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Abstract

We report 8Li spin lattice relaxation in two forms of the molecular glass TPD, one a normal glass and one prepared in an ultrastable configuration. The relaxation is remarkably fast, similar to 8Li relaxation in other organic materials and shows a stretched exponential behavior typical of glasses with a small stretching exponent $\beta = 0.3$. At low temperature, there is little or no difference between the two glasses, while above 250 K, the relaxation in the denser ultrastable form is faster. In addition, in this temperature range, the data shows a significant thermal hysteresis.

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Exploring the Dynamics of Glasses Using Beta Detected NMR

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We report ^{8}Li spin lattice relaxation in two forms of the molecular glass TPD, one a normal glass and one prepared in an ultrastable configuration. The relaxation is remarkably fast, similar to ^{8}Li relaxation in other organic materials and shows a stretched exponential behavior typical of glasses with a small stretching exponent $\beta = 0.3$. At low temperature, there is little or no difference between the two glasses, while above 250 K, the relaxation in the denser ultrastable form is faster. In addition, in this temperature range, the data shows a significant thermal hysteresis.

KEYWORDS: Molecular glasses, TPD, β-NMR

1. Introduction

Glasses combine the disordered structure of a liquid with the mechanical properties of a solid. Ordinary molecular glasses are prepared by cooling the liquid as slowly as possible while still avoiding crystallization. A glass is formed when the molecular motion becomes too slow for the constituent molecules to attain equilibrium configurations; the temperature at which this occurs is defined as the glass transition temperature (T_g). Glasses are thermodynamically unstable, and they generally anneal slowly, undergoing molecular rearrangements that explore a complex energy landscape. However, since the glass is solid-like, the process of "aging" is very slow. In contrast, ultrastable molecular glasses can be obtained by vapour deposition of a thin film onto a substrate held at a temperature below the glass transition [1-3]. The most stable of these are formed when the temperature is 70-90% of T_g. Ultrastable glasses (USG) have higher densities, and are more stable than the corresponding ordinary glasses (OG). It has even been suggested that they are equivalent to annealing the conventional glass for thousands of years [4]. Here

we use spin-lattice relaxation of implanted [8]Li to probe potential differences in the high frequency molecular dynamics between the USG and OG states of a molecular glass.

Aside from higher thermal stability, the material properties of USGs may differ substantially from ordinary glasses, with consequences for wide-ranging applications from drug delivery to organic electronics [5]. Calorimetric evaluation of the stability of ultrastable glasses reveals a higher transition temperature than the ordinary glass counterpart. It has been postulated that the improved stability is due to the kinetics of the vapour deposition process. During deposition, the surface layer is suggested to be in a liquid-like state, and thus the molecules have time to reach a more favourable configuration before freezing. Studies of the diffusion have suggested that the molecular dynamics in the two types of glasses are substantially different [1,6,7].

Glasses have extremely complex relaxational dynamics with timescales varying from picoseconds, for atomic vibrations, to thousands of years, for molecular rearrangements or "aging" [8,9]. These processes are mainly studied using dielectric spectroscopy however; this measurement is a bulk probe, and to completely understand the processes on a molecular level a local probe is essential. One such local probe is conventional NMR which can reveal information on both average properties and their intrinsic microscopic heterogeneity [10,11]. However, conventional NMR is difficult or impossible in thin films, due to the intrinsically weak signal.

Previous β-NMR experiments on polymers [12,13], demonstrated that the [8]Li spin lattice relaxation (SLR) is sensitive to molecular dynamics through the fluctuating quadrupolar interaction. In this paper, we report a preliminary exploration into the molecular dynamics in an ultrastable and an ordinary molecular glass thin film. The glass studied in this paper was made from the organic semiconductor N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine, or TPD. This medium size molecule (see Fig. 1) has a molecular weight of 516 amu, a glass transition temperature of 342.1 K, and a band gap of 3.1 eV. Due to the polyaromatic structure of TPD, we expect [8]Li to bind strongly with the phenyl rings as has been observed for polystyrene [12,13], and this will inhibit [8]Li diffusion.

2. Experimental

2.1 Sample Preparation

Two thin films of TPD glass (see Fig. 1) were vapour deposited onto sapphire substrates held at a constant temperature. For the ultrastable glass, the substrate was maintained at a temperature of 279 K (or $0.85T_g$) during the deposition, while for the ordinary glass it was 330 K [14]. The film thicknesses were determined to be 200±10 nm by ellipsometry.

Figure 1. Molecular structure of TPD, a triphenyl amine derivative with IUPAC name: N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine

2.2 Spectroscopy

Beta detected nuclear magnetic resonance (β-NMR) measurements were performed at the ISAC facility at TRIUMF. β-NMR is a magnetic resonance technique in which a
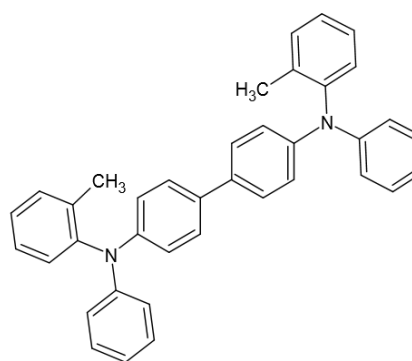
laser polarized radioactive ion beam is implanted into the sample of interest. The most common isotope used, and the one used in this experiment, is [8]Li which undergoes a beta decay. The polarization is monitored by measuring the asymmetry of the beta decay along the initial polarization direction using suitably placed detectors. By changing the energy of the incident ion beam between 0.1 and 30 keV it is possible to analyze thin films, interfaces, and surfaces, similar to Low Energy μSR, but complementary due to its much longer radioactive lifetime and additional quadrupolar relaxation channel. For this experiment, SLR measurements were performed with a pulsed beam of [8]Li, and with no applied RF. For this measurement, the asymmetry is measured as a function of time, which provides information on the different relaxation mechanisms in the system. For the SLR measurements performed in this experiment, the pulse length was 4 s, and the total measured time was 16 s.

3.   Results and Discussion

The asymmetry as a function of time for the ultrastable and ordinary glass of TPD is shown in Fig. 2 for four different temperatures at an applied field of 6.55 Tesla. The relaxation is quite fast, typical of the organic polymer glasses we have studied [12,13]. At 100 K, there is not much difference between the two glasses. However, as the temperature is increased above room temperature the difference between the two glasses increases. In fact, from a visual inspection, it appears as if the relaxation rate in the ultrastable glass becomes faster than the relaxation in the ordinary glass. In order to model the temperature dependence of the relaxation rates, the SLR spectra were fit using the following stretched exponential function:

$$P(t, t') = A_o e^{-\left(\frac{t-t'}{T_1}\right)^{\beta}}, \tag{1}$$

where t' is the time of implantation, T_1 is the spin-lattice relaxation time, and β is the stretching exponent. This is convoluted with the 4 s beam pulse in order to fit the data. Purely phenomenologically, we found that good fits to all the data could be obtained with a fixed stretching exponent (β) of 0.3. This has the practical advantage that only one parameter (T_1) is required to describe the relaxation. Examples of the fit curves can be seen overlaid with the raw data in Fig. 2. The small value of β might suggest the presence of a nonrelaxing component. For the fastest relaxation (at the highest temperature), however, allowing β to vary yields an upper limit for a nonrelaxing fraction of only a few percent. Figure 3 shows the temperature dependence of the
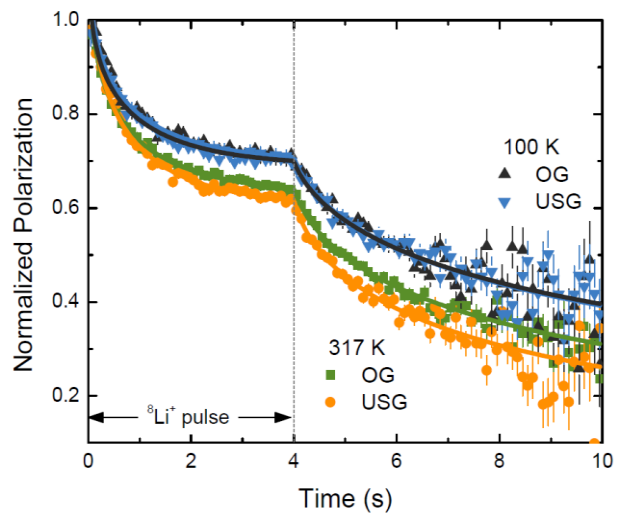

Figure 2. Comparison of the raw spin lattice relaxation spectra of the ultrastable and ordinary glasses at 100 K and 317 K. In addition, the fits to the data have been plotted with solid lines. The data was taken at 6.55 T, and 6.9 keV.

relaxation rate in the USG and OG samples upon cooling from room temperature. The relaxation rates look identical within error below 250 K however, above 250 K the relaxation in the USG becomes faster.

As in polystyrene [12,13], we expect the implanted $^8Li^+$ in TPD is rather strongly bound to one or more of the phenyl rings of the molecule. This binding is sufficiently strong that one can consider the $^8Li^+$ as bound, and not diffusing. In this situation, high frequency molecular dynamics will modulate the electric field gradient at the $^8Li^+$ site, with a spectral component at the nuclear Larmor frequency (~41.3 MHz) that causes spin-lattice relaxation. The high frequency molecular motion that gives rise to the ^8Li relaxation is probably related to the wagging and rotation of the phenyl rings, in analogy of what has been observed for polystyrene [13,14]. The quadrupolar interaction is likely the dominant source of relaxation for the ^8Li, making it qualitatively similar to that of spin 1 deuterium NMR in organic and polymeric glasses.

For polymeric glasses, such as polystyrene, compressing the polymer triaxially (causing densification) is thought to be equivalent to "aging" the material for thousands of years. ^2H NMR studies on densified polystyrene glasses, have shown an increase in the ^2H relaxation rate with increasing densification [15]. This result is still not well understood; however, the answer may be related to why the relaxation rate is higher in the ultrastable TPD glass. The temperature dependence of the relaxation rate has an activated character at higher temperatures (Inset of Fig. 3), representing the average activation barrier for a relaxation process in TPD glass. The barriers (slopes) appear quite similar, but higher temperatures are required to determine whether there is a significant difference between USG and OG states. When the samples were heated from low temperature, we found some hysteresis in the relaxation. Specifically, the relaxation rate in both samples was systematically faster than during the cooling cycle shown in Fig. 3. We do not believe this is due to incomplete thermalization of the sample during the measurements, but rather is intrinsic to the material. Further studies will be required to understand this effect.
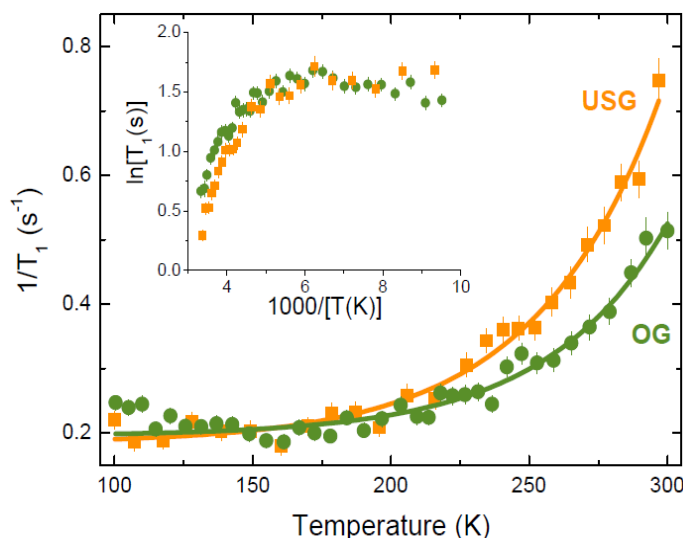

Figure 3. Relaxation rate as a function of temperature for the ultrastable and normal glass, during cooling from room temperature at an average rate of about 20 K per hour. The lines are guides for the eye. The inset shows the relaxation times on an Arrhenius scale.

4. Summary

A comparison was performed between the ^8Li relaxation rate in an ultrastable and an ordinary molecular glass of TPD. The experiments show that there is not much difference

between the ^{8}Li relaxation rates below 250 K. However above 250 K, the relaxation rate in the USG becomes faster than in the OG. Although puzzling, it is consistent with results from ^{2}H NMR on densified polystyrene glasses; where the relaxation rate was found to be faster in the "older" (denser) polystyrene [15].

The ^{8}Li relaxation rate in both molecular glasses also showed temperature hysteresis. We are confident that the temperature hysteresis does not arise from the incomplete thermalization of the molecular glass. However, the origin of the hysteresis currently remains a mystery.

Acknowledgments

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