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Dynamics of polyurethane elastomers by muon spin relaxation

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Abstract

Muon spin relaxation has been used to study the dynamics of hard domains in three polyurethane elastomers based on methylenediphenyleneisocyanate. Repolarisation curves of the muonium spin show the muon implants to the aromatic ring of the hard segments. Qualitative changes in the muon spin relaxation rate indicative of phenyl ring dynamics can be seen as the polyurethane is heated from 100 to 470 K. Interpretation of the changes seen in the muon spin relaxation rate are hampered by the absence of a detailed theoretical understanding. Further, poor muon counting statistics of this initial experiment make an accurate analysis impossible. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polyurethane elastomers are characterised by a segmented structure consisting of alternating flexible polyester or polyether segments and stiff segments formed in the reaction between methylenediphenyleneisocyanate (MDI) and chain extender molecules [1]. As the polymerisation reaction proceeds, a phase-separated morphology develops composed of glassy and rubbery domains resulting from the incompatibility of these so-called hard and soft segments. Mechanical strength is provided by the hard microdomains that can be thought of as both rigid reinforcing particles and physical crosslink sites. Clear differences are seen between the dynamics of the polymer segments in the hard and soft domains. In the hard domain, the MDI molecules are essentially rigid as shown by ^{2}H-NMR of specifically MDI labelled polyurethane [2] elastomer, whereas ^{1}H-NMR of the soft segments indicate fast pseudo-isotropic motion [3]. Upon heating the polyurethane elastomer, mechanical strength is lost, whilst at the same time there is a growth in an ^{2}H-NMR signal attributable to fast isotropic type motion. These changes are consistent with hard segments dissolving into the soft matrix, either through the loss of the smaller domains or the more disordered regions of larger hard domains. Analysis of the mobile fraction seen in the ^{2}H-NMR spectrum in terms of a disorder parameter gives an insight into the polyurethane morphology.

A wider examination of this phenomenon and in particular the study of commercially produced samples is severely limited by the need for ^{2}H isotopic labelling. One possible way to selectively label the hard domains is through the use of muons. Muons are elementary particles produced by the radioactive decay of pions produced normally by the bombardment of protons on a light element target, such as carbon [4]. Muon sources include those at the Rutherford–Appleton Laboratory (UK), PSI (Switzerland), TRIUMF (Canada) and KEK (Japan). Muons when implanted into materials may pick up an electron to form muonium which chemically react by adding preferentially to unsaturated centres creating radicals. The expectation therefore is that muons will add to the aromatic rings in the hard segments rather than the saturated polyester segments. Muonium can be considered as a light isotope of hydrogen with $I = 1/2$ with the physical properties of the radical muoniums so created in the polyurethane dominated by the muon–electron hyperfine interaction. Dynamic processes involving the reorientation of the muon–electron hyperfine interaction can be studied by muon spin relaxation in a manner analogous to ^{1}H-NMR relaxation time studies of motions although the theoretical treatment of the relaxation processes is less well understood.

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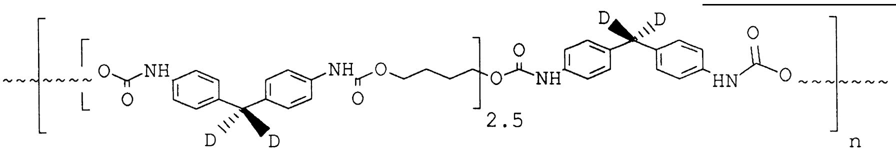
2. Experimental

Longitudinal field muon spin relaxation (LF-μSR) measurements were made on the EMU spectrometer at the ISIS muon facility, Rutherford–Appleton Laboratory, UK. In LF-μSR, the external magnetic field is applied parallel to the direction of the muon spin at the time of implantation with the muon decay events registered in the detectors placed in the forward (F) and backward (B) directions with respect to the initial muon spin direction. This defines the asymmetry $a(t)$ where [5]:

$$a(t) = \frac{F(t) - B(t)}{F(t) + B(t)}.$$

Muon beams are almost 100% spin polarised and although a proportion of this polarisation is lost on implantation, as the muons partition themselves between the coupled muon–electron spin states of the radical product, the observable polarisation is still substantial. The evolution of the polarisation with time of the systems under investigation is analogous to spin–lattice (T_1) relaxation in conventional magnetic resonance.

The main emphasis in the muon experiments was on a polyurethane elastomer which had been used earlier in the ^{2}H-NMR and SAXS experiments to permit an accurate comparison with these results [2,3]. Previous ^{2}H-NMR experiments have shown that the melting of the hard domains caused by the heating cycle is reversible. In this elastomer, the hard segments are based on MDI with 1,4-butanediol chain extender, whereas the soft block phase is a bifunctional poly(ethylene-tetramethyleneadipate) with an average molecular weight of 2000 Da. The backbone of this commercial polyester from ICI plc (Daltocast TA20) consists of adipic acid/ethylene glycol/butanediol in a molar ratio equal to 2:1:1. Given the specific stoichiometry for the reactants, the average structure of the elastomer can be represented by:



The mass fraction of the hard segments, calculated from the above composition, is 0.36. Subsequently, to examine whether the nature of the soft segment influenced the general character of the muon spin relaxation, experiments were also carried out on polyurethane elastomers with two different soft segments: in one case the soft segments were poly(propylene glycol) 2000 and in the other case polytetrahydrofuran (THF). In both cases, the hard segments were MDI and the chain extender 1,4-butanediol with a similar mass fraction of hard blocks.

Strips of the polyurethane elastomer were packed into a 2 mm deep and 40 mm diameter recess in an aluminium plate and covered with a thin Mylar film. High temperature experiments above 120°C were carried out using a titanium plate with a titanium foil screwed into place over the sample to form an airtight container. Typically 20–30 million muon decay events were accumulated for a spectrum at each field and temperature. Data analysis was carried out using an in-house non-linear least squares fitting (UDA version 13.0), according to standard models for the muon implantation and decay process. Muon relaxation decays were best fitted to two exponential decays wherein the fast relaxing component corresponds to muons undergoing some dynamic process within an appropriate correlation time and a slow decaying background component.

3. Theory

3.1. Muon spin relaxation

Molecular dynamic information can be obtained from a study of the variation in the muon spin relaxation rate with temperature [5]. Although the evolution of the muon spin polarisation involves four eigenstates and in principle three relaxation rates, numerical calculations have shown that when the relaxation times differ greatly only one has significant weight, whereas when all have similar weight, the relaxation times are of comparable magnitude [6]. Thus, muon relaxation can be defined by a unique relaxation time. Reorientation induces transitions between the muon–electron spin states, by causing anisotropic or dipolar terms in the muon–electron hyperfine interaction to fluctuate. As a consequence of these transitions, muon polarisation is lost, i.e. they depolarise. Peaks in the relaxation rate will occur when the reorientation rate matches the frequency of the dominant transition between the coupled muon–electron spin states. At an applied field of 20 mT, the muon transition frequency for a muonated benzene will be greater than ~400 MHz indicating that muon spin relaxation is sensitive to motions which have correlation times of the order of 10^{-9}s.

3.2. Repolarisation curves

An approximate value for the hyperfine coupling constant and hence the type of radical formed can be deduced using repolarisation curves [7]. These are plots of the initial asymmetry as a function of the applied field. At low fields, mixing of the muon–electron eigenstates, as shown in the

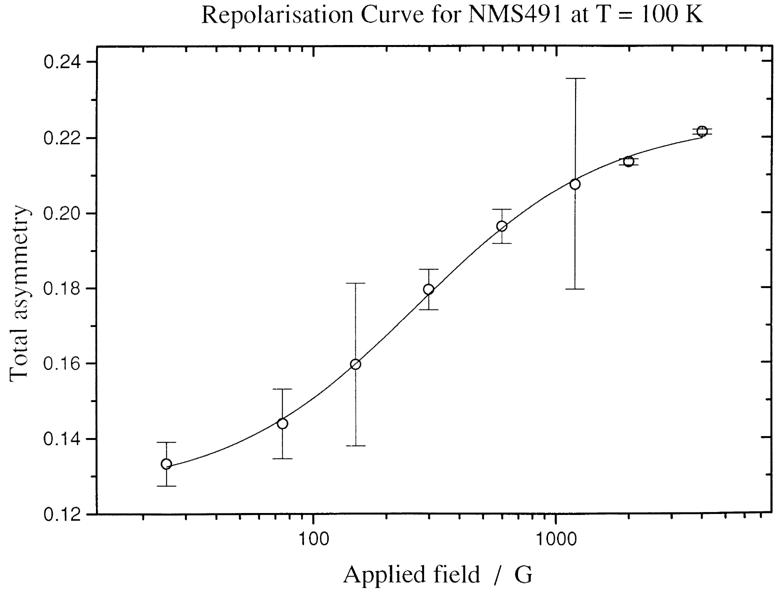


Fig. 1. Repolarisation curve showing the asymmetry of the muon spin polarisation as a function of the applied field at a temperature of 100 K.

Breit–Rabi diagram, leads to a loss of the muon polarisation. In the case of an isotropic hyperfine interaction, the zero field asymmetry has a value of 0.5 which increases with the applied field as the muon–electron states become pure eigenstates and the asymmetry tends towards 1.0, i.e. full asymmetry. The hyperfine field can be estimated from the repolarisation curve as the value of the applied field when the polarisation is 0.75. Only a rough estimate can be made because anisotropic terms and motional effects distort the analysis. Accurate values of the hyperfine coupling constant can be obtained by transverse field μSR [8] and avoided level crossing (ALC) experiments [9].

4. Results and discussion

Repolarisation of the muon asymmetry as a function of applied field at a temperature of 100 K is shown in Fig. 1. From a sigmoidal fit of the asymmetry variation with applied field, the hyperfine interaction can be estimated to be ~20 mT, similar to the value of 18.6 mT found for muonated benzene, indicating that the muon is added to the aromatic ring [10]. In the case of addition to a carbonyl group, a repolarisation field of ~0.9 mT would be expected [11]. The repolarisation curve, therefore, clearly shows that the muons have implanted on the aromatic rings which are

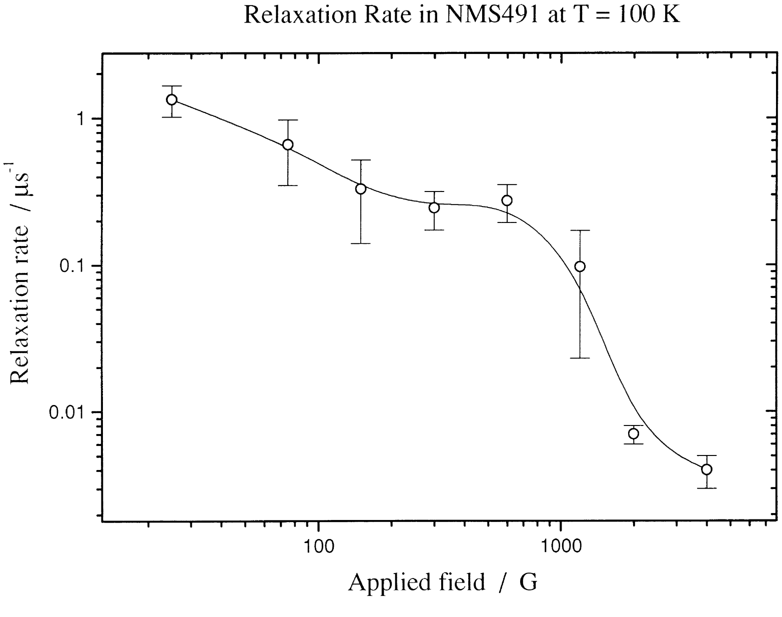


Fig. 2. Muon spin relaxation rate of the fast relaxing component as a function of the applied field at a temperature of 100 K.

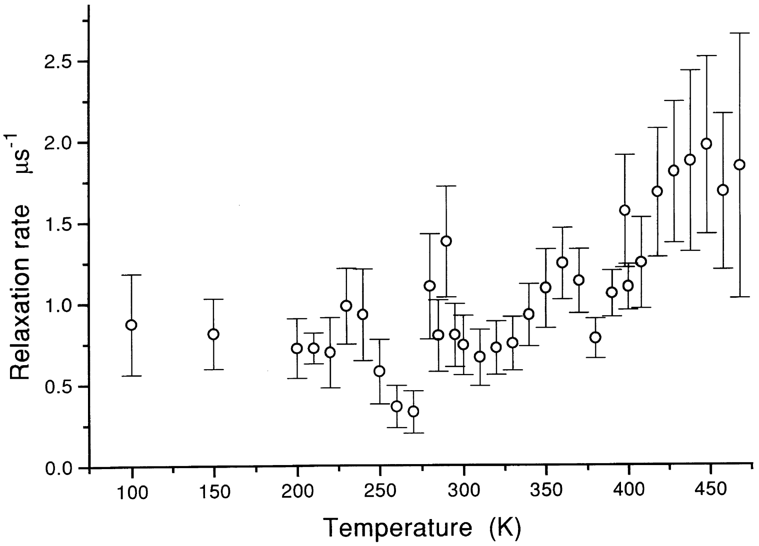


Fig. 3. Muon spin relaxation rate of the fast relaxing component of the poly(ester) urethane as a function of temperature from 100 to 470 K at an applied field of 200 G.

found only in the hard domains. Similar results were obtained for the repolarisation at 400 K indicating that the nature of the muonium radical is not affected by the changes in temperature. As expected, both the poly(propylene glycol) 2000 and poly(THF) soft segment polyurethanes showed similar repolarisation curves indicating that just as in the case of the polyester urethane, the muon is implanted in the aromatic ring.

The variation in the muon spin relaxation with applied field at 100 K from 2.5–400 mT is shown in Fig. 2. Interpretation of the relaxation rate as a function of field is not as straightforward as for NMR, as the energy of the eigenstates as shown by the Breit–Rabi diagram do not diverge monotonically with the field [7]. Thus, at low applied fields, the energy separation between the eigenstates involved in the dominant transition is effectively constant, and the relaxation rate is almost field independent. However, at high-applied fields, the eigenstates diverge. The resulting large energy separation means that the contribution local fluctuating fields can make to the relaxation decreases, with the consequence that the relaxation rate falls. Internal consistency of the repolarisation and relaxation rate data is shown by the switch over between the field independent and field dependent relaxation rates shown in Fig. 2 occurring at an applied field close to the hyperfine field deduced from the repolarisation curve.

The temperature dependence of the muon relaxation rate measured at an applied field of 20 mT is shown in Fig. 3 for

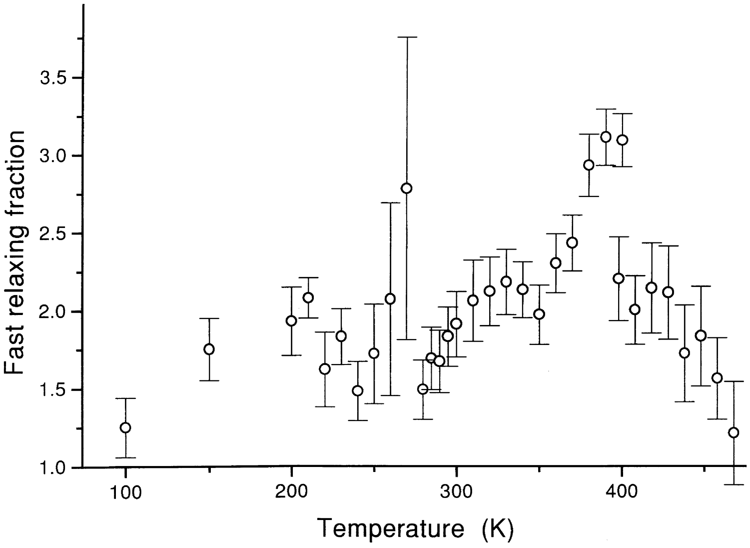


Fig. 4. Muon spin relaxation rate of the fast relaxing component of the the poly(propylene glycol) 2000 urethane as a function of temperature from 220 to 400 K at an applied field of 200 G.

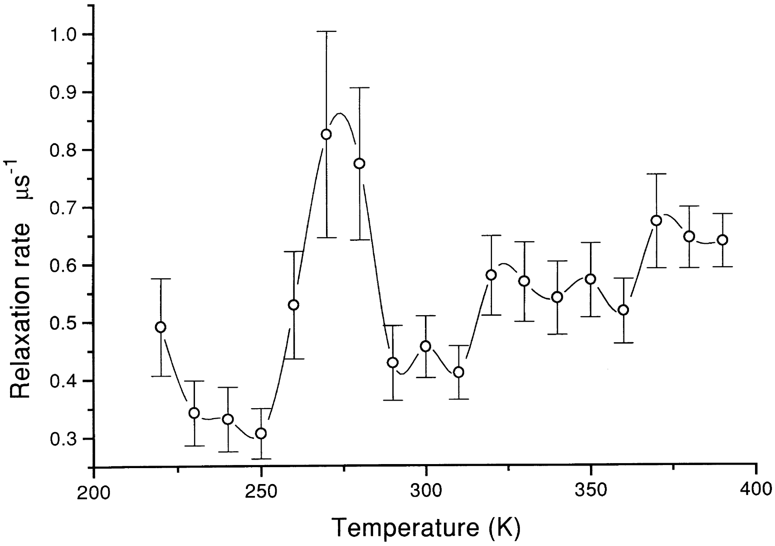


Fig. 5. Muon spin relaxation rate of the fast relaxing component of the poly(THF) urethane as a function of temperature from 220 to 400 K at an applied field of 200 G.

the poly(ester) urethane. In Figs. 4 and 5, the muon relaxation rate as a function of temperature is shown for the poly(propylene glycol) 2000 and poly(THF) urethanes. An applied field of 20 mT was chosen for the temperature studies as a compromise between a high field for regaining the full asymmetry and thus maximising the signal-to-noise ratio and a low field for seeing a fast muon spin relaxation rate which would be measurable. Overall, the data are characterised by relatively large errors in the relaxation rates, despite the large number of muon events accumulated, $20–30 \times 10^6$, which makes the analysis uncertain. Three related factors, two intrinsic to a polyurethane, explain the poor statistics. First, the aromatic ring density within the polyurethane is low given the hard segment mass fraction of only 0.36. Second, at most 16% of the muon events are found in the fast relaxing fraction. In part, this is a reflection of the low conversion of muons to paramagnetic muonium radicals caused by the low density of the aromatic rings. However, perhaps, more importantly, because of the distribution in rates for a dynamic process, at any given temperature, the fraction of aromatic rings exhibiting the appropriate dynamics for fast muon relaxation is small. The rest contributes to the background relaxation. Third, two exponential fittings to noisy data carry with it large errors in the fitted parameters. Despite the rather poor quality of the relaxation rate data, a striking feature of all three polyurethanes is a rather complex variation in the relaxation rate indicative of a number of dynamic processes. In the case of a single dynamic process with a well-defined correlation time, a narrow bell-shaped curve is predicted, with a relaxation rate maximum occurring when the correlation time, τ, matches the condition $\omega\tau = 1$ with ω the appropriate transition frequency from the Breit–Rabi diagram. For a polymer, a distribution in correlation times is expected for any given dynamic process with the consequence that the maximum relaxation rate will be reduced and the curve broadened. At the same time, single exponential fits to the muon relaxation decay curve will show poorer fitting statistics as the mean correlation time approaches the appropriate value for the muon spin–lattice relaxation time. Statistically better fits can be obtained to relaxation decay curves described by a distribution in relaxation times by using a stretched exponential. Although such fits have the added advantage that the value of the exponent gives an indication of the width of the distribution, the flexibility of the function can lead to problems in the interpretation of the parameters especially when the data are of low signal-to-noise ratio.

The changes in the muon relaxation rate below 300 K demonstrate that phenyl ring motion is present before the onset of a more generalised motion caused by “melting” of the hard domains. Pseudo-isotropic line narrowing, reflecting chain melting, is only seen in the ^{2}H-NMR spectra of the methylene deuterated MDI above 295 K. However, the precise nature of the ring dynamics, small angle librations, π flips or continuous rotation cannot be deduced from the relaxation rate data. At a fundamental level, this reflects the lack of detailed descriptions of the muon spin–lattice relaxation rates under conditions of anisotropic motion. Work is in progress to extend the existing theory to deal with this question. Two peaks are seen in the region below 300 K for the poly(ester) urethane: the one at ~240 K coincides with the T_g of the soft phase. Both peaks can be attributable to the dynamics of hard segments dispersed in the soft phase. Upon transition of the soft segments from the glassy the fluid phase at the T_g, the constraints on the hard segments are reduced allowing initially a limited motion of the phenyl rings, in all probability a libration. As the temperature increases further, the spatial constraints are relaxed further and the dispersed hard segments are able to execute larger amplitude motions. Finally at 290 K, the

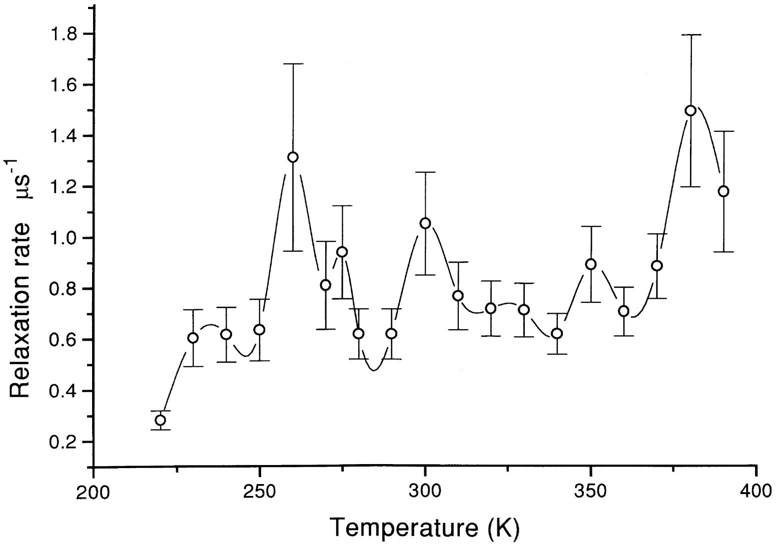


Fig. 6. Fraction of the muon spin polarisation undergoing fast relaxation in the poly(ester) urethane as a function of temperature from 100 to 470 K at an applied field of 200 G.

dispersed hard segments are able to execute the larger amplitude ring motion, in all likelihood a phenyl ring flip, at the requisite frequency for muon relaxation. Thus, 290 K does not correspond to any formal transition as seen in the differential scanning calorimetry or differential mechanical thermal analysis because it represents a dynamic muon "transition" as described above. The absence of changes in the ^{2}H-NMR spectrum of the methylene group demonstrate the limited nature of the overall mobility. Similar low-temperature peaks associated with the phase transitions of soft segment matrix are seen for both the poly(THF) urethane and the poly(propylene glycol) 2000 urethane. For the poly(THF) urethane, the muon relaxation peaks observed at 260 and 300 K correspond closely to those observed in the DSC at ~250 and 293 K. The first thermal transition corresponds to the T_g of the soft block, and the latter the T_m arises from the semicrystalline nature of the soft matrix. It is not possible to identify the muon relaxation peaks with specific phenyl ring dynamics. By analogy with NMR, only the dynamically averaged hyperfine coupling constants from transverse muon spin rotation or ALC experiments can give accurate information about the type of motion. In contrast, for the poly(propylene glycol) 2000 urethane, only a single muon relaxation peak is seen at the temperature, 275 K, well above the soft phase T_g of ~230 K. The most likely explanation is that the onset of the limited phenyl ring motion occurs around or below 220 K, just outside the temperature range studied for this sample. Indeed, there is some evidence to support this from the higher muon relaxation rate observed at 220 K than at 230 K. The observed muon relaxation peak at 275 K thus corresponds to the onset of the high frequency larger amplitude motion. for the hard segments dispersed in the soft matrix.

Above 300 K, the hard domains begin to melt and dissolve into the soft segment matrix, this is accompanied by an increase in the relaxation rate for all three polyurethane samples. No difficulties arise from the motional model in this case, because in the rigid-to-mobile transition, the phenyl ring goes from a rigidly held state to a quasi-isotropic motion. Similar behaviour for the relaxation rate is seen for benzene where the transition from the solid to liquid is associated with a jump in the muon spin relaxation rate [9]. Interpretation of the fast relaxing fraction, shown in Fig. 6 for the poly(ester) urethane, and thus quantitation of the muon relaxation results in terms of a fraction of hard segments undergoing a rigid-to-mobile transition, is complicated by three factors. First, the effect of the muon instrument dead time. As the muon relaxation becomes faster, an increasing fraction will not be observed, as the muons will have relaxed back to thermal equilibrium before data collection. Second, the derived relaxation rate may be an artificial single parameter describing the muon relaxation rate for muons executing a motion with a range in frequencies. The difficulty here is a lack of knowledge about the physical characteristics of the soft-hard segment melt in polyurethanes. For example, to what extent is the soft matrix homogeneous with the dispersed hard segments and the newly dissolving the hard segments. Third, the muon relaxation rate operates as a window of observation on the mobile fraction, it will only "sense" those with the appropriate frequency. Once the motion is of a high enough frequency so that the correlation time for the motion satisfies the condition $\omega\tau < 1$, the muon relaxation rate will decrease, and the muon implanted on the highly mobile phenyl ring will not be differentiated from one on a rigid ring. A critical question here is whether the hard segment when it undergoes the rigid-to-mobile transition immediately adopts the dynamics characteristic of the soft matrix at the transition temperature. Only in the case of the instrument dead-time can the muon technique itself be held responsible for the difficulties in interpretation. The other two factors highlight a weakness in our understanding of the dynamic processes affecting hard segments in polyurethanes as a function of temperature and have only been brought to light by attempts to interpret the muon relaxation data. Accurate experimental data would allow muon relaxation data to be used to explore questions such as the homogeneity of the hard segment dynamics in the soft matrix.

The underlying limitation in these studies of the dynamic processes in polyurethanes by muon spin relaxation is the poor signal-to-noise ratio coupled with the need for at least two exponential fitting. As muon beams are already essentially 100% polarised, an improved signal-to-noise can only be achieved by a higher muon flux. At the Rutherford–Appleton laboratory, the muon beam intensity is comparable to other pulsed sources with an order of 20 million events per hour on the spectrometer used. Significant improvements on this counting rate are, however, possible, for example, the RIKEN-RAL spectrometer ARGUS at the Rutherford laboratory can give ~60 million events per hour. Comparisons with the signal-to-noise achievable in NMR experiments is complicated by the different detection efficiencies. In practical terms, though, the acquisition times involved in muon experiments are of the same order as low resolution natural abundance ^{13}C-NMR. Despite typical muon experiments only measuring 10^7 muons, the polarisation is 100% and the detection efficiency through single particle counting is close to 100%. In contrast, for the NMR experiment, a much larger number of spins are usually involved, 10^{20}, but the polarisation is low 10^{-5}, and the radiofrequency detection efficiency is poor.

5. Conclusion

Repolarisation of the muon asymmetry shows that muonium addition to the aromatic ring takes place. Despite the poor signal-to-noise ratio resulting from the limited number of muon events collected, the relaxation rate can be seen as having a rather complex temperature dependence indicative of a number of dynamic processes. Muon relaxation peaks below 300 K could be correlated with phase transitions occurring in the soft phase. Of particular note is the fact that increased phenyl ring dynamics are associated with the glass transition of the soft segments. Although an increase is seen in the relaxation rate as hard domain melting occurs, no marked differences were seen between the different polyurethanes. Accurately, quantification of the fast relaxing fraction and thus the mobile fraction of hard segments was not possible. To a large extent this was caused by an incomplete knowledge of the dynamic processes affecting the hard segments in polyurethanes and their influence on the observable muon relaxation decay. A contributing factor was the lack of sensitivity in the muon relaxation time analysis caused by the poor counting rates.

Dynamic studies in general of complex heterogeneous polymers such as polyurethanes using muon spin relaxation are limited by the poor counting statistics. Further studies are required on homopolymers to establish in principle whether the improved signal-to-noise ratio possible on the ARGUS spectrometer or a continuous muon source such as PSI will permit dynamic studies. In addition, the interpretation of the relaxation data is further limited by the absence of a detailed theoretical treatment of muon spin–lattice relaxation rates for different models of anisotropic motion. ALC experiments are required to ascertain whether the shape of the ALC peak will allow motional models to be tested in polymeric systems.

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