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Structural Analysis of Linear PEEK via MALDI-TOF Mass Spectrometry

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S *Supporting Information*

Poly(ether ether ketone) (PEEK) is an important member of the poly(aryl ether ketones) (PAEKs). These polymers can be synthesized either by nucleophilic aromatic substitution of a halogenated or nitrated benzophenone with a phenol in the presence of a base[1] or by acid promoted condensation of aromatic carboxylic acids or acid chlorides with phenyl ethers.[2] PEEK has excellent thermal and mechanical properties, as well as a high degree of solvent resistance, as a result of the semicrystalline nature of the material.[3] Indeed, unmodified PEEK is insoluble in conventional organic solvents at room temperature and can only be dissolved at very high temperatures (>300 °C) or through protonation of the carbonyl groups in the polymer backbone by strong acids such as trifluoroacetic acid.[4] This inherent insolubility, while responsible for the desirable properties of PEEK, renders detailed structural analysis of the polymer problematic. In particular, characterization of the end-groups of the polymer is limited to solid-state techniques such as NMR, IR, and Raman spectroscopy. Several methods have been reported whereby PEEK has been converted to a form that is soluble at room temperature. Commonly, PEEK is rendered water-soluble by sulfonation of the aromatic backbone with concentrated sulfuric acid.[5] More recently, Colquhoun et al. have reported the quantitative protection of the carbonyl groups in the polymer backbone by dithioacetalization to form a product that is soluble in common organic solvents such as tetrahydrofuran and dichloromethane and, as such, can be characterized by NMR spectroscopy, gel permeation chromatography, and MALDI-TOF mass spectrometry.[6] This method, while useful, is an indirect way of characterizing the polymer that requires an extra synthetic step with harsh reaction conditions, in particular the use of the strong acid TFA. MALDI-TOF mass spectrometry has also been used for the analysis of cyclic PEEK oligomers that are soluble in common organic solvents.[7]

Herein, we report a general procedure under which unmodified PEEK may be characterized, directly and unambiguously, by MALDI-TOF mass spectrometry. This technique,[8] while widely used for the structural characterization of a wide range of polymers, has hitherto not been reported for the analysis of linear PEEK to the best of our knowledge. All mass spectra obtained by this method clearly display the repeat unit of PEEK, and as a result, the mass of the two polymer end-groups can readily be calculated. In order to demonstrate the effectiveness of the technique, a series of PEEK oligomers were synthesized by the reaction of 4,4′-difluorobenzophenone (BDF) and hydroquinone (HQ) in the presence of a carbonate base.[9]

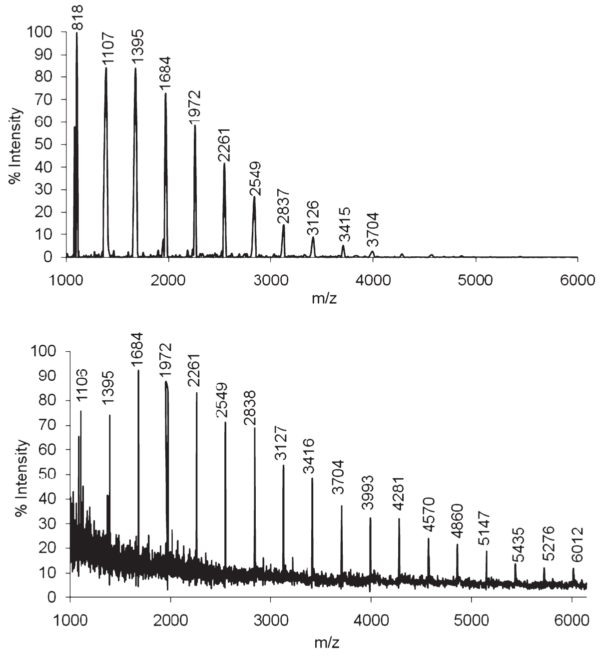

Figure 1. MALDI-TOF mass spectra of PEEK oligomers **1** and **2** (top and bottom, respectively).

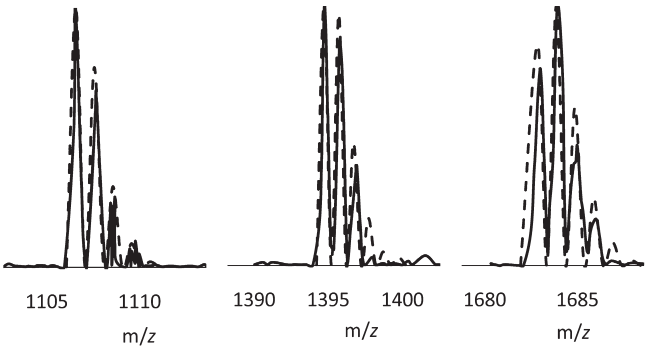

Figure 2. Calculated (dashed line) and observed (solid line) isotopic distributions for n = 3, 4, and 5.

Received: July 11, 2011
Revised: September 29, 2011
Published: October 21, 2011

Oligomers **1**, **2**, and **3** were prepared by adjusting the ratio of BDF to HQ (with BDF in excess) and the values of M_n were determined to be 1400, 4300, and 2400 Da, respectively (molecular weights determined by GPC after conversion of the oligomers to their thioacetal-protected forms via a previously reported method).[6,10] A 1 mg mL^{-1} solution of each oligomer in a 1:1 mixture (w/w) of phenol and 1,2,4-trichlorobenzene was obtained by heating the mixture to 214 °C for several minutes. Importantly, the oligomers stayed in solution after cooling to room temperature. This polymer solution was then mixed with an appropriate amount of matrix solution, prepared with the same solvent system, and the oligomer matrix solution was then spotted onto a MALDI plate and the solvents were removed by gentle heating. For the oligomers **1** and **2** (Figure 1), the best spectra were obtained with dithranol as the matrix and sodium iodide as the cationating agent, with the sodiated molecular ions of each polymeric species being observed. For oligomer **3**, both dithranol and DCTB were found to be equally effective as the matrix.

The mass spectra of oligomers **1** and **2** (Figure 1) both display a single polymeric series with a repeat unit of 288/289 g mol^{-1}— the molar mass of the PEEK repeat unit (see Figure 3). The expected end groups of a PEEK oligomer formed using an excess of BDF should have masses of 19 g mol^{-1} (F) and 199 g mol^{-1} ($C_{13}H_8OF$) (Figure 3). The predicted masses for this sodiated polymeric series (n = 2, 3, 4, 5, 6, etc.) are therefore 818, 1107, 1395, 1684, 1972 g mol^{-1}, etc. The m/z ratio for the observed peaks in Figure 1 is consistent with the formation of these oligomers as the exclusive product of the reaction. Figure 1 shows a smoothed representation of the MALDI-TOF mass spectra obtained, listing only the main ion peaks. The isotopic distributions obtained experimentally by this technique were in good agreement with the predicted values, as demonstrated for the trimer, tetramer, and pentamer in Figure 2.[7]

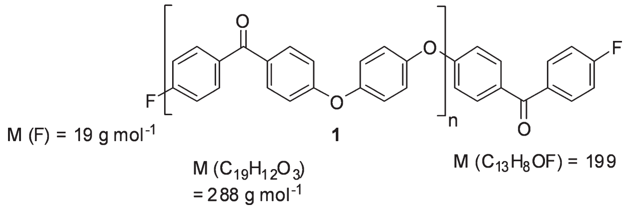

Figure 3. Mass units of di-F-terminated PEEK.

The MALDI-TOF mass spectrum of oligomer **3** (Figure 4) shows the presence of a secondary polymeric series with an m/z of 1196, 1485, 1774, 2062, 2351, etc. This series of peaks corresponds to a sodiated PEEK species with a terminal F (19 g mol^{-1}) and a terminal H (1 g mol^{-1}). The presence of this secondary species can be attributed to the reaction with an excess of BDF not going to completion. This example clearly shows the efficiency of the MALDI-TOF mass spectrometry method developed for identifying the polymer microstructure. However, because of the tendency of MALDI-TOF mass spectrometry to favor the ionization of lower molecular weight species, the spectra of polydisperse polymers, such as those prepared via a condensation process, should not be considered to represent the true molecular weight distribution.[11]

The method developed can also be used, in conjunction with solid-state NMR, to monitor subsequent end-capping reactions of F-terminated PEEK (Figure 1). Oligomer **1** was reacted with 4-*tert*-butylphenol in diphenyl sulfone at 300 °C using potassium carbonate as the base to produce a PEEK oligomer bearing *tert*-butyl terminal substituents (Figure 5). The *tert*-butyl group in the end-capper was selected to provide a clear and unambiguous signal in the solid-state ^{13}C NMR spectrum of the end-capped product, via the methyl carbons. The product was analyzed by MALDI-TOF mass spectrometry employing the method described above and the solid-state ^{13}C NMR spectrum (see Supporting Information for method).

The best mass spectra were obtained using dithranol as the matrix and using the mass spectrometer in linear mode. The main polymeric series observed (Figure 6) has peaks with masses that correspond closely to those expected for the fully end-capped product (predicted masses = 1077, 1365, 1654, 1942, and 2230 g mol^{-1} for sodiated n = 2—6). Solid-state ^{13}C NMR of the product (Figure 7) provided further confirmation that the desired product had been formed, with the methyl carbons of the end-capper being observed at 31.6 ppm, in addition to the expected signals for the PEEK backbone.[12] This demonstrates that the analysis technique can be used for monitoring reactions on PEEK oligomers. These compounds can be used as models for the reactivity of commercial grade PEEK, which would generally be above the mass range of MALDI-TOF mass spectrometry.

In conclusion, a method for the direct analysis of linear PEEK oligomers using MALDI-TOF mass spectrometry is reported. The mass spectra obtained can be used to identify the polymer end-groups and confirm the polymer microstructure. This is

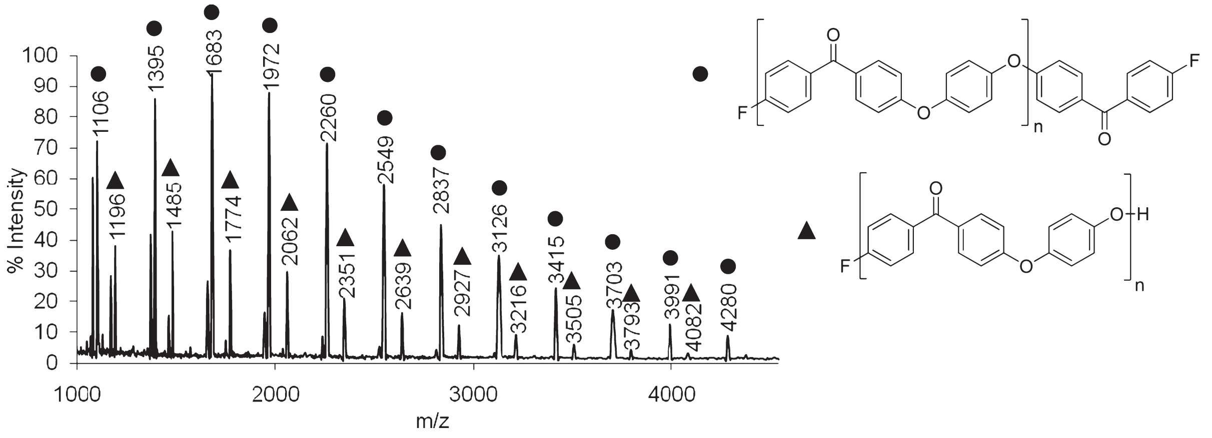

Figure 4. MALDI-TOF mass spectrum of PEEK oligomer **3**. Inset: structures of primary (●) and secondary (▲) species.

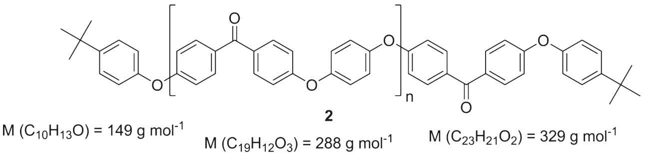

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Figure 5. Mass units of *tert*-butyl-substituted PEEK.

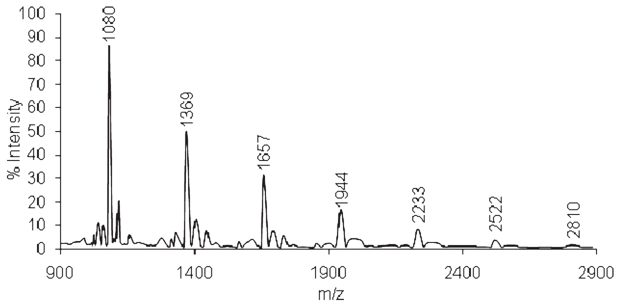

Figure 6. MALDI-TOF mass spectrum of *tert*-butyl-capped PEEK.

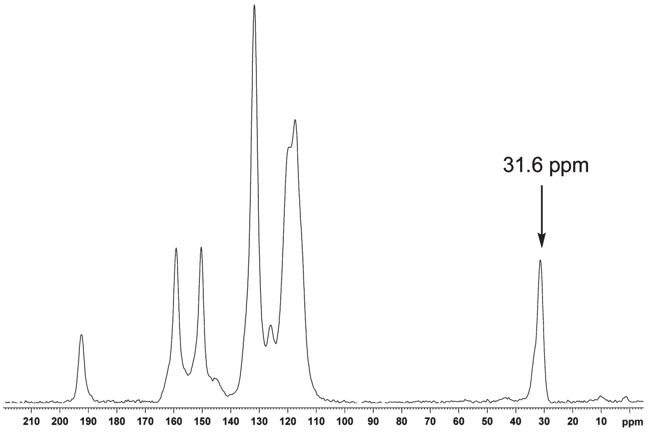

Figure 7. Solid-state ^{13}C NMR spectrum of *tert*-butyl-capped PEEK.

particularly useful where more than one series of polymers is obtained from a polymerization or where the end-groups are to be functionalized by further reaction. The mild nature of this characterization technique is expected to allow for its general use in characterizing PEEK oligomers and other insoluble PAEKs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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