Analysis of End-Functionalized Polymers Using ESI-Quadrupole Ion Trap Mass Spectrometry and IRMPD

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Introduction. Polymer analysis involves characterization of the backbone as well as the endgroups of the polymer. Endgroup functionality is indicative of the polymerization process and influences the polymer's physical properties. Backbone and endgroup structure elucidation is difficult using low-energy collision-induced dissociation (CID) on sodiated polymers. This type of dissociation is inefficient, and dissociation conditions (i.e., high q_z values) prevent detection of low-mass ions. Infrared multiphoton photodissociation (IRMPD) has been shown to be effective in dissociating simple, sodiated polymers[1] for backbone analysis. Here, IRMPD is shown to provide information about polymer endgroups in addition to backbone structure.

Methods. Polyethylene glycol (PEG) and dicarboxymethyl-polyethylene glycol (CM-PEG) polymers (Shearwater Polymers) were prepared as 0.5 mM solutions in methanol with an equal concentration of sodium acetate. Polymers were analyzed using a modified Finnigan ITMS quadrupole ion trap with a custom-built nanoelectrospray (nanoESI) source. The beam from a Synrad 48-series CO_2 laser (50 watts, 10.6μm) was directed through a hole in the ring electrode of the quadrupole ion trap for IRMPD experiments. Irradiation times ranged from 10 to 350 ms at 100% laser power. A small amount of helium (<0.3 mTorr) was used for collisional cooling of ions prior to dissociation. Conventional CID was performed at a helium pressure of 0.7 mTorr. Product ion spectra using CID were compared to those using IRMPD.

Discussion. CM-PEG is a polyether containing a carboxylic acid functionality on each end as depicted in Figure 1. Four distinct ion series appear in IRMPD MS/MS spectra of sodiated oligomers (Figure 2). These ion series correspond to partial or complete rearrangement and loss of the acid functionality from the end of the polymer. As has been noted with IRMPD of PEG[1], both C-O and C-C bond cleavages occur during IRMPD of CM-PEG. All four ion series exhibit peaks corresponding to C-O and C-C bond cleavages. C-C bond cleavages are not present in CID spectra of CM-PEG. CID spectra of low-mass, singly-charged oligomers show an ion series exhibiting loss of one endgroup and a second series resulting from endgroup rearrangement (Figure 3). These ions are formed only if the oligomer is very small (~10 monomer units). Distinct ions with a proposed cyclic structure appear only in the IRMPD spectrum.

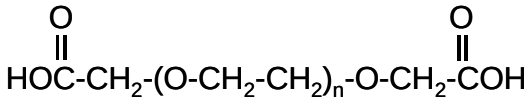

Figure 1. Structure of CM-PEG

Polymers with MW>800 Da are known to form adducts with multiple Na+ ions during ESI. CID of multiply charged PEG and CM-PEG ions results almost exclusively in charge stripping of the parent ions, so that the above polymer characterization would not be possible with a polymer ion of appreciable size. MS^3 has been performed on product ions generated from CM-PEG via IRMPD. Both CID and IRMPD of MS^2 ions provide informative MS^3 spectra. Because MS^2 ions are singly sodiated and are of relatively small size, CID is an effective dissociation method in MS^3 experiments. CID and IRMPD MS^3 spectra are identical in most cases and provide complementary information about the polymer in others.

In general, IRMPD product ions appear in greater abundance and variety than do CID product ions. More low-mass product ions are detected in IRMPD spectra because the low-mass cutoff is not raised in IRMPD as it is for CID. Cleavage of the C-O bond in the polymer backbone is observed in both spectra, but cleavage of the C-C bond appears in IRMPD spectra only. IRMPD efficiency is not hampered by either the molecular weight of the polymer or its charge state. In addition, IRMPD does not require the high collision gas pressures or parent ion isolation necessary for CID, both of which degrade polymer signal. IRMPD provides a greater variety of polymer product ions than CID, allowing more complete structural information about the polymer to be obtained. Because many types of bonds are cleaved, this technique has the potential to complicate analysis of polymers with complex endgroup structure. We have found that IRMPD of CM-PEG produces informative spectra with a finite number of ion series.

References.

1. McGrath, SC; Glish, GL. *Proc 49th ASMS Conference*; Chicago, IL, 2001

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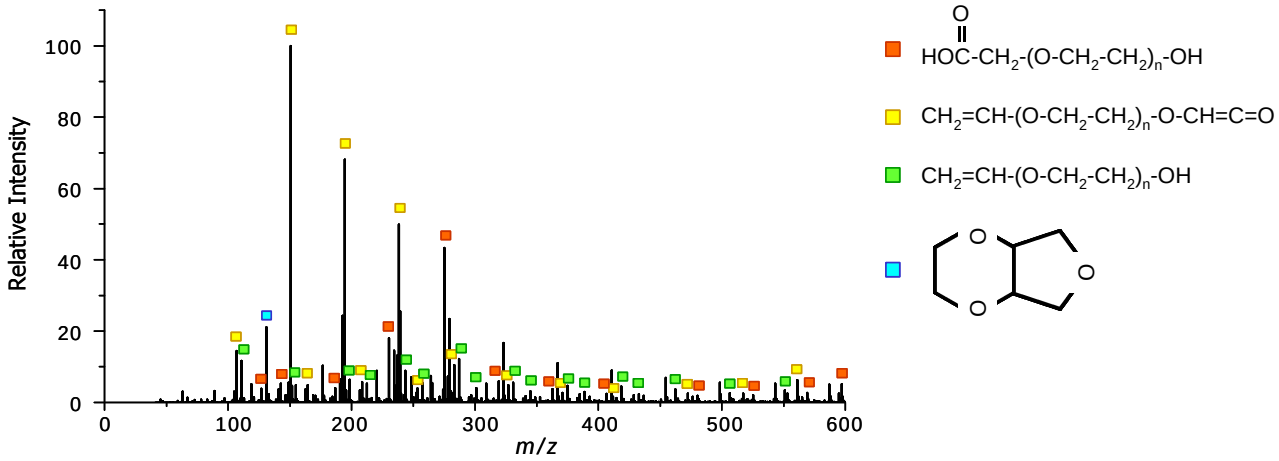

Figure 2. IRMPD products of CM-PEG

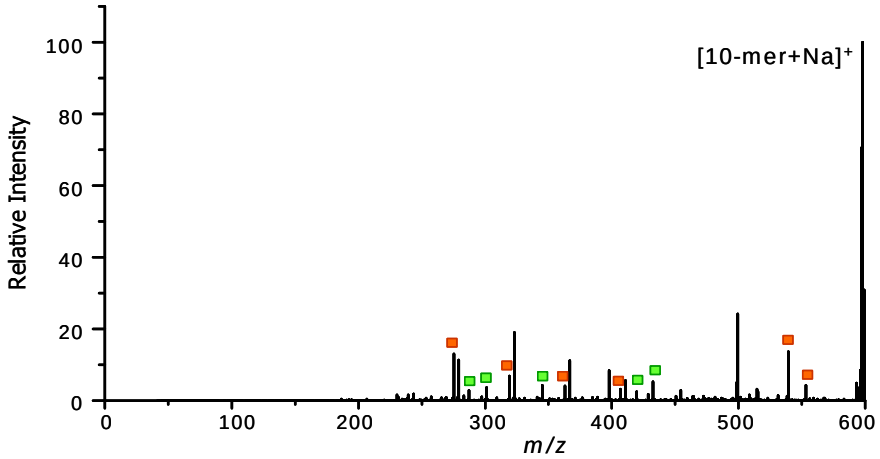

Figure 3. CID products of CM-PEG