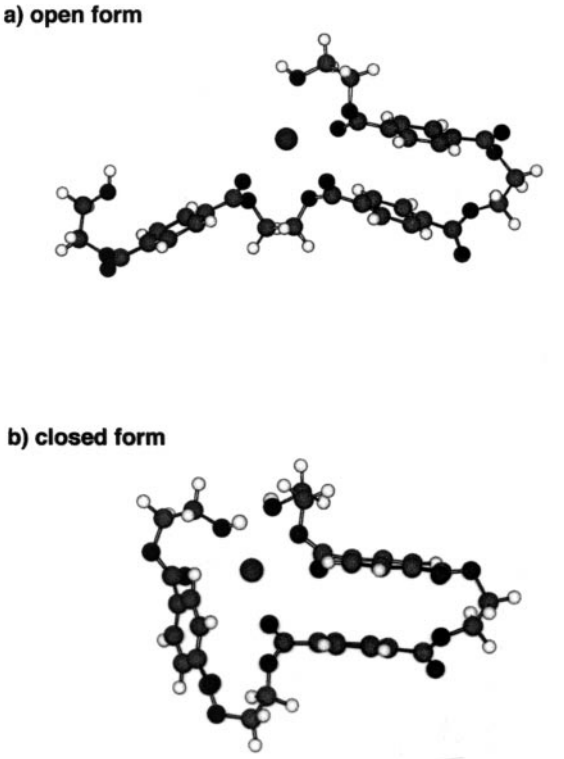


Fig. 11. Typical low-energy structures of the (a) open and (b) closed form of the sodiated trimer of poly(ethylene terephthalate) (PET).

7. Gas phase conformations of synthetic polymers

The ability of mass spectrometry to select an oligomeric cation of known mass-to-charge ratio has been shown in the MALDI-CID experiments. Recently work has been undertaken to better understand the interactions of various polymer systems with cations and to attempt to study the conformation of these ions in the gas phase [95–100]. The experimental technique used was the ion-mobility-based ion chromatography (IC) approach [101]. Ion chromatography is based on the principle that ions with different conformations will have different mobilities when drifting through a buffer gas under the influence of a weak electric field. Theoretical methods are then used to generate candidate structures of the ions and calculate their corresponding mobilities for compari-

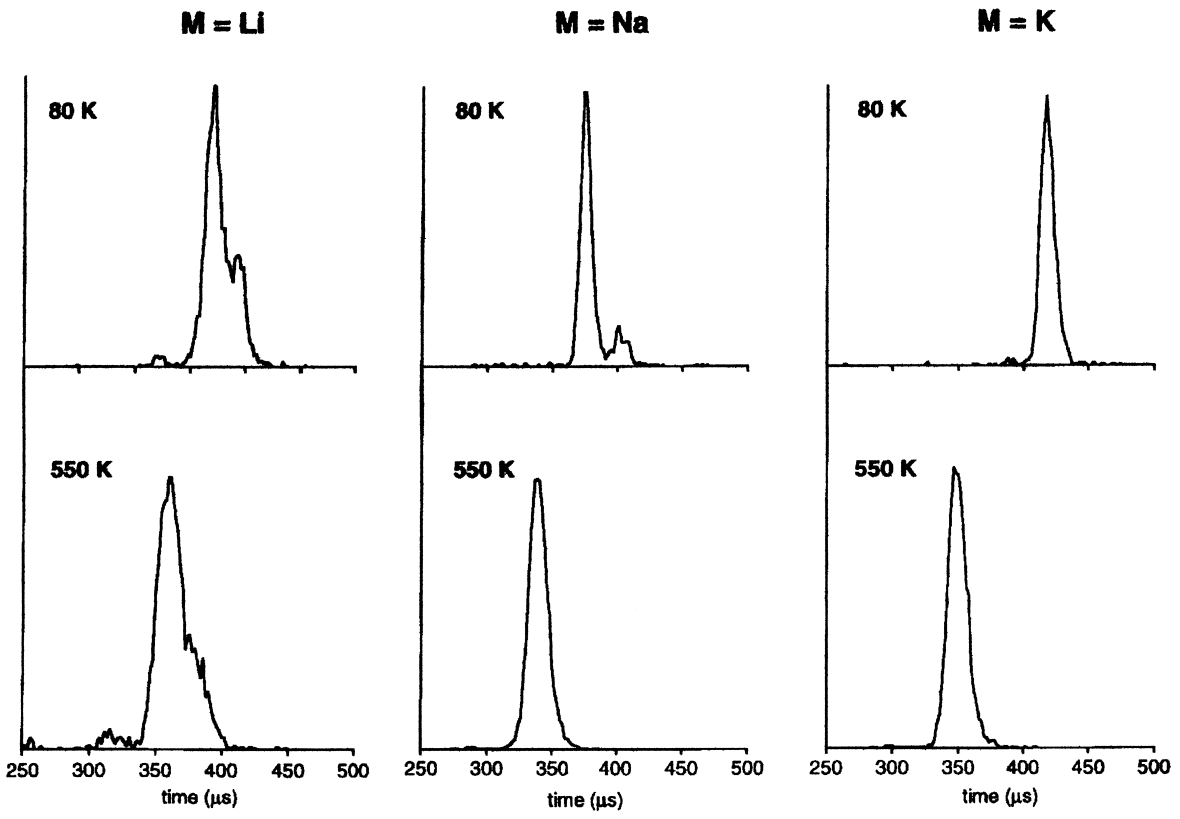


Fig. 12. Arrival time distributions for lithiated, sodiated and potassiated trimers of poly(ethylene terephthalate) (PET) at 80K and 550K.

son to experiment. Figure 11 shows the calculated typical low-energy structures of the sodium cationised trimer of poly(ethylene terephthalate). These are calculated to exist in closed and open forms. Figure 12 shows the arrival time distributions for the trimers, with different cations, at 80K and 550K. The two isomeric forms are in dynamic equilibrium at 550K, with a measured arrival time observed as an average between the open and closed forms. The isomerisation is frozen out at the lower temperature and two peaks are observed for lithiated and sodiated species, in good agreement with the calculated values for open and closed forms. For the potassium-cationised species, even at the lower temperature, only one peak is observed. This experimental result gives weight to the validity of the calculations employed. The approach has recently been extended to neutral species [95]. It is clear that, if mass spectrometry is to have a wider influence on the characterisation of synthetic polymer systems, then more fundamental work of this type is required to overcome some of the currently existing lack of understanding.

8. The future

The introduction of ionisation techniques such as ESI and MALDI and the continued development of analyser technology such as TOF and FTICR has had a major impact on the potential utility of mass spectrometry to characterise synthetic polymer systems. The analytical challenge presented by a commercial polymer formulation makes direct study difficult for all but the simplest systems. Considerable progress has been made, however, in the direct characterisation of low polydispersity systems and,

via links with chromatographic approaches such as GPC, systems of higher polydispersity. The nature of the end groups present may be inferred from the molecular masses or obtained more directly from ion selection methods such as MALDI-CID. Polymer microstructural issues such as block and random copolymer structure are beginning to be addressed, and fundamental work on cation attachment and polymer conformations is being undertaken. It is clear that this area of science is still developing and that the use of mass spectrometry to characterise polymer systems will increase. It is important to point out that mass spectrometry is only one tool and that the maximum benefit can be obtained by linking the results with those obtained from other spectroscopic and chromatographic methods.

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References

[1] M Karas, F. Hillenkamp, Anal. Chem. 60 (1988) 2299.
[2] K. Tanaka, H. Waki, Y. Ido, S Akita, Y. Yoshida, T. Yoshida. Rapid Commun. Mass Spectrom. 2 (1988) 151.
[3] J.B. Fenn, M. Mann, C.K. Meng, S.F. Wong, C.M. Whitehouse. Mass Spectrom. Rev. 9 (1990) 37.
[4] P.J. Flory. Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1953.
[5] H.R. Schulten, R.P. Lattimer. Mass Spec. Rev. 3 (1984) 231.
[6] G. Montaudo. Br. Polymer J. 18 (1986) 231.
[7] P. Vouros, J.N. Kyranos. J. Appl. Polymer Sci., Appl. Polymer Symp. 43 (1989) 211.
[8] J.H. Scrivens. Advances in Mass Spectrometry, Vol. 13, John Wiley, New York, 1995.
[9] M.W.F. Nielen. Mass Spec. Rev. 18 (1999) 309.
[10] R.P. Lattimer, R.E. Harris. Mass Spec. Rev. 4 (1985) 369.
[11] R.P. Lattimer. Rubber Chem. Technol. 63 (1988) 658.
[12] R.P. Lattimer, H. Muenster, H. Budzikiewicz. Rubber Chem. Technol. 63 (1990) 298.
[13] R.P. Lattimer, J. Anal. Appl. Pyrolysis 26 (1993) 65.
[14] A.T. Jackson, K.R. Jennings, J.H. Scrivens, Rapid Comm. Mass Spectrom. 10 (1996) 1449.
[15] A.T. Jackson, A. Buzy, K.R. Jennings, J.H. Scrivens. Eur. Mass Spectrom. 2 (1996) 115.
[16] A.T. Jackson, K.R. Jennings, J.H. Scrivens. Rapid Comm. Mass Spectrom. 10 (1996) 1459.
[17] G. Montaudo, E. Scamporrino, D. Vitalini. Macromolecules 22 (1989) 627.
[18] P.A. Barnes. Anal. Proc. (London) 27 (1990) 150.
[19] T.G. Blease, G.A. Paterson, J.H. Scrivens. Br. Polymer J. 21 (1989) 37.
[20] J.J. Boon. Int. J. Mass Spectrom. Ion Processes 118 (1992) 755.
[21] P.J. Gale, B.L. Bentz, W.L. Harrington, RCA Rev. 47 (1986) 380.
[22] L. Prokai. Field Desorption Sass Spectrometry, Vol. 9, Marcel Dekker, New York, 1990.
[23] K. Rollins, J.H. Scrivens, M.J. Taylor. Rapid Comm. Mass Spectrom. 4 (1990) 355.
[24] J.H. Scrivens, K. Rollins, Fundamentals of gas phase ion chemistry. K.R. Jennings (Ed.), Kluwer Academic, Dordrecht, The Netherlands 1991.
[25] J.H. Gross, S.M. Weidner. Eur. J. Mass Spectrom. 6 (2000) 11.
[26] C.E. Carraher, Jr. Polymer Chemistry, 4th ed., Marcel Dekker, New York, 1996.
[27] K. Martin, J. Spickermann, H.J. Raeder, K. Muellen. Rapid Comm. Mass Spectrom. 10 (1996) 1471.
[28] R.S. Lehrle, D.S. Sarson. Rapid Comm. Mass Spectrom. 9 (1995) 91.
[29] R.S. Lehrle, D.S. Sarson. Polymer Degradation and Stability 51 (1996) 197.
[30] P.M. Lloyd, K.G. Suddaby, J.E. Varney, E. Scrivener, P.J. Derrick, D.M. Haddleton. Eur. Mass Spectrom. 1 (1995) 293.
[31] N. Sakurada, T. Fukuo, R. Arakawa, K. Ute, K. Hatada. Rapid Comm. Mass Spectrom. 12 (1998) 1895.
[32] J. Axelsson, E. Scrivener, D.M. Haddleton, P.J. Derrick. Macromolecules 29 (1996) 8875.
[33] W.J. Feast, L.M. Hamilton, S. Rannard. Polymer Bulletin 39 (1997) 347.
[34] C.N. McEwen, C. Jackson, B.S. Larsen. Polym. Prepr. 17 (1996) 314.
[35] C.N. McEwen, C. Jackson, B.S. Larsen. Int. J. Mass Spectrom. Ion Processes 160 (1997) 387.
[36] D.C. Schriemer, L. Li. Anal. Chem. 69 (1997) 4176.
[37] H. Zhu, T. Yalcin, L. Li. J. Am. Soc. Mass Spectrom. 9 (1998) 275.
[38] B.S. Larsen, W.J. Simonsick, Jr., C.N. McEwen. J. Am. Soc. Mass Spectrom. 7 (1996) 287.

[39] E. Scamporrino, P. Maravigna, D. Vitalini, P. Mineo. Rapid Comm. Mass Spectrom. 12 (1998) 646.
[40] A.T. Jackson, H.T. Yates, W.A. McDonald, J.H. Scrivens, G. Critchley, J. Brown, M.J. Deery, K.R. Jennings, C. Brooks. J. Am. Soc. Mass Spectrom. 8 (1997) 132.
[41] H.Rashidzadeh, B. Guo, J. Am. Soc. Mass Spectrom. 9 (1998) 724.
[42] J.P. Barry, W.J. Carton, K.M. Pesci, R.T. Anselmo, D.R. Radtke, J.V. Evans. Rapid Comm. Mass Spectrom. 11 (1997) 437.
[43] D.C. Schriemer, L. Li. Anal Chem 69 (1997) 4169.
[44] G. Montaudo, E. Scamporrino, D. Vitalini, P. Mineo. Rapid Comm. Mass Spectrom. 10 (1996) 1551.
[45] M.W.F. Nielen, Anal. Chem. 70 (1998) 1563.
[46] R.S. Brown, J.J. Lennon. Anal. Chem. 67 (1995) 1998.
[47] W.S. Wiley, I.H. McLaren. Rev. Sci. Inst. 26 (1955) 1150.
[48] D.C. Schriemer, L. Li. Anal. Chem. 68 (1996) 2721.
[49] A.T. Jackson, H.T. Yates, C.I. Lindsay, Y. Didier, J.A. Segal, J.H. Scrivens, G. Critchley, J. Brown. Rapid Comm. Mass Spectrom. 11 (1997) 520.
[50] J.S. Cottrell, M. Koerner, R. Gerhards. Rapid Comm. Mass Spectrom. 9 (1995) 1562.
[51] G. Montaudo, M.S. Montaudo, C. Puglisi, F. Samperi, M. Sepulchre. Macromol. Chem. Phys. 197 (1996) 2615.
[52] C.G. de Koster, M.C. Duursma, G.H. van Rooij, R.M.A. Heeren, J.J. Boon. Rapid Comm. Mass Spectrom. 9 (1995) 957.
[53] J.T. Mehl, R. Murgasova, X. Dong, D.M. Hercules. Anal. Chem. 72 (2000) 2490.
[54] G. Wilczek-Vera, P.O. Danis, A. Eisenberg. Macromolecules 29 (1996) 4036.
[55] G. Wilczek-Vera, P.O. Danis, A. Eisenberg, Y. Yisong, K. Waddell. Rapid Comm. Mass Spectrom. 13 (19990 764.
[56] V. Francke, H.J. Rader, Y. Geerts, K. Mullen. Macromol. Rapid Comm. 19 (1998) 275.
[57] M. Dey, J.A. Castoro, C.L. Wilkins. Anal. Chem. 67 (1995) 1575.
[58] P.B. O'Connor, M.C. Duursma, J.J. Boon, R.M.A. Heeren, G.J. van Rooij. Anal. Chem. 69 (1997).
[59] S. Koster, M.C. Duursma, J.J. Boon, R.M.A. Heeren. J. Am. Soc. Mass Spectrom. 11 (2000) 536.
[60] C.G. de Koster, M.C. Duursma, G.J. van Rooij, R.M.A. Heeren, J.J. Boon. J. Am. Soc. Mass Spectrom. 7 (1996) 449.
[61] S.D-H. Shi, C.L. Hendrickson, A.G. Marshall, W.J. Simonsick, Jr., D.J. Aaserud. Anal. Chem. 70 (1998) 3220.
[62] E.R.E. van der Hage, M.C. Duursma, R.M.A. Heeren, J.J. Boon, M.W.F. Nielen, A.J.M. Weber, C.G. de Koster, N.K. de Vries. Macromolecules 30 (1997) 4302.
[63] G.J. van Rooij, M.C. Duursma, C.G. de Koster, R.M.A. Heeren, J.J. Boon, P.J.W. Schuyl, E.R.E. van der Hage. Anal. Chem. 70 (1998) 843.
[64] A.N. Verentchikov, W. Ens, K.G. Standing. Anal. Chem. 66 (1994) 126.
[65] C. Puglisi, F. Samperi, S. Carroccio, G. Montaudo. Polymer Preprints 41 (2000) 680.
[66] R.P. Lattimer, M.J. Polce, C. Wesdemiotis. J. Anal. Appl. Pyrolysis 48 (1998) 1.
[67] R.P. Lattimer. Polymer Preprints 41 (2000) 667.
[68] K.K. Murray. Mass Spectrom. Rev. 16 (1997) 283.
[69] P.J. Wyatt. Analytica Chemica Acta 272 (1993) 1.
[70] H.G. Barth, B.E. Boyes, C. Jackson. Anal. Chem. 70 (1998) 251R.
[71] C.Jackson, B. Larsen, C. McEwen. Anal. Chem. 68 (1996) 1303.
[72] M.W.F. Nielen, S. Malucha. Rapid Comm. Mass Spectrom. 11 (1997) 1194.
[73] G. Montaudo, M.S. Montaudo, C. Puglisi, F. Samperi. Rapid Comm. Mass Spectrom. 9 (1995) 1158.
[74] G. Montaudo, D. Garozzo, M.S. Montaudo, C. Puglisi, F. Samperi. Macromolecules 28 (1995) 7983.
[75] M.S. Montaudo, G. Montaudo, C. Puglisi, F. Samperi. Macromolecules 31 (1998) 3839.
[76] M.S. Montaudo, G. Montaudo, C. Puglisi, F. Samperi. Rapid Comm. Mass Spectrom. 12 (1998) 519.
[77] P.O. Danis, D.A. Saucy, F.J. Huby. Polymer Preparations 17 (1996) 311.
[78] T.I. Stevenson, J.A. Loo. LC-GC 16 (1998) 54.
[79] J. Dwyer, D. Botten. Am. Lab. (1996) 51.
[80] D.J. Aaserud, L. Prokai, W.J. Simonsick, Jr. Anal. Chem. 71 (1999) 4793.
[81] D.J. Aaserud, W. Zhong, W.J. Simonsick, Jr. Polymer Preprints 41 (2000) 657.
[82] M.F.W. Nielen, F.A. Buijtenhuijs. Anal. Chem. 71 (1999) 1809.
[83] I.A. Mowat, R.J. Donovan, R.R.J. Maier. Rapid Comm. Mass Spetrom. 11 (1997) 89.
[84] A.R. Bottrill, A.E. Giannakopulos, C. Waterson, D.M. Haddleton, K.S. Lee, P.J. Derrick. Anal. Chem. 71 (1999) 3637.
[85] A.T. Jackson, H.T. Yates, J.H. Scrivens, G. Critchley, J. Brown, M.R. Green, R.H. Bateman. Rapid Comm. Mass Spectrom. 10 (1996) 1668.
[86] A.T. Jackson, H.T. Yates, J.H. Scrivens, M.R. Green, R.H. Bateman. J. Am. Soc. Mass Spectrom. 8 (1997) 1206.
[87] A.T. Jackson, H.T. Yates, J.H. Scrivens, M.R. Green, R.H. Bateman. J. Am. Soc. Mass Spectrom. 9 (1998) 269.
[88] A.T. Jackson, A. Bunn, L.R. Hutchings, F.T. Kiff, R.W. Richards, J. Williams, G.R. Green, R.H. Bateman. Polymer 41 (2000) 7437.
[89] I.V. Chernushevich, W. Ens, K.G. Standing, Anal. Chem. 71 (1999) 452A.
[90] H.R. Morris, T. Paxton, A. Dell, J. Langhorne, M. Berg, R.S. Bordoli, J. Hoyes, R.H. Bateman. Rapid Comm. Mass Spetrom. 10 (1996) 889.
[91] A. Shevchenko, I. Chernushevich, W. Ens, K.G. Standing , B. Thompson, M. Wilm, M. Mann. Rapid Comm. Mass Spectrom. 11 (1997) 1015.
[92] A.N. Krutchinsky, A.V. Laboda, V.L. Spicer, W. Ens, K.G. Standing. Rapid Comm. Mass Spectrom. 12 (1998) 508.
[93] A.N. Krutchinsky, W. Zhang, B.T. Chait. J Am. Soc. Mass Spectrom. 11 (2000) 493.
[94] J.H. Scrivens, A.T. Jackson, H.T. Yates, M.R. Green, G. Critchley, J. Brown, R.H. Bateman, M.T. Bowers, J. Gidden. Int. J. Mass Spectrom. Ion Proc. 165/166 (1997) 363.
[95] J. Gidden, T. Wyttenbach, A.T. Jackson, J.H. Scrivens, M.T. Bowers. J. Am. Chem. Soc. 122 (2000) 4692.
[96] J. Gidden, T. Wyttenbach, J.J, Batka, Jr., P. Weis, A.T.

Jackson, J.H. Scrivens, M.T. Bowers. J. Am. Soc. Mass Spectrom. 10 (1999) 883.
[97] J. Gidden, T. Wyttenbach, J.J. Batka, Jr., P. Weis, A.T. Jackson, J.H. Scrivens, M.T. Bowers. J. Am. Chem. Soc. 121 (1999) 1421.
[98] J. Gidden, A.T. Jackson, J.H. Scrivens, M.T. Bowers. Int. J. Mass Spectrom. Ion Proc. 188 (1999) 121.
[99] G. von Helden, T. Wyttenbach, M.T. Bowers. Science 267 (1995) 1483.
[100] G. von Helden, T. Wyttenbach, M.T. Bowers. Int. J. Mass Spectrom. Ion Proc. 146/147 (1995) 349.
[101] M.T. Bowers, P.R. Kemper, G. von Helden, P.A.M. van Koppen. Science 260 (1993) 1446.