Structural characterization of a poly(methacrylic acid)/poly(methylmethacrylate) copolymer by activated electron photo-detachment dissociation

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ABSTRACT

Tandem mass spectrometry of co-oligomers composed of methacrylic acid (MAA) and methyl methacrylate (MMA) units was performed after activated electron photo-detachment dissociation (activated EPD). In this technique, doubly charged MAA/MMA co-oligomers were first produced in negative mode electrospray ionization. Species produced upon electron photo-detachment (220 nm) of these doubly charged co-oligomers were observed to spontaneously eliminate a carbon dioxide molecule. The so-formed radical anions were then activated by collision. In contrast to CID of negatively charged MAA/MMA co-oligomers, which does not provide informative data with regards to the end-groups, activated EPD is shown here to promote efficient radical-induced dissociation reactions thanks to the oxidation of a carboxylate pendant group upon laser irradiation. Product ions generated after backbone bond cleavages only contained the anionic initiating group. Combining these MS/MS results with the sum of the end-group masses determined from MS data allowed the terminating group to be characterized. As compared to activated EPD data obtained for a PMAA homopolymer holding the same end-groups, an additional product ion series was generated in the case of MAA/MMA copolymers, strongly suggesting that the hydrogen bond network established between neighboring MAA monomers is disrupted when MMA units are inserted in the polymeric backbone.

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1. Introduction

The performance of polymeric materials highly depends on their structure, and a whole set of parameters should be determined to describe a polymer, such as molecular weight distribution, monomer and end-groups [1]. In particular, end-group analysis is extremely informative on polymerization mechanisms. Presence or absence of specific terminations can cause significant changes in the final material properties but also in the polymer reactivity. For molecules composed of two different repeating units, random or block nature of copolymer and balance between hydrophobic and hydrophilic segments are additional crucial information [2]. Unambiguous characterization of copolymer microstructure can be efficiently addressed using mass spectrometric techniques [3].

Using soft ionization techniques to produce intact gas phase ions, individual oligomers can be measured in a MS spectrum, allowing the nature of the repeat unit and of the end-groups to be confirmed and copolymers to be distinguished from homopolymers [3]. Tandem mass spectrometry (MS/MS) is however required to characterize chain terminations of unknown molecules, and to distinguish block copolymers from random copolymers [4]. Since each co-monomer exhibits different dissociation behavior, fragmentation pathways along the chain usually allow copolymers to be sequenced, as previously reported for a variety of polyether-based [4–8] and polyester-based [9–13] copolymers.

A useful analysis of MS/MS data obtained for copolymers first requires the dissociating behavior to be understood for homopolymers consisting of each of the co-monomers. In most cases, major fragmentation routes induced by collisional activation of polymeric adducts proceed *via* backbone cleavages, yielding product ions containing either the initiating or the terminating group [14]. In some cases, however, dissociation of polymer adducts fails at providing useful structural information, as observed for example for poly(methacrylic acid) (PMAA). Indeed, conventional collision induced dissociation (CID) of PMAA, ionized either in the negative [15] or in the positive [16] ion mode, mainly consists of multiple

dehydration steps proceeding between adjacent pending acidic groups. A similar mechanism was observed to be the major process during CID of a copolymer composed of methacrylic acid (MAA) and methyl methacrylate (MMA) units [17]: water elimination occurred from any two contiguous MAA units while MAA–MMA pairs gave rise to the loss of methanol. Although this dissociation behavior revealed that the co-monomers were randomly distributed and allowed co-monomeric composition to be determined, the lack of reactions involving backbone cleavages such as those expected for PMMA [18–23] did not permit the end-groups to be individually mass characterized.

Using an alternative activation method developed for the gas phase dissociation of polyanions [24–28], namely activated electron photo-detachment dissociation (activated EPD), we recently addressed the issue of end-group analysis for PMAA [29]. Multiply deprotonated PMAA oligomers produced in negative-ion mode electrospray ionization (ESI) were oxidized into radical anions upon electron photo-detachment using a 220 nm laser wavelength, and further activated by collision. Fragmentation of these odd-electron species was shown to proceed *via* a radical-induced decarboxylation, followed by reactions involving backbone bond cleavages, giving rise to product ions containing one or the other oligomer termination. Activated EPD experiments were thus evaluated here to characterize the PMAA/PMMA random copolymer previously studied in CID [17].

2. Experimental

2.1. Chemicals

HPLC grade methanol (MeOH) was purchased from Sigma–Aldrich (Saint Quentin Fallavier, France). The copolymer synthesis was previously described in details elsewhere [17] and is summarized in Supplementary Information. The copolymer (5 mg) was dissolved in 1 mL of methanol, further diluted using methanol to a final 50 μg mL^{-1} concentration and introduced in the ionization source at a 5 μL min^{-1} flow rate using a syringe pump.

2.2. Mass spectrometry

The experimental setup has been described in details elsewhere [26] and is only briefly presented here. It consists of a mass spectrometer coupled to a vis/UV tunable optical parametric oscillator (OPO) laser. The mass spectrometer is a quadrupole linear ion trap (LTQ, Thermo Fisher Scientific, San Jose, USA). A quartz window was fitted on the rear of the LTQ chamber to allow the introduction of the laser beam. The laser is a nanosecond frequency-doubled tunable

Panther^{TM} EX OPO laser pumped by a Surelite^{TM} II Nd:YAG laser (both from Continuum, Santa Clara, CA, USA). EPD experiments were performed at λ = 220 nm. The output laser power was around 4 mW at a repetition rate of 10 Hz. The laser beam passes through two diaphragms (2 mm diameter), lenses and a mechanical shutter electronically synchronized with the mass spectrometer, after which it is injected on the axis of the linear trap. The mechanical shutter is used to synchronize the laser irradiation with the trapping of the ions. To perform laser irradiation for a given number of laser pulses, we add in the ion trap RF sequence an MS^n step with an activation amplitude of 0%, during which the shutter located on the laser beam is opened. Laser irradiation was performed during 5000 ms (*i.e.*, 50 laser pulses). Activation by collision (CID) of the oxidized ions was performed by using an additional step in the RF sequence. This was accomplished using helium gas with a normalized collision energy of 30% for 30 ms. The activation q value was set to 0.25 for CID and for activated EPD. An m/z window of 3 Th was applied for ion precursor isolation for both methods.

3. Results and discussion

3.1. Negative mode ESI-MS of the PMAA/PMMA sample

Based on nuclear magnetic resonance analyses [17], the studied sample would actually be composed of two PMAA/PMMA copolymers, referred hereafter as **I** and **II**, holding different ω end-groups (Scheme 1). However, owing to the nature of the co-monomers and to the 14 Da mass difference between ω terminations proposed for each co-polymeric species, co-oligomers **I** containing n MAA and m MMA units, noted **I**$(n;m)$, are to be expected at the same m/z values than **II**$(n+1;m-1)$.

Negative mode ESI of the copolymer sample gave rise to a complex mass spectrum, where multiple polymeric distributions could be distinguished in the 400–2000 m/z range (Fig. 1). Electrosprayed ions were mostly in the 2$^-$ charge state, as indicated by their isotopic pattern. Homologue series could thus be defined from each peak by adding or substracting 50.0 or 43.0 m/z, *i.e.*, the half mass of neutral MAA and MMA unit, respectively (see inset of Fig. 1). Two main co-oligomeric distributions could be defined, with calculated end-group masses such as $m_\alpha + m_\omega = 355.1$ and $m_\alpha + m_\omega = 369.1$. This result is consistent with the termination structures respectively proposed for copolymers **I** and **II** (Scheme 1), when considering that the sulfonate moiety in the α end-group is desodiated and the second negative charge results from deprotonation of any one carboxylic acid group of the molecules, either within a MAA unit of the polymeric skeleton or in the chain terminations. Monomer composition of each ion in both distributions could be calculated from MS data and is
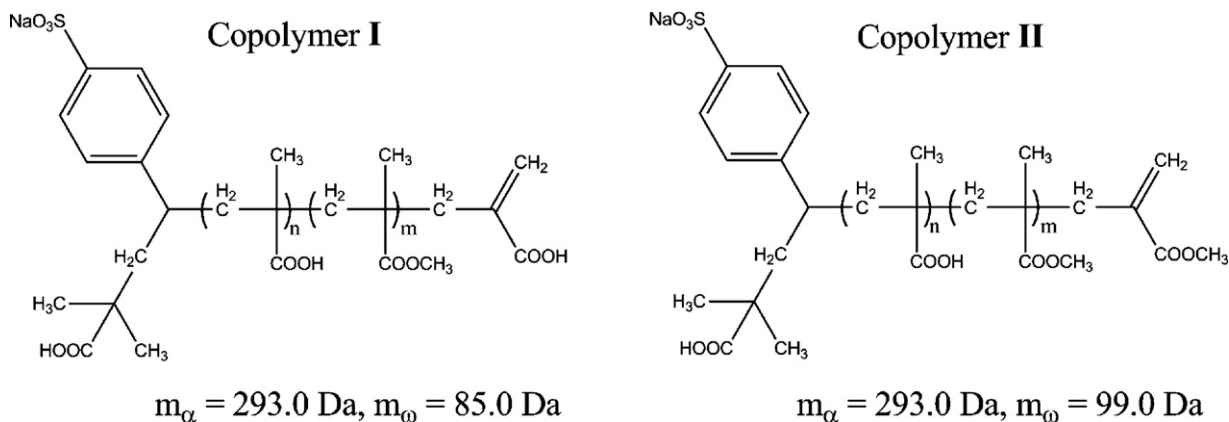
Scheme 1. Structure proposed from NMR analysis for the two PMAA/PMMA copolymers.