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Dan Alan Patterson [a] , Marco Roy Plumley [a] , Edward Gelerinter [a] & Johanan Isaac Spielberg [a]

[a] Kent State University, Physics Department, Liquid Crystal Institute, Kent, Ohio, 44242

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Saturation Studies of Spin Probes Dissolved in a Glass Forming Nematic Liquid Crystal MBBA

DAN ALAN PATTERSON, MARCO ROY PLUMLEY, EDWARD GELERINTER,† and JOHANAN ISAAC SPIELBERG

*Kent State University, Physics Department and Liquid Crystal Institute,
Kent, Ohio 44242*

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We have performed saturation studies of spin probes dissolved in the glass forming nematic liquid crystal MBBA that are similar to our previously reported studies of probes dissolved in an isotropic liquid. We have also repeated the measurements using a technique that eliminates a systematic error and find a similar functional form for the spin-lattice relaxation time (T_1) vs. temperature even though the absolute values are somewhat different. Both sets of data show evidence of the previously reported main glass and chain melting transitions.

1. INTRODUCTION

Spielberg and Gelerinter have published a series of papers in which they use electron paramagnetic resonance (epr) of spin probes to study the molecular dynamics of glass forming liquids and liquid crystals.[1,2,3,4,5,6] In the last of these papers, which we will refer to as *SG′*, the authors observed, in the ordered nematic liquid crystal a decrease in the intensity of the observed epr signal as the temperature is decreased towards the glass transition. This intensity decrease is attributed to saturation of the epr signal at lower temperature due to an increase in the spin-lattice relaxation time T_1 as the tumbling of the probe slows down. In order to confirm this, they use an expression for the rotational correlation time vs. temperature derived from

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†To whom all correspondence should be addressed.

a modification of the glass theory of Grest and Cohen[7,8,9] and combine this with an expression for $1/T_1$ for a molecule tumbling in an anisotropic magnetic field.[10] The calculated T_1 is then used to calculate a form for the intensity vs. temperature curve using simple saturation theory.[11,12,13] There are more sophisticated saturation studies in the literature inspired by the observation of major changes in observed line shapes,[14] but these were not used in this study since drastic line shape changes were not present. *SG′* matched their curve to the integrated intensity of the spectra observed above and near the glass transition with limited success.

In this work we perform a more direct test of *SG′*'s assumption that the intensity decrease is due to saturation effects by performing a series of saturation studies of both probes used in *SG′*. The resulting saturation curves are then used to predict the variation in intensity with temperature, and the prediction is compared with the data from *SG′*. We do not match our form for T_1 vs. temperature because of the difficulty in obtaining saturation data in the supercooled liquid region, but we do calculate a theoretical intensity using the values of T_1 measured in this study and compare the results to the integrated intensities of our data. We are successful in the temperature region above the glass transition thus strengthening the view put forth in *SG′* that saturation effects due to reduced tumbling times are responsible for the decrease in signal intensity as the sample temperature is lowered. The samples used in these studies are the same as those used in *SG′*. Subsequently, we prepared fresh samples and repeated the saturation studies using a technique that eliminated a systematic error in the calculation of the value of Q. The functional form of T_1 vs. temperature was similar, but, as might be imagined, the absolute values were substantially different.

2. EXPERIMENTAL

Most of the details of the equipment and experimental techniques appear in *SG′* and in Reference 4, so that only an abbreviated description will be given here. The samples used were the same ones used in *SG′*. They consisted of 1 mM solutions of piperdinooxy-4-hydroxy-2,2,6,6-tetramethyl-*p*-nitrocinnamate (N-6) and 2,2,6,6-tetramethyl-4-oxopiperidinooxy (D-Tempone) in the glass forming liquid crystal MBBA *n*-(*p*-methoxybenzylidene)-*p*-butylaniline.

The experimental techniques using the Varian 4500 X-band spectrometer were previously described.[4] The fresh samples were run on an IBM 200D-SRC epr spectrometer with an ER 044 MRDH X-band microwave bridge. This bridge could vary the power over a 90 db range thus removing some of the difficulties previously discussed. We were able to get a large linear portion on the saturation curves. Also, we used the literature value for the corner microwave field (0.1067 G) for the saturation curve of a 1 mM solution of PADS (potassium nitrosodisulfonate or Fremy's salt) in a 10 mM K_2CO_3 solution in water[15] to calibrate our microwave field by observing a saturation curve for PADS using a sample geometry similar to the one used in the rest of the experiments. The PADS sample and the new MBBA samples were deoxygenated using freeze-thaw pumping cycles.

3. RESULTS AND DISCUSSION

Epr spectra were observed vs. power at temperatures from 110 to 300 K, and the log of the relative amplitude of the central line was plotted vs. the log of the relative power in db to obtain a saturation curve. The low power portion of the curve is expected to be linear and was matched with a straight line of the correct theoretical slope.[3,10,11,12,16]

Since all of *SG*''s data were taken at a power level of 10 db we turn our attention to this portion of the saturation curves. The following discussion applies to the data observed using the Varian spectrometer and the older samples. Above 280 K, we find that the observed 10 db amplitudes lay on, or close to, the linear portion of the saturation curves, and below 220K the 10 db amplitudes fall below the linear portion indicating that the signal is partially saturated. We also find that the line shapes of the 10 and 15 db spectra are quite similar, so that we assume that the amplitude of the central line is a measure of the integrated intensity. This assumption becomes progressively worse as the temperature is reduced below the main glass transition. We further assume that the intensity of the unsaturated spectra follows a Curie law and is proportional to 1/T. Using these assumptions, we plot the intensities at 10 db vs. 1/T in Figures 1a and b. A straight line is drawn and the unsaturated data are plotted on this line. As saturation sets in at lower temperature the saturation curves are used to determine the fractional decrease of the amplitude of the central line from the unsaturated value. The corresponding point is plotted in Figure 1 with the same fractional decrease in height below the line. The technique is illustrated on the typical saturation curve shown in Figure 2. The ratio of the vertical values of the ob-

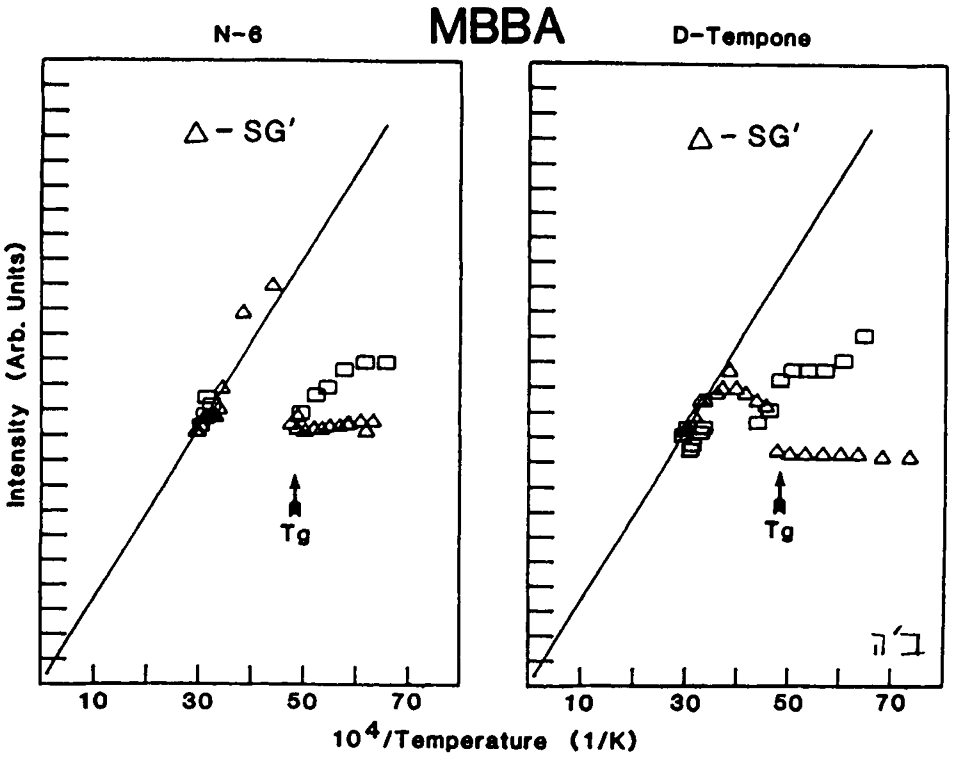


FIGURE 1 a. Intensity of spectra from N-6 vs. the reciprocal of the temperature: (□) this study; (Δ) data from *SG′*. b. Intensity of spectra from D-Tempone vs. the reciprocal of the temperature: (□) this study; (Δ) data from *SG′*.

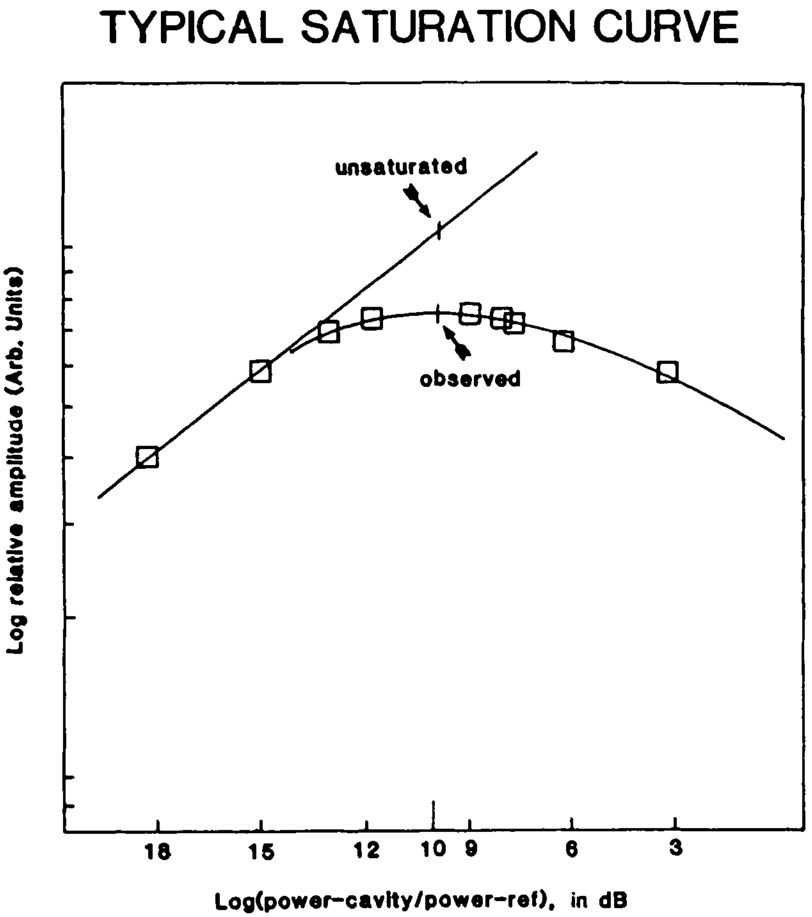


FIGURE 2 A typical saturation curve showing the actual and unsaturated signal heights at 10 db.

served to unsaturated points is noted and a point on Figure 1 corresponding to the value on the straight line multiplied by this ratio is plotted. One sees that the temperature at which the data begin to deviate from the line is the temperature at which saturation becomes important, and increased deviation corresponds to increased saturation. The integrated intensity data from *SG′*, corrected to the same scale, are also plotted in Figures 1a and b. The two sets of data for each of the spin probes are in very good agreement above 290K. *SG′*'s data clearly follow the Curie law at higher temperature and deviate from the Curie law at a temperature corresponding to the onset of saturation. This is in agreement with the model put forth in *SG'*. We present no saturation data between 290 and 220 K since the sample readily crystallizes in this temperature region before saturation data can be gathered. The data at and just above the glass transition still show good agreement, but the data below the glass transition do not match nearly as well. This is probably due to the fact that the differences between the 10 and 15 db data are greater in this temperature range, so that the central line height is no longer a good indicator of the intensity.

In Figures 3a and b, we display our calculated values of T_1. These values were obtained using methods previously described.[3,4,10,11,12,13] The product T_1T_2 is obtained from the saturation curves and T_1 is then calculated using the value of T_2 reported by *SG'*. We note the following general features in Figures 3a and b: T_1 is approximately constant above 290 K, and then rises as the temperature is decreased towards and below the glass transition. If one looks carefully, one can see evidence of both the chain and main glass melting transitions which have previously been reported.[2] Below the glass transition we were able to gather data with the director parallel and perpendicular to the magnetic field and the data from both orientations are presented. We see that their values are similar, but their variation with temperature are somewhat different. For the case of the D-Tempone probe, the 90° data appear to be more sensitive to the chain melting than the 0° data. For the case of the N-6 probe, we see evidence of chain melting in the data taken at both orientations. Looking at the 0° D-Tempone data we see a general downward trend with increasing temperature for T_1 except for an upward tick at the main glass transition temperature. The 90° data show a milder downward trend with an uptick at the chain melting temperature. The N-6 0° data also show a downward trend with increasing temperature, but they become choppy near the glass and chain melting transitions. The 90° T_1 data decrease until the chains melt and then assume a nearly constant value. It is interesting to note that N-6 is sensitive to the chain melting even though it is a rather large molecule. One might argue that the accuracy of the saturation technique makes the above comments suspect, and the variations displayed are just random results. However, most of these same features also appear in the T_1 data obtained from the fresh samples studied six months later using the IBM spectrometer.

One can compare the measured spectral intensity values with those theoretically expected from the measured T_1 lattice relaxation values

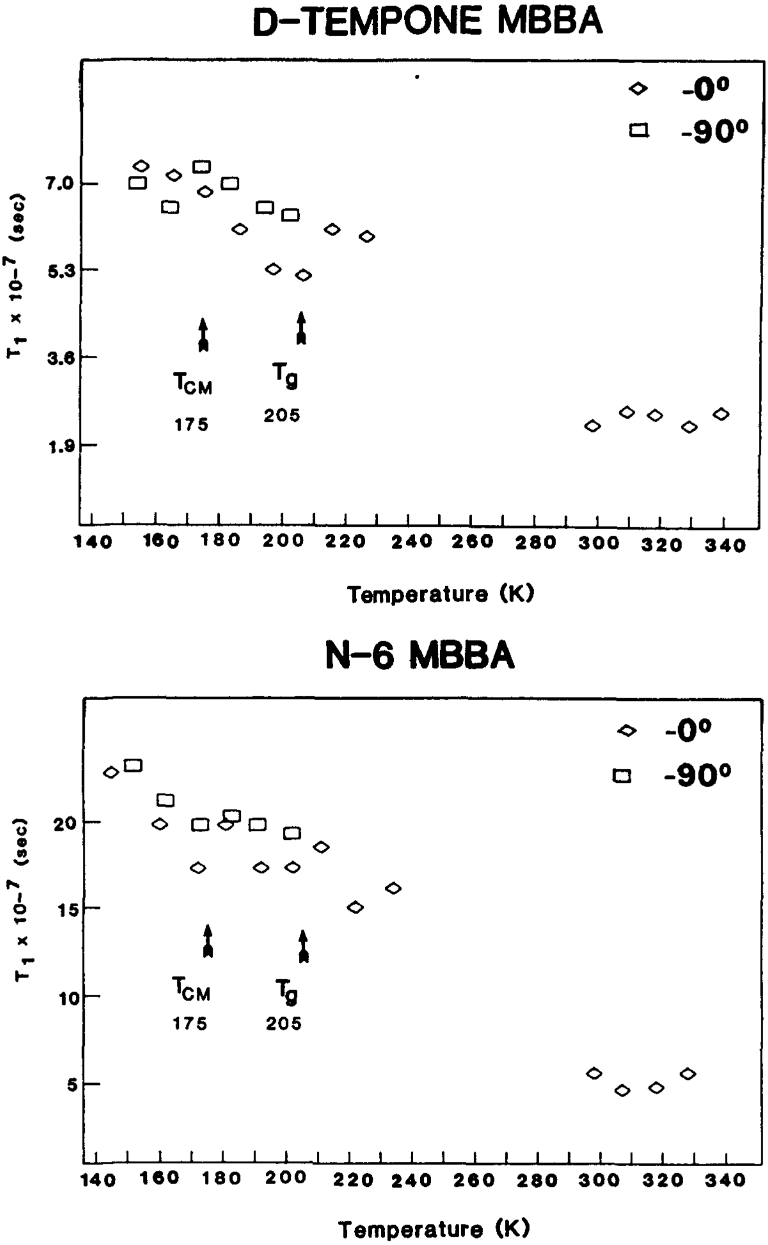


FIGURE 3 a. The spin-lattice relaxation time vs. temperature for D-Tempone. b. The spin-lattice relaxation time vs. temperature for N-6. These data were obtained using the Varian 4500 Spectrometer.

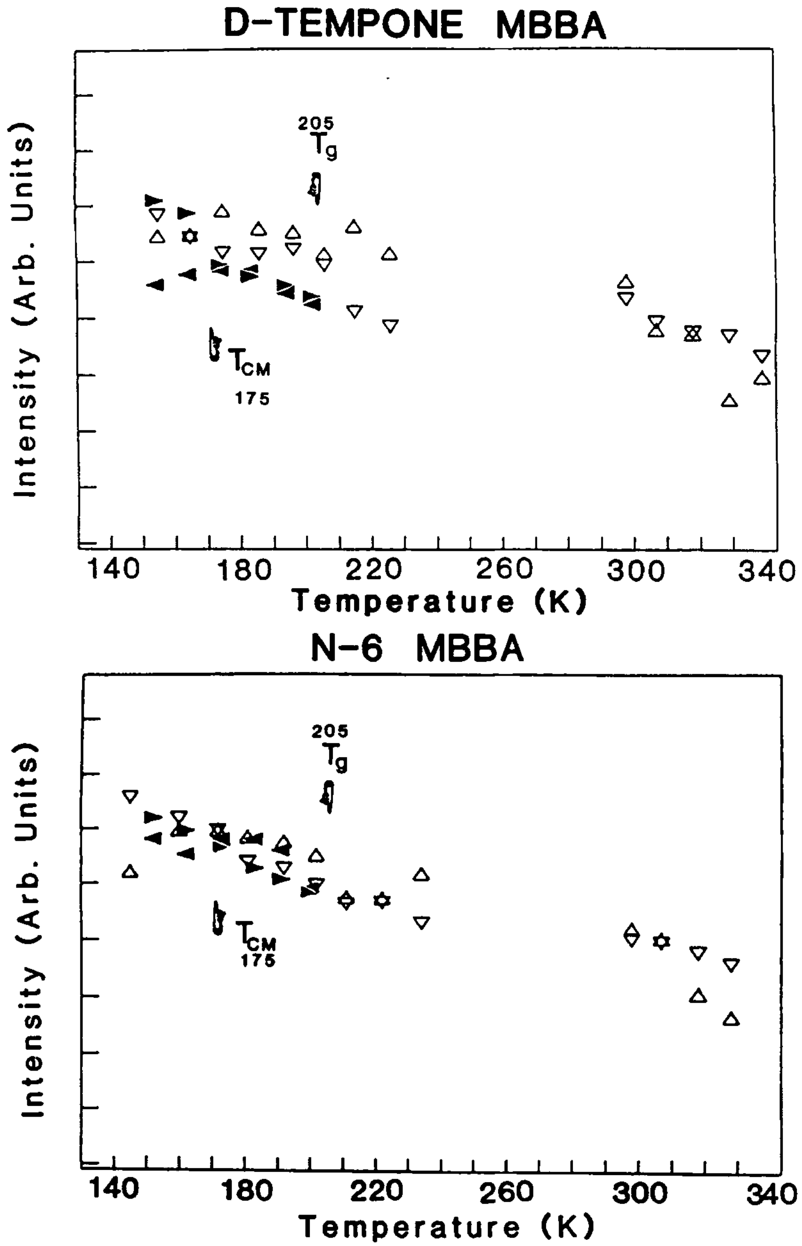


FIGURE 4 a. Integrated intensity vs. temperature for D-Tempone: (△,◀) this study; (▽,▶) calculated using the values of T_1 measured in this study and eqn. 1; $P_{expr} = 0.56 \times 10^6$, $P_{calc} = 0.79 \times 10^5$. b. Integrated intensity vs. temperature for N-6: (△,◀) this study; (▽,▶) calculated using the values of T_1 measured in this study and eqn. 1; $P_{expr} = 1.3 \times 10^6$, $P_{calc} = 1.1 \times 10^6$. The open symbols indicate 0° data and the closed symbols indicate 90° data.

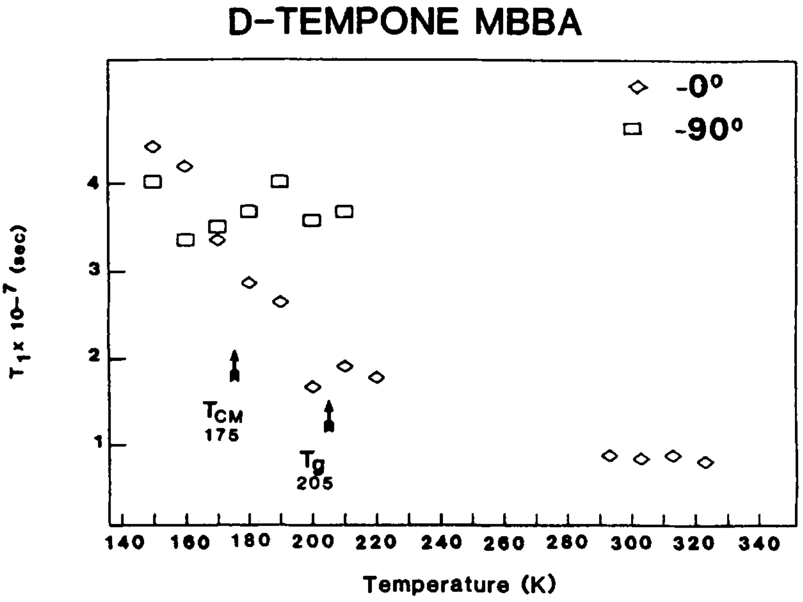
using this saturation equation,[3,10]

$$I(T) = n/T + b = \frac{n^0/T}{1 + 2PT_1} + b, \tag{1}$$

where $n = n_l - n_u$ is the difference in population of the lower and upper energy levels, P is the stimulated emission coefficient and may be found from $P = \gamma^2 H_1^2 T_2$, where H_1 is the radio interaction magnetic field, n^0 is the thermal equilibrium population difference, and b accounts for the background. Our fits to this equation are shown in Figure 4. Here the intensity values are the area under the integrated 10 db first derivative epr spectra, and the integrations were carried out with an Intel 8080 assembler language program that iteratively solves for the proper baseline.[3] The closeness of the fit shows the reasonableness of the saturation model.

In addition, the value of P found from the matches may be compared with the theoretical value from the definition. The values generated are indicated in the figure legends. The results for N-6 are amazingly close. The D-Tempone results, while not as close, are still within experimental error.

In Figure 5 we show the results obtained using the fresh samples and the IBM spectrometer. The high temperature D-Tempone values for T_1 are constant as before, but have a value approximately one-half that obtained from the earlier sample. Similarly, the low temperature data have values that are approximately one-half those obtained from the earlier sample. As before, we can describe the 0° results as generally decreasing with increasing temperature with a break at the main glass transition. The 90° results again show a dip at the chain melting temperature. The low temperature results for N-6 are approximately one-half the values obtained from the older N-6 sample. The 0° data display the upticks discussed previously. The 90° data are more scattered than before, but appear to change their behavior at the chain melting temperature. No high temperature data are shown since the sample did not saturate at 290K or above. We tried to saturate the old sample using the IBM spectrometer and did so with some difficulty. Using the newer technique on the older sample we obtained a value for T_1 of approximately 0.8×10^{-8} sec at room temperature. Part of the difficulty in saturating the N-6 sample at room temperature stems from the fact that the output of the IBM goes through a power leveler which reduces the output power to 200 mW while the Varian can output nearly 700mW. In the worst case, the difference in the data from the two experiments is about a



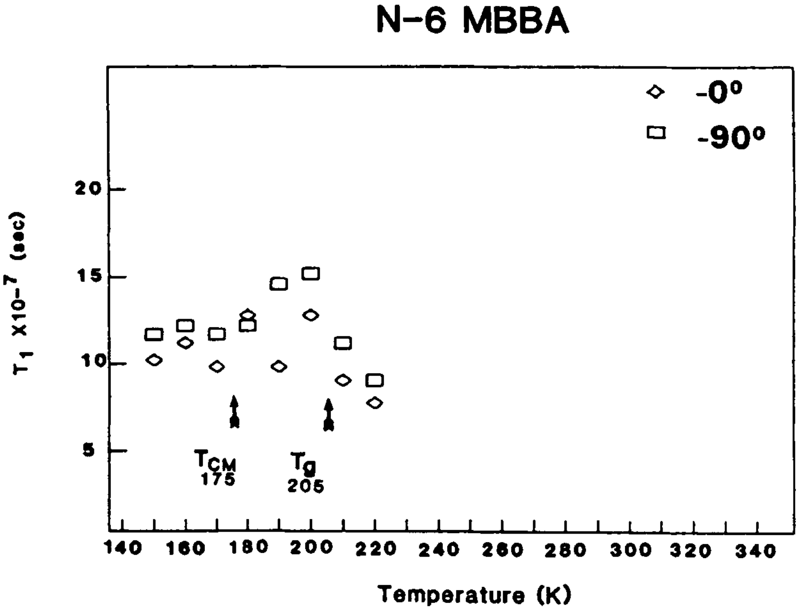


FIGURE 5 The spin-lattice relaxation time vs. temperature obtained from data gathered on the IBM 200D-SRC spectrometer and calculated using the reported corner value of H_1 from the saturation curve for PADS. a. Data for D-Tempone. b. Data for N-6.

factor of five which is well within our estimate[4] of the systematic error involved in measuring Q.

4. CONCLUSIONS

We have presented data from two different sets of epr saturation studies, and both sets of data lead us to the same conclusions. In particular, they verify the conclusions of SG' that the loss of epr signal intensity as the temperature is reduced, is due to the increased spin-lattice relaxation time as was the case for our previously reported studies of the isotropic liquid, dibutyl phthalate. There is also evidence that both the small spherical probe, D-Tempone, and the longer probe, N-6, are sensitive to the melting of MBBA's chains. D-Tempone is presumably forced out into the nonpolar chain region when the MBBA is in the supercooled and glassy temperature regions.[2,17] The motions of the MBBA chains must affect the motions of the N-6 chains and hence its T_1. If we think about it in this manner, then we are not surprised to see that these probes are sensitive to the chain melting transition. It is interesting to note that both the main glass and the chain melting transitions were observed as changes in epr signal heights four years ago.[2] In the current work we again detect these transitions as changes in the plots of T_1 vs. temperature in agreement with our previous interpretations.

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