Synthetic oligomer analysis using atmospheric pressure photoionization mass spectrometry at different photon energies

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HIGHLIGHTS

- Atmospheric pressure photoionization was performed using synchrotron radiation.
- Photoionization of oligomers in THF with 10% CH_2Cl_2 produces intact $[M+Cl]^-$ ions.
- The photon energy required corresponds to ionization potential of the solvent.
- Polymer distributions depend on source parameters such $T^\circ C$ and applied voltages.
- Liquid chromatography was coupled to MS using an APPI interface for polymer analysis.

GRAPHICAL ABSTRACT

Atmospheric pressure photoIonization mass spectra of synthetic oligomers were recorded in the negative mode by varying the photon energy using synchrotron radiation. Photon energy required for an efficient ionization of the polymer was correlated to ionization potential of the solvent (for example 9.4 eV for tetrahydrofuran).
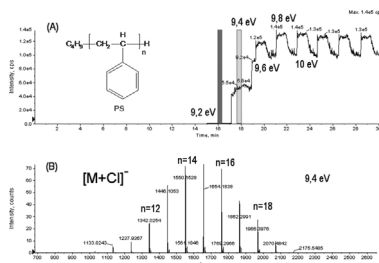
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ABSTRACT

Atmospheric pressure photoionization (APPI) followed by mass spectrometric detection was used to ionize a variety of polymers: polyethylene glycol, polymethyl methacrylate, polystyrene, and polysiloxane. In most cases, whatever the polymer or the solvent used (dichloromethane, tetrahydrofuran, hexane, acetone or toluene), only negative ion mode produced intact ions such as chlorinated adducts, with no or few fragmentations, in contrast to the positive ion mode that frequently led to important in-source fragmentations. In addition, it was shown that optimal detection of polymer distributions require a fine tuning of other source parameters such as temperature and ion transfer voltage. Series of mass spectra were recorded in the negative mode, in various solvents (dichloromethane, tetrahydrofuran, hexane, toluene, and acetone), by varying the photon energy from 8 eV up to 10.6 eV using synchrotron radiation. To these solvents, addition of a classical APPI dopant (toluene or acetone) was not necessary. Courtesy of the synchrotron radiation, it was demonstrated that the photon energy required for an efficient ionization of the polymer was correlated to the ionization energy of the solvent. As commercial APPI sources typically use krypton lamps with energy fixed at 10 eV and 10.6 eV, the study of the ionization of polymers over a wavelength range allowed to confirm and refine the previously proposed ionization mechanisms. Moreover, the APPI source can efficiently be used as an interface between size exclusion chromatography or reverse phase liquid chromatography and MS for the study of synthetic oligomers. However, the photoionization at fixed wavelength of polymer standards with different molecular weights showed that it was difficult to obtain intact ionized oligomers with molecular weights above a few thousands.

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1. Introduction

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) is currently the most popular MS technique for polymer analysis [1,2]. This technique allows characterization of repeat units and end-groups of synthetic polymers. From a MALDI mass spectrum, reliable values of number average molecular weight (M_n), weight average molecular weight (M_w) and of polydispersity index of a molecular weights distribution (PDI, defined by M_w/M_n) can be deduced for narrow polydispersity polymers (PDI <1.2) [3,4]. Tandem MS experiments with MALDI-TOF–TOF instruments bring an additional dimension in structural characterization of polymers [5]. Nowadays, MALDI-MS is the most widespread MS technique for polymer analysis, but alternative ionization techniques are desirable for direct coupling with liquid chromatography (LC) or for compounds that are difficult to be ionized by MALDI. Polymer analyses using ambient ionization methods such as desorption-electrospray ionization (DESI) [6–11], direct analysis in real time (DART) [12] and atmospheric solids analysis probe (ASAP) [13] techniques, were recently published, but these latter techniques cannot be directly used as interfaces with liquid chromatography (LC). Among the commonly used techniques as LC–MS interfaces, such as electrospray ionization (ESI) [14,15], atmospheric pressure chemical ionization (APCI) [16,17] and atmospheric pressure photoionization (APPI) [18,19], the last appears to be as a promising ionization technique for MS and LC–MS analyses of synthetic polymers, especially for nonpolar compounds, despite the small number of articles recently published [20–23]. Only three articles from Zsuga et al., deal with the use of APPI for polymer analysis [20–22]. Low mass polyethylene and polyisobutylene with different end-groups were studied using a commercial APPI source (Photomate) equipped with a Kr discharge lamp emitting vacuum ultraviolet (VUV) photons of 10.0 eV and 10.6 eV in an intensity ratio of 4:1. This APPI source was combined with a hybrid Q-TOF mass analyzer. In the positive ion mode, significant fragmentation was noted by Zsuga et al. whereas in the negative mode, abundant chlorinated adduct ions were produced from chlorinated solvents such as carbon tetrachloride in the presence of toluene as dopant [20–22]. The reported results were all in the flow injection mode only, and at fixed wavelength.

In the present work, the potential of the vacuum ultraviolet (VUV) photons for the ionization of polymers was explored over a wavelength range from 8 eV up to 10.6 eV using the coupling of an APPI source with a VUV synchrotron radiation beamline (DISCO) at the SOLEIL synchrotron radiation facility in France. Using this set-up as described by Giuliani et al. [24], the ionization of guanine in the positive mode was recently studied by Touboul et al. as a function of the photon energy [25]. The use of the coupling of the synchrotron radiation with MS was also reported by Le Naour et al. for the characterization of peptide palmitoylation, a major post-translational modification of membrane proteins [26].

By studying the formation of gaseous ions by APPI-MS from various synthetic polymers (polyethylene glycol, polymethyl methacrylate, polydimethyl siloxane and polystyrene) at different wavelengths, one of our objectives was to gain a better understanding of the mechanism of formation of ions. The crucial questions for polymer analysis that are related to the sensitivity, mass range, and the kind of polymer able to be analyzed by APPI-MS were also addressed. In addition, we report here the first coupling experiments of LC with APPI-MS for synthetic polymer analysis. LC–MS coupling can be a powerful tool for polymer analysis [27]. The combination of chromatographic separation and identification by APPI-MS may reduce the complexity of the analysis of polymers. Finally, this work was completed by tandem MS experiments in order to evaluate the amount of information that could be obtained by CID-MS/MS from the chlorinated adducts produced by APPI.

2. Experimental

2.1. Materials

Polydimethyl siloxane (PDMS 20 cs, $M_n \sim 2000\,\mathrm{g\,mol^{-1}}$), was purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France), used without further purification. Polyethylene glycol (PEG, M_p 620 g mol^{-1}, 1080 g mol^{-1}, 1470 g mol^{-1} and 4120 g mol^{-1}), and polymethyl methacrylate (PMMA, M_p 855, 1970, 2710 g mol^{-1}), and polystyrene (PS, M_p 580 g mol^{-1}, 1355 g mol^{-1} and 4950 g mol^{-1}) were obtained as Gel Permeation Chromatography (GPC) standards from Polymer Laboratories (now a part of Varian, Santa Clara, CA, USA). M_p corresponds to the most probable molecular weight of the molecular distribution given by the supplier determined by GPC. All polymers were used after dissolution in solvent (10^{-3} M). No salt was added. All solvents were HPLC grade. Dichloromethane unstabilized, dichloromethane stabilized with amylene, toluene and tetrahydrofurane unstabilized were purchased from Fisher Scientific (Illkirch, France). Dibromomethane and acetonitrile were acquired from Sigma-Aldrich (Saint Quentin Fallavier, France). Acetone was purchased from Merk (Fontenay Sous Bois, France) and tetrahydrofurane stabilized with BHT (3,5-di-tert-butyl-4-hydroxytoluene) was from Acros organics (Illkirch, France).

2.2. Instrument set-up

Experiments were carried out using a hybrid Q-TOF (Q STAR Pulsar i, ABSciex) mass spectrometer equipped with a Photospray^{TM} Source (APPI). The APPI source has been modified to allow the introduction of photons from the DISCO beamline [28] of a synchrotron radiation facility (SOLEIL) by substitution of the standard UV krypton lamp [24]. Photon energy was tunable from 5 eV (248 nm) to 20 eV (62 nm) with a precision of 0.1 nm. Source temperature was 300–500 °C. In the negative ion mode, typical applied voltages were −100 V for focusing potential, 10 V for declustering potential (1) and −15 V for the declustering potential (2). The gas pressures (N$_2$) in the APPI source were set at 40 psi for GAS 1 and 20 psi for GAS 2. The curtain gas pressure was 20 psi and that of collision gas was 3 psi. The samples were introduced using the flow-injection analysis (FIA) method: 20 μL of the sample solution at 10^{-3} mol L^{-1} was loaded into an injection loop and pushed through the APPI source by the solvent at a flow rate of 200 μL min^{-1}.

All LC-MS experiments (RPLC and SEC) were performed using an HP1100 liquid chromatograph (Agilent Technologies). Reversed-phase chromatographic separation was performed on a C$_{18}$ column (Fused-Core Ascentis, 100 × 3 mm, diameter particle 2.7 μm) with the following gradient: linear gradient from acetonitrile (with 5% acetone) to 65% of dichloromethane, return to acetonitrile with 5% acetone within 5 min, and equilibrate the column at those conditions for 10 min, at a flow rate of 200 μL min^{-1}.

SEC analyses were carried out using a PLgel column in isocratic mode (Polymers Labs, France), 300 × 8 mm, pore diameter 1000 Å, particle diameter 5 μm (polydivinylbenzene/polystyrene copolymer). THF at a flow rate of 200 μL min^{-1} was used as eluent. The injection volume was 20 μL (concentration 10^{-3} M) for all LC and SEC-MS analyses. In mass spectra, the chemical background induced by the solvent was systemically removed by signal subtraction.