Investigating the compatibility of PEEK polymer for the fabrication of sample cells for use in muon spin spectroscopy

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Abstract. Polyether ether ketone (PEEK) is a thermoplastic polymer with a wide range of applications due to its chemical inertness and thermal stability, and for these reasons sample cells for gas and liquid phase μSR have been constructed from PEEK. Muon level-crossing resonance (μLCR) studies of PEEK revealed a broad, strong μLCR signal that, we hypothesize, is due to multiple overlapping resonances from the various muonium (Mu) adducts of PEEK. To investigate this, two monomer units from PEEK (4,4′-dihydroxybenzophenone and para-dimethoxybenzene) were studied in solution using transverse-field muon spin rotation (TF-μSR) and μLCR. Two different muoniated radicals were formed by Mu addition to 4,4′-dihydroxybenzophenone and one radical was formed in para-dimethoxybenzene. The μSR spectra were assigned by comparing the experimentally measured muon and proton hyperfine coupling constants with values calculated for the possible structures using Gaussian-09 software with the B3LYP functional and 6-31G basis set. Good agreement was found for cyclohexadienyl-type radicals formed by Mu addition to the benzene rings of the monomer units. We can also infer that these radicals are being formed in PEEK, and based on this we conclude that sample cells made of PEEK are unsuitable for many types of μSR experiment.

1. Introduction

Materials used for μSR sample cell construction should have a number of important properties. They should be chemically inert and non-magnetic, withstand high pressure and temperature conditions, yet allow the fabrication of thin enough entrance windows to facilitate muon penetration with minimum stops and scattering in the window itself to optimize muon stops inside the cell cavity containing the target material. In addition, for radio-frequency experiments the sample cell should be electrically non-conducting to prevent the RF cavity from interacting with the cell material [1].

In this context polyether ether ketone (PEEK) was considered an ideal material for sample cell construction. It is a thermoplastic polymer with a wide range of application due to its chemical inertness and thermal stability up to 533 K [2]. Muons stop in this material with only a small amount of diamagnetic polarization (P_D \sim 0.1 \% with about 90\% missing fraction) and cells have been fabricated for gas samples up to 50 bar of pressure [1].
In a study of muon implantation in inert gases, a large (∼30%) muonium (Mu) signal was detected in a sample of high purity neon in a PEEK sample cell. This was a magnitude larger than previous measurements on neon carried out over a large pressure range. It was suggested that a charge neutralization reaction occurs with an unknown impurity outgassing from the PEEK polymer cell: NeMu$^+$ + X → NeX$^+$ + Mu. In addition, longitudinal-field repolarization studies suggested the formation of a radical state in the cell body.

The objective of the study reported here was to determine whether muoniated radicals are formed in PEEK, which would make it an unsuitable material for sample cells of experiments studying Mu and muoniated radicals, and to identify the structures of the resulting radicals. PEEK is a polymer consisting of alternating aromatic ring structures, a 4,4′-substituted benzophenone and a para-substituted benzene, with ether linkages. It is well established that Mu adds to substituted benzene rings to produce cyclohexadienyl radicals [3], and that Mu also adds to ketone groups [4]. We have performed muon level-crossing resonance (µLCR) measurements on PEEK and transverse-field muon spin rotation (TF-µSR) and µLCR measurements on two monomer units from PEEK (4,4′-dihydroxybenzophenone and para-dimethoxybenzene) in solution. The structures of these molecules are shown in Figure 1.

![Figure 1. The structure of the polyether ether ketone (PEEK) repeating unit and the sub-units of para-dimethoxybenzene and 4,4′-dihydroxybenzophenone.](image)

2. Experimental

2.1. Sample Preparation
A 6.5 mm thick sheet of PEEK was purchased from Goodfellow Inc and a 4 cm × 4 cm sample was cut from this sheet. Para-dimethoxybenzene and 4,4′-dihydroxybenzophenone were purchased from Sigma-Aldrich and dissolved in anhydrous tetrahydrofuran and ethanol, respectively. The sample solutions were deoxygenated by the freeze-pump-thaw technique and sealed in stainless-steel cells fitted with windows made of 25 µm thick foils of the same material.

2.2. TF-µSR and µLCR Experiments
The µLCR measurement on PEEK was performed with the ALC spectrometer on the πE3 beam line of the Paul Scherrer Institute, Villigen AG, Switzerland. This measurement was made at 360 K and no field modulation was used. µSR experiments on para-dimethoxybenzene and 4,4′-dihydroxybenzophenone were performed using the HELIOS spectrometer on the M20 surface muon channel at the TRIUMF cyclotron facility in Vancouver, Canada. The magnetic field was aligned along the beam direction, and the beam was tuned to give transverse spin-polarization for TF-µSR experiments, and longitudinal spin-polarization for µLCR experiments.
wave field modulation (approx. ±80 G amplitude) was used to suppress baseline fluctuations in \( \mu \)LCR. These measurements were made at 298 K.

3. Results and Discussion

The raw \( \mu \)LCR spectrum of PEEK at 360 K is shown in Figure 2(left). There is a broad feature between 14 and 23 kG that is superimposed on a non-linear background. This background can be attributed to the magnetic field effect on the muon beam spot and positron trajectories in the ALC spectrometer [5]. In keeping with previous practice [6, 7] the background was modelled with a polynomial, which in this case was 4th order. The background-subtracted \( \mu \)LCR spectrum of PEEK is shown in Figure 2(right). Our hypothesis is that this spectral feature is due to multiple overlapping resonances of cyclohexadienyl radicals with restricted rotation. To confirm this we turn to the study of the PEEK sub-units.

![Figure 2.](image)

The TF-\( \mu \)SR results are displayed as Fourier power spectra in Figure 3. The signal at 131 MHz arises from muons in diamagnetic environments whereas muoniated radicals give rise to a pair of precession frequencies almost symmetrically placed about the diamagnetic peak. Data was collected from positron detectors in phase quadrature, so that negative precessions can be distinguished via complex Fourier transformation. The signal at -131 MHz in the right-hand spectrum is an artifact (ghost frequency of the strong diamagnetic signal caused by imperfect quadrature). A single radical was detected from the \textit{para}-dimethoxybenzene sample and two from 4,4'-dihydroxybenzophenone. The precession frequencies were determined by fitting the original \( \mu \)SR time spectra, and the muon hyperfine constants were calculated either from the separation of radical precession frequencies or from the stronger radical precession and the diamagnetic frequency, using standard formulae:

\[
A_\mu = \nu_{R2} - \nu_{R1}
\]

\[
A_\mu = 2\left(\nu_e + \nu_{R1}\right)\left(\nu_\mu - \nu_{R1}\right)\left(\nu_e - \nu_\mu + 2\nu_{R1}\right)
\]

where \( \nu_{R1} \) and \( \nu_{R2} \) are the radical precession frequencies, and \( \nu_e \) and \( \nu_\mu \) are the electron and muon Larmor frequencies. All three radicals exhibit large hyperfine constants (Table 1) characteristic of substituted cyclohexadienyl radicals. There was no evidence to support the formation of a ketyl radical by Mu addition to the ketone group of the 4,4'-dihydroxybenzophenone.
Figure 3. Transverse-field μSR spectra at 9.65 kG obtained from (left) 1.5 M para-dimethoxybenzene in tetrahydrofuran; and (right) 1.05 M 4,4′-dihydroxybenzophenone in ethanol. Radical precession signals are marked with arrows.

Table 1. Muon hyperfine constants ($A_\mu$) determined from TF-μSR and calculated $\Delta_1$ avoided level-crossing fields ($B_{\Delta_1}^{\text{LCR}}$).

| Parent molecule                  | $A_\mu$ / MHz | $B_{\Delta_1}^{\text{LCR}}$ / kG |
|----------------------------------|----------------|----------------------------------|
| para-dimethoxybenzene           | 426.8(1)       | 15.668(4)                        |
| 4,4′-dihydroxybenzophenone       | 473.8(1)       | 17.394(4)                        |
| 4,4′-dihydroxybenzophenone       | 504.2(3)       | 18.510(11)                       |

The $\mu$LCR results also support the conclusion that one cyclohexadienyl-type radical is formed from the para-dimethoxybenzene and two such radicals from 4,4′-dihydroxybenzophenone. The resonances displayed in Figure 4 are typical for the methylene (-CHMu-) fragment of a cyclohexadienyl. Proton hyperfine constants were calculated from the resonance field positions using the standard formula [8],

$$B_{\text{LCR}} = \frac{1}{2} \left[ \frac{(A_\mu - A_p)}{(\gamma_\mu - \gamma_p)} - \frac{(A_\mu + A_p)}{\gamma_e} \right]$$

and are included in Table 2. In principle there is ambiguity in assigning the two resonances from dimethoxybenzene to the two radicals detected by TF-μSR. In practice the relative signal

Table 2. Proton hyperfine constants ($A_p$) determined from $\Delta_0$ avoided level-crossing fields ($B_{\Delta_0}^{\text{LCR}}$), and the hyperfine isotope effect.

| Parent molecule                  | $B_{\Delta_0}^{\text{LCR}}$ / kG | $A_p$ / MHz | $A_\mu/A_p$ |
|----------------------------------|----------------------------------|-------------|-------------|
| para-dimethoxybenzene            | 16.999(2)                       | 109.0(1)    | 1.23        |
| 4,4′-dihydroxybenzophenone       | 19.064(4)                       | 117.4(1)    | 1.27        |
| 4,4′-dihydroxybenzophenone       | 20.402(8)                       | 122.8(4)    | 1.29        |
Figure 4. Avoided level-crossing spectra obtained from (left) 1.5 M para-dimethoxybenzene in tetrahydrofuran; and (right) 1.05 M 4,4ʻ-dihydroxybenzophenone in ethanol.

amplitudes and the consistent ratio of muon to proton hfcs leaves little doubt that the assignment of Table 2 is correct.

DFT calculations were carried out to help assign structures to the three radicals detected experimentally. The Gaussian 09 suite of programs was used to optimize molecular geometries of potential muoniated radicals and compute their isotropic hyperfine constants, using the unrestricted B3LYP hybrid density functional and the 6-31G basis set. The muonium atom was explicitly included in the calculations as an isotope of H with mass 0.113429 u and magnetic moment 8.6578226 $\mu_N$. It is thus possible to take account of isotope effects by calculating vibrationally averaged hyperfine constants. Table 3 lists hyperfine constants calculated for the reference geometry (identical for all H isotopes) and vibrationally averaged at 298 K. In the final column the experimentally determined values are compared with calculated values for the reference geometry, because that is the isotope effect most often quoted in the literature. The structures of the radicals are displayed in Figure 5.

Table 3. Muon and proton hyperfine constants calculated for the reference geometry ($A_0$) and as vibrationally averaged at 298 K ($A_{298}$).

| Parent molecule     | Radical | Nucleus | $A_0$ / MHz | $A_{298}$ / MHz | $A_{exp}/A_0$ |
|---------------------|---------|---------|-------------|-----------------|--------------|
| para-dimethoxybenzene | 1       | $\mu$   | 425.6       | 520.9           | 1.00         |
| para-dimethoxybenzene | 1       | $p$     | 138.0       | 132.3           | 0.79         |
| 4,4ʻ-dihydroxybenzophenone | 2 | $\mu$   | 425.5       | 538.7           | 1.11         |
| 4,4ʻ-dihydroxybenzophenone | 2      | $p$     | 138.1       | 133.1           | 0.85         |
| 4,4ʻ-dihydroxybenzophenone | 3      | $\mu$   | 448.5       | 510.7           | 1.12         |
| 4,4ʻ-dihydroxybenzophenone | 3      | $p$     | 154.9       | 139.3           | 0.79         |

The similarity of isotope effects for Mu adducts of 4,4ʻ-dihydroxybenzophenone supports the assignment of structures implicit in the ordering of data in Table 3. Calculations were also carried out for the radical formed by Mu addition to the benzophenone ketone. As expected, the muon hyperfine constant is much smaller than those determined by TF-$\mu$SR, nor could such a radical account for the LCR resonances. Finally, the Mu addition to ketones is known to be much slower than addition to aromatic rings [9]. This possibility is therefore rejected.
Figure 5. Muoniated radicals identified in this work.

Inspection of Tables 1-3 shows that there is reasonable agreement between the calculated hyperfine constants and the experimental results. However, although the inclusion of vibrational averaging addresses the isotope effect, there is still not a perfect match. Possible factors for the discrepancy include the use of a relatively modest basis set, the neglect of solvent effects, and inaccurate calculation of vibrational frequencies, which leads to overestimation of the temperature effect (cf. $A_{01}$ and $A_{298}$ in Table 3). Preliminary investigations suggests that this last factor is the major source of the discrepancy.

4. Conclusions
Extrapolating the results of this investigation of the monomer subunits of PEEK, it is clear that overlapping resonances from radicals formed by Mu addition to benzene rings in the polymer can account for the broad $\mu$LCR signal observed in PEEK. It is therefore concluded that PEEK sample cells are unsuitable for many types of $\mu$SR experiment, in particular those involving muonium or muoniated free radicals, because the PEEK polymer can produce signals which could interfere with those of the sample under study.

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References
[1] Johnson C, Cottrell S P, Ghandi K and Fleming D G 2005 J. Phys. B: At. Mol. Opt. Phys. 38 119
[2] Patel P, Hull T R, McCabe R W, Flath D, Grasmeder J and Percy M 2010 Polym. Degrad. Stab. 95 709
[3] Roduner E, Brinkman G A and Louwrier P W F 1982 Chem. Phys. 73 117
[4] Cox S F J, Geeson D A, Rhodes C J, Roduner E, Scott C A and Symons M C R 1986 Hyp. Int. 32 763
[5] Stoykov A, Scheuermann R, Sedlak K, Shiroka T and Zhuk V 2009 Physica B 404 986
[6] McKenzie I, Scheuermann R and Sedlak K 2012 J. Phys. Chem. A 116 7765
[7] McKenzie I, Cammidge A N, Gopee H, Dilger H, Scheuermann R, Stoykov A and Jayasooriya U A 2013 Phys. Rev. E 87 012504
[8] McKenzie I 2013 Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. 109 65
[9] Barnabas M V and Walker D C 1991 Can. J. Chem. 69 1252