Electrospray ionisation mass spectrometry (ESI MS) of poly(methyl methacrylate) and acrylic statistical copolymers

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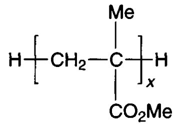
ESI MS is found to an effective tool for the analysis of poly(methyl methacrylate); optimum conditions involve the use of K^+ counter ion at relatively high cone voltage; ESI MS is used for end-group and copolymer compositional analysis.

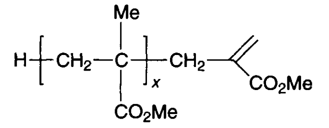
Mass spectrometry might, in principle, be expected to be the definitive analytical technique for polymer science.[1] It provides information on both relative molecular mass and molecular structure. A variety of ionisation methods has recently been developed that enable relatively high-mass synthetic polymers to be ionised with little or no fragmentation. These include secondary-ion mass spectrometry,[2] field desorption[3] and matrix-assisted laser desorption ionisation (MALDI)[4–6] as well as electrospray ionisation (ESI).[7] We have recently demonstrated the use of MALDI with time-of-flight detection (TOF) for the analysis and end-group determination of a range of poly(methyl methacrylate) homopolymers from a variety of polymerisation chemistry.[8] Electrospray ionisation has developed as an excellent technique for the mass characterisation of hydrophilic polymers such as poly(ethyleneglycol) where polymers with masses in excess of 5 000 000 Da have been observed, as multiply charged species.[7] More recently the application of ESI MS has been demonstrated for low molar mass poly(methyl methacrylate) (PMMA) monodisperse macromolecules (degree of polymerisation = 25, 50)[9] as well as for the compositional analysis of poly(methyl methacrylate–co-butyl acrylate) with ESI MS coupled to size exclusion chromatography.[10] In the previously reported ESI MS of PMMA the only spectra reported show extensive multiple charging (1–4 charges per molecule) which resulted in overlapping, and unresolved peaks thus hindering analysis. In this communication we report ESI MS of PMMA with a range of cations and cone voltages so as to determine the optimum conditions for end-group analysis and ESI MS of acrylic copolymers allowing compositional analysis.

ESI MS experiments were carried out using a Fisons 'Quattro II' triple quadrupole mass spectrometer equipped with an atmospheric pressure ionisation source operated in the nebuliser-assisted electrospray mode.† ESI MS of three poly(methyl methacrylate) homopolymers of number average molar mass (M_n) 1073, 1779 and 4322 (polydispersity index, PDi, 1.11, 1.10 and 1.10, respectively,‡ with structure **1**) were measured with Na^+, K^+, Cs^+ and Ag^+ counter ions and cone voltages of 30, 60, 80, 120 and 180 V. In each, an increase in cone voltage gives rise to two important features. First, low cone voltages favour ionisation of lower mass macromolecules biasing the molecular mass distribution to low mass; this effect is reduced by operating above an appropriate threshold. An increased cone voltage also increases the amount of fragmentation observed for PMMA as loss of MeO, 31 Da. In all cases the most intense series of peaks arise from singly charged macromolecules. Precise structural information is available; for example a peak observed at 1241.7 Da is from **1** where $x = 12$ (calculated mass 1241.61 Da) . The number of cations attached to each macromolecule is highly dependent on the choice of cation. Although for PMMA of $M_n = 1073$ ionisation occurred for all cations at all cone voltages the two higher mass polymers required cone voltages in excess of 60 V for ionisation with either Li^+ or Ag^+. As the polymer mass is increased there is an increased probability of multiple charging such that in the case of PMMA with $M_n = 4322$ and Cs^+, doubly charged species are almost as intense as singly charged; triply charged species also occur. Although multiple charging is often desirable in ESI MS this is *not always* the case for synthetic polymers which are invariably a complex mixture of macromolecular species of varying mass. For the analysis of PMMA homopolymers from acetone solution, K^+ results in the highest quality spectra when run at the highest cone voltage possible, while avoiding fragmentation.

Poly(methyl methacrylate) homopolymer of $M_n = 2158$, PDi = 2.21 was prepared by catalytic chain-transfer polymerisation (CCTP).§ Although mass averages from ESI MS are unreliable, extremely useful information regarding absolute masses of each individual macromolecular species is available, yielding structural information. Of particular interest is analysis of polymer end-groups so as to obtain information on both polymerisation initiation and termination mechanisms. CCTP results in competitive initiation from primary radical and Co^{III}–H with termination almost exclusively, at low mass, *via* hydrogen-atom transfer to Co^{II} to give polymers of structure **2** and **3**, respectively. Fig. 1 shows the ESI MS of the CCTP prepared PMMA at a cone voltage of 80 V. No fragmentation is observed. Series from both **2** and **3** are observed indicating initiation to be predominantly from Co^{III}–H and termination by H-atom



1



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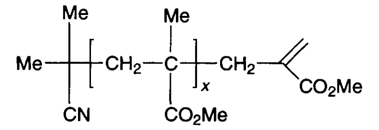

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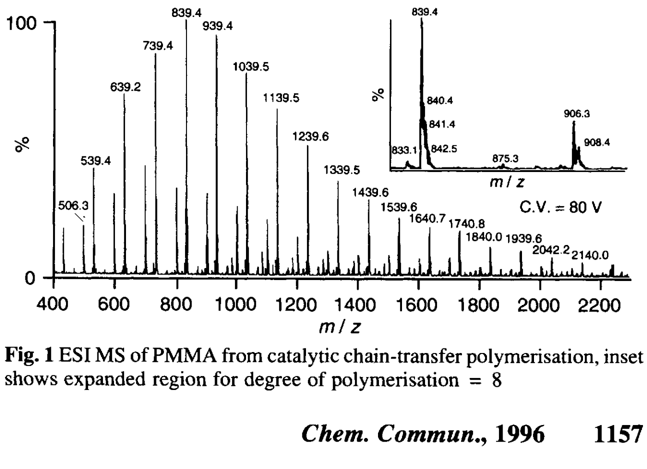

Fig. 1 ESI MS of PMMA from catalytic chain-transfer polymerisation, inset shows expanded region for degree of polymerisation = 8

abstraction, as expected. The observed masses are accurate to the first decimal place, Table 1, whereas with MALDI-TOF mass numbers are only accurate to within 2 Da, for these polymers. Low-intensity peaks are observed from doubly cationised macromolecules as are polymers which show termination by combination of two primary radical initiated polymers.

Two statistical copolymers from monomer feeds containing 8.7 mole% methacrylic acid (MAA) and 12.4 mole% styrene (STY) with 92.3 mole% and 87.6 mole% methyl methacrylate, respectively, of low mass were prepared using CCTP.[¶] In both cases, excellent spectra showing incorporation of the secondary monomer, were observed. For each individual degree of polymerisation a range of compositions is observed. For example, for degree of polymerisation 8 we observe MMA_8, MMA_7STY_1, MMA_6STY_2, MMA_5STY_3, MMA_4STY_4 as individually resolved peaks (839.2, 843.2, 847.1, 851.2. Calc. 839.4, 843.4, 847.4, 851.4 Da); the most abundant species being MMA_7STY_1. The number of styrene units incorporated increases with the length of the chain as is expected from statistical polymerisation. Copolymers of hydrophobic STY with, relatively, hydrophilic MMA can not only be easily distinguished but the resolution is sufficient to identify accurate composition; even though the difference in mass between the two monomers is approximately 4 Da. The copolymer of 8.7% MAA–92.3%MMA, Fig. 2, also shows the composition of each individual macromolecule. For degree of polymerisation of 10, MMA_{10}, MMA_9MAA_1, MMA_8MAA_2, are observed (1039.5, 1025.4, 1011.4. Calc. 1039.5, 1025.5, 1011.4 Da), the most abundant being MMA_{10}. Thus this technique can be used to examine copolymers containing a diverse range of monomers. No evidence for either fragmentation or multiple charging was observed for any copolymer.

Table 1 Selected observed and calculated masses for PMMA from CCTP with structures **2** and **3**

Structure	x^a	Obs. mass/Da	Calc. mass/Da
2	7	839.4	839.4
2	8	939.4	939.4
2	9	1039.5	1039.5
2	10	1139.5	1139.5
3	7	906.3	906.4
3	8	1006.6	1006.5
3	9	1106.4	1106.5
3	10	1206.4	1206.6

^{a} Degree of polymerisation.

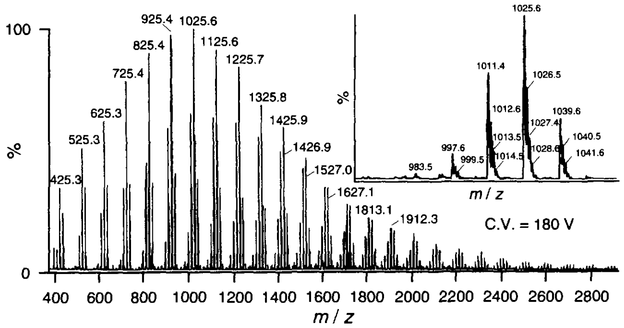

Fig. 2 ESI MS of 8.7% MAA–92.3% MMA statistical copolymer, inset shows degree of polymerisation = 10

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Footnotes

[†] Only the first quadrupole mass analyser was used. The spectrometer was calibrated with CsI with mass spectra acquired over the range *m/z* 4000–350 during a 10 s scan; several scans were summed to produce the final spectrum. Polymer samples were prepared at a concentration of 0.05 μg l^{-1} by dissolving 5 mg of polymer in 1 ml of the appropriate salt solution (5 mg LiCl, KI, CsI, CF_3CO_2Ag in 10 ml acetone; methanol in the case of MMA–MAA copolymer). Aliquots of 20 μl were injected into the ion source at a flow rate of 10 μl min^{-1} by means of a Wilson model 607 L.C. pump.

[‡] Narrow molecular-mass size exclusion chromatography standards from Polymer Laboratories. M_n and PDi as given by the manufacturer.

[§] 10 ml of deoxygenated, inhibitor-free MMA and 500 mg of azo(isobutylnitrile) were dissolved in 20 ml of butanone. 0.25 ml of a stock solution of [bis(dimethylglyoximato)](tetrafluorodiborato)cobalt (2.5 mg in 5 ml of butanone) were heated at 60 °C for 24 h under an atmosphere of nitrogen. The polymer was isolated by precipitation from hexane.

[¶] Standard Schlenk-line conditions were used for all manipulations. In a typical polymerisation *e.g.* MMA/MAA copolymer, MMA (25.51 g, 0.2548 mol), MAA (2.09 g, 0.0243 mol), AIBN (0.0436 g, 2.65×10^{-3} mol) and [bis(dimethylglyoximato)](tetrafluorodiborato)cobalt (6.19×10^{-4} g, 1.38×10^{-6} mol) were mixed. 10 ml of this mixture was heated in a sealed ampoule at 60 °C for 150 min. Final conversion was 22.5% (gravimetry) with $M_n = 2150$, $M_w = 4200$ (SEC against narrow PMMA standards). The styrene copolymer showed a conversion of 10.2% ($M_n = 2450$, $M_w = 4950$).

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