A Brief Survey of $\beta$-Detected NMR of Implanted $^8\text{Li}^+$ in Organic Polymers

F H McGee, I McKenzie, T Buck, C R Daley, J A Forrest, M Harada, R F Kiefl, C D P Levy, G D Morris, M R Pearson, J Sugiyama, D Wang and W A MacFarlane

1 Department of Physics, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada
2 TRIUMF, Vancouver, B.C. Canada, V6T 2A3
3 Department of Chemistry, Simon Fraser University, Burnaby, B.C. Canada, V5A 1S6
4 Department of Physics and Astronomy, University of Waterloo, Waterloo, Ont. Canada N2L 3G1
5 Toyota Central Research and Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan
6 Canadian Institute for Advanced Research, Canada
7 Chemistry Department, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada

E-mail: wam@chem.ubc.ca, iain.mckenzie@triumf.ca

Abstract. Unlike the positive muon, we expect the chemistry of the implanted $^8\text{Li}^+$ $\beta$-NMR probe in organic polymers to be simply that of the monovalent ion, but almost nothing is known about the NMR of isolated $\text{Li}^+$ in this context. Here, we present a brief survey of $^8\text{Li}^+$ $\beta$-NMR in a variety of insulating polymers at high magnetic field, including polyimide, PET, polycarbonate, polystyrene and polyethylene oxide. In all cases, we find a large-amplitude, broad Lorentzian resonance near the Larmor frequency, consistent with the expected diamagnetic charge state. We also find remarkably fast spin-lattice relaxation rates $1/T_1$. There is very little dependence of either linewidth or $1/T_1$ on the proton density, the main source of nuclear dipolar magnetic fields, leading us to conclude the main contribution to both broadening and spin relaxation at room temperature is quadrupolar in origin. This behaviour is very different from crystalline insulators such as MgO and Al$_2$O$_3$, and suggests that $^8\text{Li}^+$ $\beta$-NMR will be an important probe of polymer dynamics. Additionally, we note dramatically different behaviour of one sample above its glass transition, motivating the construction of a high temperature spectrometer to enable further exploration at elevated temperature.

1. Introduction

Our understanding of polymers has made great strides in recent years thanks to the emergence of new analysis techniques, but many of their properties remain a mystery. One area where this is particularly true is the study of depth-dependent properties of polymers. $\beta$-detected NMR ($\beta$-NMR) has a depth resolution on the order of a few nanometers in the surface layer, allowing detailed studies of depth dependence. This technique, analogous to low energy $\mu$SR, uses the anisotropic beta decay to measure magnetic resonance and relaxation of extremely dilute implanted radioactive probes. At TRIUMF’s Isotope Separator and Accelerator (ISAC) facility [1] a dedicated system for producing high intensity spin polarized beams of $\beta$-NMR probes is routinely used to study depth dependent phenomena in crystalline solids [2], but only recently...
has this capability been applied to more disordered materials such as glassy organic polymers. Here we present the results of preliminary experiments conducted on several polymers to assess the viability of the β-NMR technique (using the $^8\text{Li}^+$ probe) as a tool to study their properties across a wide range of temperatures and conditions.

2. Experimental

β-NMR measurements for this experiment were performed at the ISAC facility at TRIUMF, using an optically pumped, highly polarized beam of radioactive $^8\text{Li}^+$ to implant ions into the sample at varying energies in the range 0.1-30 keV. The $^8\text{Li}$ nucleus has spin $I = 2$, gyromagnetic ratio $\gamma = 6.3015 \text{ MHz/T}$, and electric quadrupole moment $Q = +31.4 \text{ mb}$. The spin is polarized by in-flight optical pumping to polarization $\sim 70\%$. Resonances were acquired with continuous wave (CW) transverse radiofrequency (RF) magnetic field with frequency stepped slowly relative to the $^8\text{Li}$ lifetime of 1.21 s through a frequency range around the $^8\text{Li}^+$ Larmor frequency. A static magnetic field of 6.55 T was applied perpendicular to the sample surface (parallel to both the beam and the spin polarization).

Three of the samples (Kapton (polyimide), PC (polycarbonate) and PET (polyethylene terphthalate)) were freestanding polymer foils used as templates for nanowire growth in swift heavy ion tracks produced at the GSI [3]. The polystyrene (PS) films were spin-coated on $\text{Al}_2\text{O}_3$ substrates [4]. Polystyrene-d3 and d5 are deuterated along the molecular backbone and phenol side-groups respectively, while polystyrene-d8 is fully deuterated. Polyethylene oxide (PEO) was also spin-coated on $\text{Al}_2\text{O}_3$[5]. All of the thin films were approximately 200 nm thick. At the implantation energies used, we expect none of the $^8\text{Li}^+$ to penetrate through to the substrate. The polymer properties are summarized in Table 1 and the structures are shown in Figure 1. All data was taken at room temperature, except the PEO which was somewhat colder at 260 K.

| Sample                          | $\rho_p$ (mol/cm$^3$) | $T_g$ (K) |
|---------------------------------|-----------------------|-----------|
| Polystyrene-d8 (0.9 kg/mol) film| 0.000                 | 270       |
| Polystyrene-d5 (25.3 kg/mol) film| 0.030                 | 373       |
| Polymide (Kapton 50HN) foil     | 0.037                 | 658       |
| Polystyrene-d3 (22.3 kg/mol) film| 0.050                 | 373       |
| PET (Hostaphan RN) foil         | 0.058                 | 342       |
| Polycarbonate foil              | 0.066                 | 420       |
| Polystyrene (1.140 kg/mol) film | 0.081                 | 293       |
| Polyethylene oxide film          | 0.103                 | 223       |

3. Results and Discussion

β-NMR spectroscopy provides information about the local environment of lithium ions, which will be interacting with the different functional groups of the polymers. The lithium ion will preferentially stop in regions of high electron density. We propose stopping sites based on the structures of the polymers. The main areas where $^8\text{Li}^+$ is likely found would be adjacent to a phenyl or aromatic ring system, where it is bound via the cation-π interaction, bound to the oxygen of a carbonyl group and bound to an ether or ester oxygen. The final location of $^8\text{Li}^+$ will be a delicate balance of the interactions with all the neighbouring functional groups.
Figure 1. Structures of the polymers studied with β-NMR

We have used DFT calculations (RB3LYP/6-311+G(d,p)) of model compounds (benzene, dimethyl ether, acetone and ethylene carbonate) to estimate the binding energy ($BE$) for Li$^+$ bound to the different functional groups present in the polymers (Figures 1,2). The calculations were performed with the Gaussian 09 package. $BE = [E(\text{Li}^+ + E(X)] - E(\text{Li}^+ - X)$, where $E$ is the internal energy and $X$ is the molecule to which the lithium ion is bound. The calculated $BE$ values are shown in Table 2 and are in good agreement with experimental values and previous calculations by Blint [6]. All of the sites have quite large $BE$, although the interaction with carbonyl groups is preferred. In PS it is likely that Li$^+$ is sandwiched between two adjacent phenyl rings with a total $BE$ of 265.3±15.1 kJ/mol [7]. In the other polymers Li$^+$ is likely to interact with multiple functional groups, so that the effective $BE$ will be larger than that of a single molecule. The preferred interaction with carbonyl groups means that in most of the polymers studied here the $^8\text{Li}^+$ is not likely to be close to protons.

Table 2. Summary of experimental and calculated Li$^+$ binding energies for model compounds

| Molecule                     | Experimental $BE$ | Experimental $BE$ | B3LYP/6-311+G(d,p) $BE$ |
|------------------------------|-------------------|-------------------|--------------------------|
|                              | kJ/mol            | kJ/mol            | kJ/mol                   |
| Benzene                      | 161.1±13.5$^c$    | –                 | 160.6                    |
| Dimethyl ether               | 165.0±10.6$^d$    | 165               | 170.1                    |
| Acetone                      | 186$^e$           | 200               | 202.6                    |
| Ethylene carbonate           | –                 | 218               | 215.8                    |

$^a$Ref [6] $^b$Present work $^c$Ref. [7] $^d$Ref. [8] $^e$Ref. [9]
Figure 2. Structures of lithium ions (purple) bound to (a) benzene, (b) dimethyl ether, (c) acetone and (d) ethylene carbonate. Carbon = grey; oxygen = red; hydrogen = white.

Figure 3. (a) $\beta$-NMR resonance spectrum of $^8\text{Li}^+$ in the fully deuterated PS film at 300 K and 6.55 T and (b) the resonance linewidth in the full set of polymer samples as a function of the proton density. The measurements were made at 300 K except for PEO, which was studied at 260 K.

An example of a time-integral resonance spectrum is shown in Figure 3a. All of the resonance spectra were fit with a single Lorentzian function and the linewidth does not appear to depend on the proton density (Figure 3b). An example of a time-differential relaxation measurement is shown in Figure 4a. The relaxation was fit to the stretched-exponential function $e^{-t/(T_1)^\beta}$ with $\beta$ fixed to 0.5. The root exponential relaxation is probably the result of a distribution of relaxation times due to the microscopic inhomogeneity of the $^8\text{Li}^+$ stopping sites. Stretched exponential relaxation has been observed in dielectric relaxation [10] and NMR [11, 12] studies of glassy materials. The relaxation is remarkably fast in all the polymer samples compared to wide band gap crystalline insulators we have studied at comparably high magnetic fields (e.g. $\text{Al}_2\text{O}_3$ and MgO). $1/T_1$ does not depend significantly on the proton density except for PEO, where the spin-lattice relaxation is much faster than in the other polymers.

The spin relaxation rate will depend on the EFG as well as on the distance between $^8\text{Li}$ and surrounding protons. The linewidth of the resonance does not depend on the proton density and this is most dramatically apparent among the polystyrene samples with varying levels of
Figure 4. (a) Spin-lattice relaxation measurement of PEO film at 300 K and 6.55 T and (b) the spin-lattice relaxation rate versus proton density for the full set of polymer samples.

deuteration, which have almost identical FWHM values. This suggests that the nuclear magnetic dipolar field from the protons (i.e. dipolar broadening) plays a negligible role in broadening the resonance. Contributions from other nuclear moments ($^{13}$C etc.) are even smaller, so we conclude the linewidth is unrelated to the magnetic dipolar interaction.

One possible source of magnetic fields that could contribute to both the resonance and relaxation is long-lived paramagnetic radical species produced via radiolysis during the $^8$Li$^+$ implantation. Electronic magnetic moments would produce a large hyperfine field on the $^8$Li. In the simplest case of isolated nearby radicals, however, such fields would behave as an isolated local moment with net fields scaling as $B/T$. Temperature dependent studies in PEO [5] and PS [4] do not reveal such temperature dependence.

Instead, we suspect that the quadrupolar interaction between the $^8$Li $^+$'s small nuclear electric quadrupole moment and the local electric field gradient (EFG) at the $^8$Li$^+$ site must be the dominant source of both resonance broadening and spin lattice relaxation. For a single well-defined site, the quadrupolar interaction splits the resonance into a pattern of four quadrupole satellites centred on the undisturbed resonance frequency, e.g. in bismuth [13] or Al$_2$O$_3$ [14]. In a noncrystalline glassy material such as a polymer, the EFG varies based on the local configuration of polymer surrounding $^8$Li$^+$, resulting instead in a single broadened quadrupolar “powder pattern”. The EFG is expected to be somewhat material dependent, but would be independent of proton density as observed. This hypothesis will be tested by measuring the magnetic field dependence of the linewidth. In the case of quadrupolar broadening, the width should be field independent in contrast to the electronic magnetic fields of radicals.

Fluctuations of the EFG due to motion of the polymer chains or $^8$Li$^+$ itself will give rise to spin relaxation. Quadrupolar relaxation is important in conventional NMR of quadrupolar nuclei [15]. The similar behaviour in Kapton, PET, PC and high-molecular-weight ($M_w$) PS is perhaps not surprising as the measurements were made significantly below $T_g$ where the polymer chains are not highly mobile. The spin relaxation is dominated by the static characteristics of the local environments of $^8$Li$^+$ which are likely similar. The strength of the interaction between $^8$Li$^+$ and the functional groups of the polymers suggests that $^8$Li$^+$ is not diffusing at the temperatures where the measurements were made.

The measurements on low-$M_w$ PS were made above $T_g$ and suggest that the polymer dynamics are faster than the high-$M_w$ polymer [4]. We suggest that $^8$Li$^+$ is not diffusing above $T_g$ because of the strength of the interaction with the neighbouring phenyl rings and that these phenyl rings
cause it to be partially encapsulated. We have recently measured the depth dependence of the average spin-lattice relaxation rate and shown that there is a layer near the surface \(\sim 10\ \text{nm}\) thick with faster dynamics than the bulk [4].

PEO is well known to be a Li\(^+\) ionic conductor [16] and the measurements were made above \(T_g\). \(^8\text{Li}^+\) diffusion is likely important in PEO because the lithium ion is not encapsulated as in PS and motion of the polymer chains will bring suitable sites close to \(^8\text{Li}^+\) and make it favourable to hop. The hopping of \(^8\text{Li}^+\) results in a fluctuating EFG and leads to the much faster \(1/T_1\). The temperature dependence of the average spin-lattice relaxation time up to 317 K was used to determine the activation energy for hopping in pure PEO and PEO with 30 wt.% of LiCF\(_3\)SO\(_3\) [5].

4. Conclusions
We believe that \(^8\text{Li}^+\) will be an important probe of the dynamics of polymeric materials, particularly in thin films and near the free surface where other techniques (notably conventional NMR) have very limited applicability. It will be particularly informative to make measurements closer to \(T_g\) but the maximum temperature of the current spectrometer is \(\sim 320\ \text{K}\). We are currently designing a high temperature spectrometer to enable measurements through the glass transition in all the polymers in the current study.

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