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Proton Spin-Spin Relaxation Time in MBBA

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The proton spin-spin relaxation time of the liquid crystal, N-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA), was obtained by a modified Carr–Purcell method in the temperature range from −110 to 65°C. The measurements were carried out both on the warming and cooling processes of the sample. Two discrete relaxation times were found in either the solid or the nematic phase of the sample. The origin of these two relaxation times was discussed on the basis of the fraction of each component. In the solid phase an anomalous temperature dependence of these two relaxation times was observed over 0 ~ 15°C only on the warming process, and it was interpreted as an indication of the structural change toward a closer molecular packing. In the nematic phase, two relaxation times showed a different temperature dependence around 20 ~ 25°C and then came to show a similar temperature dependence at higher temperature. This was explained in terms of a steric hindrance between adjacent MBBA molecules enhanced by the molecular alignment in the magnetic field.

INTRODUCTION

N-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) exhibits two different solid phases (metastable and stable phases), which are obtained by rapid or slow cooling of the nematic phase;[1,2] and many efforts have been made to study the difference between them.[3–6] On the basis of the thermodynamic data, Andrews[3] has explained the difference in terms of disorder arising from restricted rotation of the methoxy group and melting of the *n*-butyl chain. On the other hand, Kronberg and Gilson[6] have suggested on the basis of broad line NMR measurements that the metastable phase shows the reorientation of the benzylidene ring about the para axis, while such a reorientation of the benzylidene ring is prohibited in the stable phase. Thus more extensive studies on the molecular motions are necessary to improve our understanding of the structure and properties of MBBA.

Nuclear magnetic relaxation gives useful information on the structural changes and molecular motions of the material on the microscopic scale. The most frequent work in this field has been concerned with the dynamics of the nematic state by means of the spin-lattice relaxation time measurements.[7–13] The advantages of the spin-spin relaxation time are that when several components with different proton environments are present, the individual relaxation times and the fraction corresponding to each component can be evaluated without receiving any influence of spin diffusion.

In this paper we report on the temperature dependence of the spin-spin relaxation times and the fraction of each component of MBBA and discuss the relation between the structural changes and molecular dynamics over the temperature range from solid to isotropic states.

EXPERIMENTAL

The liquid crystal MBBA obtained from Chisso Co. Ltd., Japan, was purified by vacuum distillation. The sample was packed in a glass tube and sealed in a vacuum by the freeze-melt method. The NMR measurements were performed with a JEOL pulsed NMR spectrometer (JSE-5B), operating at a frequency of 60 MHz. The sample temperature was regulated to ± 0.5°C by a nitrogen gas flow thermostat and monitored by a copper-constantan thermocouple which was placed near the sample tube. The spin-spin relaxation times were obtained by a modified Carr-Purcell method ($90^\circ_x - \tau - 90^\circ_y - 2\tau - 90^\circ_y - - -$).[14] In this study the pulse interval (τ) and the pulse width have been adjusted to be 15 and 2 μsec, respectively. The relaxation time (T_2^*) obtained by this method is qualitatively different from T_2 obtained by the free induction decay or the spin echo method. The present method is more suitable for estimating the degree of dipolar averaging effects in each phase of a system by observing pulse interval (τ) dependence of T_2^*. Thus, in the solid and nematic phases, the τ dependence of T_{2l}^* was also investigated at several temperatures. Echo train signals of the sample displayed on the oscilloscope were photographed by a Polaroid camera and the signal intensity was read directly from the photograph.

When the sample is cooled from the isotropic phase at a rate faster than 10°C min^{-1}, almost all the portion of the supercooled nematic phase of MBBA is known to be metastable.[15] In the present study, the sample was first cooled in a sample coil from 25 to -110°C over 15 min and then measurements of T_2^* were carried out on the warming process. The apparent cooling rate is about 10°C min^{-1}, which suggests that the sample is likely to be in a metastable state. When the measurements for the cooling process were

carried out, the sample was cooled slowly from the isotropic state in the applied magnetic field.

RESULTS AND DISCUSSION

Figure 1 shows the logarithm of the echo train heights of MBBA at 8°C plotted against time. The original photograph of the echo train signals used for this plot is also included at the upper right in Figure 1. A typical nonexponential decay is found and the short T_2^* component is large enough to permit a graphical separation of the two relaxation times. The long and short relaxation times obtained by this method are denoted as T_{2L}^* and T_{2S}^*, respectively. In the solid and nematic phases two discrete relaxation times were obtained; however, in the isotropic phase only one T_2^* value could be calculated because the nonexponential nature of the decay was less pronounced.

In order to study on the origin of T_{2L}^* and T_{2S}^*, the fraction of T_{2L}^* component was estimated from the value at the intersection of the vertical axis (time $t = 0$) and each straight line obtained by the decomposition procedure. The fraction of T_{2L}^* component on the warming process of MBBA was

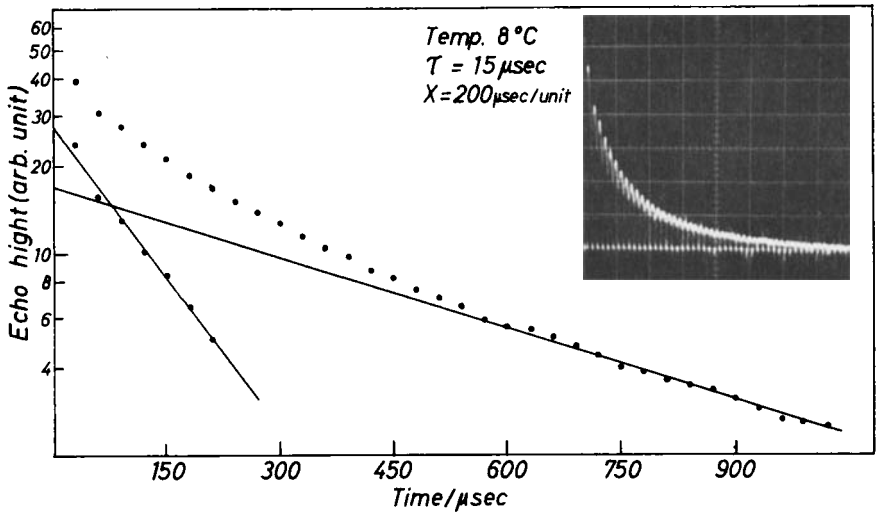

FIGURE 1 Analysis of the echo train signals in MBBA. The original photograph of the echo train signals is also included at the upper right in the figure.

plotted against temperature in Figure 2. The fraction of T_{2L}^* component begins to increase at around $-70°C$. A sharp decrease (-10 to $15°C$) followed by an abrupt increase ($>15°C$) in the fraction is observed.

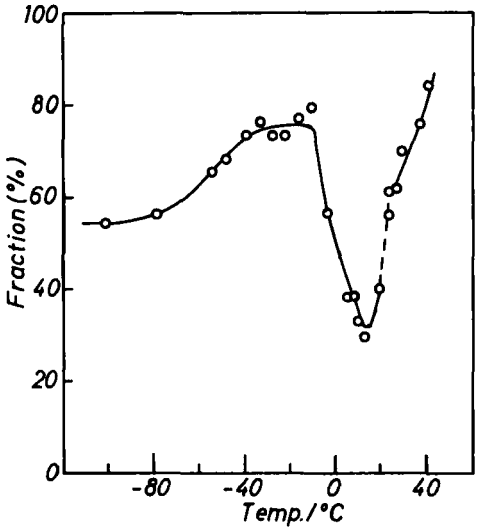

FIGURE 2 Temperature dependence of the fraction of T_{2L}^* observed on the warming process.

Origin of T_{2L}^* and T_{2S}^* components

The origin of multiple components is usually interpreted as resulting from the existence of groups with different mobility in the system or from the effects of chemical shift. The chemical shift for hydrogen at the usual magnetic field strength is very small and is observed only when the intra- and inter-dipole interactions are motionally averaged. In the solid phase, both intra- and inter-dipole interactions may be large. In order to study the effects of dipolar averaging on T_{2L}^* in the nematic phase, T_{2L}^* was measured as a function of τ in the solid and nematic phases of MBBA and shown in Figure 3. T_{2L}^* of nematic phase is much longer than that of solid phase. Nevertheless, T_{2L}^* of each phase exhibits a similar τ dependence. When the dipolar averaging is enough, T_{2L}^* should have a constant value irrespective of the variation of τ. In agreement with the previous work by Dong *et al.*[16] the present results indicate that even in the nematic phase, the dipolar averaging is not so pronounced as in the isotropic liquid. Therefore, the two discrete components observed in this study arise from the existence of two groups with different mobility in a system.

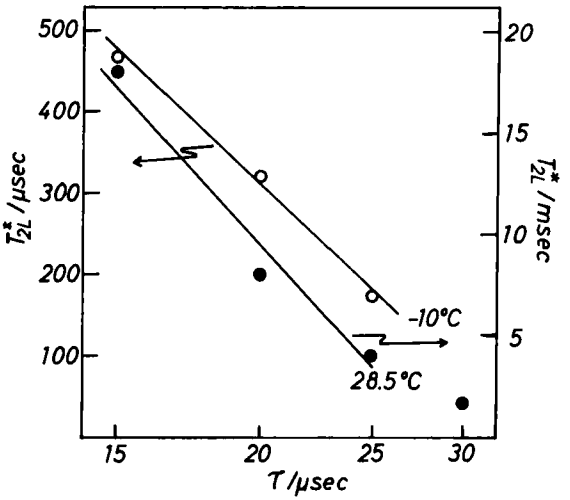

FIGURE 3 Pulse interval (τ) dependence of T_{2L}^* in the solid and nematic phases of MBBA.

In semicrystalline polymers, the appearance of two relaxation times is known to be due to the atoms of the same element being present in two phases (crystalline and amorphous) in the system with different molecular structure or different mobility in the two phases. Their relative intensities determined from the decomposition of a decay curve are correlated with the crystallinity of the system. However, the x-ray diffraction patterns suggested no clear crystalline phase even at the temperature where NMR showed the percentage of T_{2L}^* component to be 50% or less. Similar x-ray results have been reported by Lydon and Kessler.[5] Froix and Pochan[17] found that the liquid crystalline anisotropy of MBBA was retained in the metastable state on quenching the nematic state in the magnetic field. However, in the present study, no detectable anisotropy was observed in the free induction decay signal for the solid phase obtained by quenching from 25°C (the nematic state) in the magnetic field. This indicates that the content of the anisotropic liquid crystalline structure retained in the metastable state may be negligible. Thus, such a two-phase model (crystalline-amorphous) is inapplicable to the same used in this study.

It is appropriate to consider that the two discrete components observed in this study may arise from the existence of two groups with different mobility in a MBBA molecule. As shown in Figure 2, the fraction of T_{2L}^* component is about 55% at around -100°C and remains almost constant up to -70°C. A number of possible molecular mechanisms responsible for T_{2L}^* and T_{2S}^* may be postulated. Kronberg and Gilson, using broad line NMR method, have recently studied the internal rotations of various groups (e.g., phenyl rings, methyl groups, and *n*-butyl chain) of MBBA and

reported that only end methyl groups rotate at around $-100°C$.[6] The fraction of T_{2L}^* component, calculated based on a simple assumption that this T_{2L}^* component is responsible for only the rotation of end methyl groups, is 30% which is only one half of the value observed at around $-100°C$ (Figure 2). Additional motional parts in a molecule combined with end methyl group rotation must be considered. Watkins and Johnson[9] have also investigated the broad line NMR of MBBA and reported that the resonance spectrum observed for the nematic phase showed two components. The narrow and wide splitting widths were connected with the fast molecular motional parts such as end alkyl groups and with the slow molecular motional parts such as aromatic rings, respectively. It is generally considered that end alkyl groups are more mobile than the aromatic rings. The calculation, assuming rotation of both the methyl and *n*-butyl groups of MBBA, gives a mobile fraction of 57% which is in a good agreement with the experimental value of about 55%. Therefore, it is plausible to conclude that T_{2L}^* at around $-100°C$ is responsible for the rotations of methyl and *n*-butyl groups of MBBA. The fraction begins to increase from $-70°C$ and almost levels off in the temperature range from -40 to $-10°C$ with the value of 75%. This increase suggests the participation of other groups to the T_{2L}^* component. The most probable group which is responsible for this increase may be one of the two phenyl rings in a MBBA molecule. It is noted that the temperature at which the fraction begins to increase coincides with the glass transition temperature of MBBA,[1,17] but as will be shown in the next section no abrupt increase of T_{2L}^* was observed in this temperature region. At the glass transition temperature of polymeric materials, the molecular motions are greatly activated and as a result, an abrupt increase of spin-spin relaxation time is usually observed. Therefore, it seems that the molecular mechanism for the glass transition of MBBA is somewhat different from that of polymeric materials.

At around $-10°C$ the fraction begins to decrease and reaches a minimum value of about 30% at around 15°C, followed by an abrupt increase in the fraction. This decrease of the fraction suggests a structural change of MBBA which will be discussed in combination with the temperature dependence of T_{2L}^* and T_{2S}^* in the following section. The sudden increase of the fraction at around 20°C may be due to the solid to nematic transition. It is noted that at 22°C the fraction is about 60% which is nearly equal to that at around $-100°C$ where both the end methyl and butyl groups contribute to the T_{2L}^* component. The fraction increases rapidly with increasing temperature and reaches about 80% at the temperature near the nematic-isotropic transition. These results indicate that a gradient of flexibility occurs along the two phenyl rings of MBBA; these two rings may have a different mobility as first suggested by Dong *et al.*[18]

Temperature dependence of T_{2L}^* and T_{2S}^*

In order to discuss the structural changes and molecular dynamics in MBBA, T_{2L}^* and T_{2S}^* were plotted as a function of temperature for the warming process in Figure 4. Two discrete relaxation times are seen in either solid or nematic phase; however, the difference in the two T_2^* values is not so large.

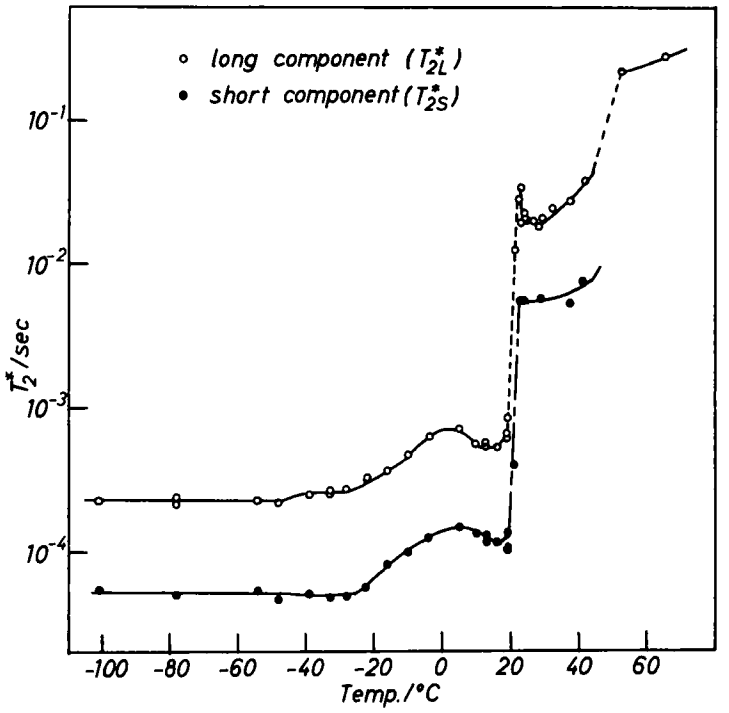

FIGURE 4 T_2^* values as a function of temperature on the warming process in MBBA.

The degree of molecular mobility is evaluated directly from the usual spin-spin relaxation time (T_2) but the evaluation is difficult from T_2^* because the latter value is considerably prolonged by the spin locking and dipolar averaging effects.[14] The usual spin-spin relaxation time (T_2) was obtained by the spin echo method and was compared with T_2^* at around -100°C. Two discrete relaxation times were also expected for T_2 as in the case of T_2^*. Nonetheless, only one T_2 with about 15 μsec was observed. It has been reported that the precision of two T_2 values extracted from a non-exponential decay is affected by the ratio of the two relaxation times and the fraction of the long component.[19] The fact that the fraction of T_{2L}^* component which may correspond to the long T_2 component is sufficiently

large (about 55% around −100°C), suggests that the unexpected result that only one T_2 was observed might be due to only a small difference in mobility between two phases. The T_2 value of 15 μsec around −100°C means that the mobility of MBBA molecules is much constrained at this temperature.

Two relaxation times (T_{2L}^* and T_{2S}^*) show a similar temperature dependence in the range from −110 to 45°C except 20–25°C, where a reverse temperature dependence is found; T_{2L}^* decreases sharply, while T_{2S}^* increases slowly with temperature. A small transition in T_{2L}^* is found at around −50°C. As described in the previous section, this transition may correspond to the glass transition of MBBA. At around −25°C both T_{2L}^* and T_{2S}^* begin to increase with temperature. A gradual decrease in T_{2L}^* and T_{2S}^* is found from 0 to 15°C, followed by a sharp increase at about 20°C. As is shown in Figure 2, the fraction of T_{2L}^* component decreases abruptly and reaches the minimum value of about 30% at around 15°C. It is generally considered that thermal expansion causes an increase of interproton distance and consequently, T_2^* increases. Therefore the present unusual T_2^* change observed over 0 to 15°C indicates an occurrence of a closer packing of molecules on the warming process. A similar consideration has been presented in the x-ray study of Lydon *et al.*[5] They reported that the increase of diffracted intensity at $2\theta = 5.2°$ suggests an occurrence of the reorientation or structural changes in the solid state of the quenched MBBA during the warming process. The decrease of the fraction of T_{2L}^* component around −10 to 15°C suggests that the closer packing of MBBA molecules induces an increase of the less mobile component due to the steric hindrance between adjacent MBBA molecules.

A sudden increase in T_{2L}^* and T_{2S}^* at around 20°C is due to the solid to nematic phase transition. In the nematic region, T_{2L}^* initially decreases sharply and then increases gradually with increasing temperature, while T_{2S}^* increases monotonically. The reason for the decrease in T_{2L}^* with temperature is not clear at the present stage; however, the decrease in T_{2L}^* may not be due to a structural change as observed around −10 to 15°C because in this temperature region T_{2S}^* and the fraction increase with temperature. MBBA molecules well orient at the solid to nematic transition along the applied magnetic field due to the diamagnetic property of the phenyl rings in the molecules. The alignment of these rings may also, more or less, force methoxy and butyl groups to align along the direction. As a consequence the steric hindrance between adjacent MBBA molecules may influence the mobility of the methoxy and butyl groups. Above 25°C, T_{2L}^* and T_{2S}^* come to show again a similar temperature dependence. This means that the motional restriction imposed on the T_{2L}^* component is relaxed above 25°C.

Figure 5 shows the temperature dependence of T_{2L}^* and T_{2S}^* on the cooling process. The dotted lines indicate T_{2L}^* and T_{2S}^* on the warming process shown in Figure 4. Both T_{2L}^* and T_{2S}^* show a similar temperature dependence and they decrease with decreasing temperature. The abrupt decreases of T_{2L}^* and T_{2S}^* at around 15°C are due to the nematic to solid transition which was shifted to the lower temperature by a supercooling effect in the phase transition of MBBA. The anomalous temperature dependence of T_{2L}^* and T_{2S}^* observed around 0 to 15°C on the warming process was not found in the cooling process. This means that the molecular mobilities are gradually restricted except at the nematic to solid transition.

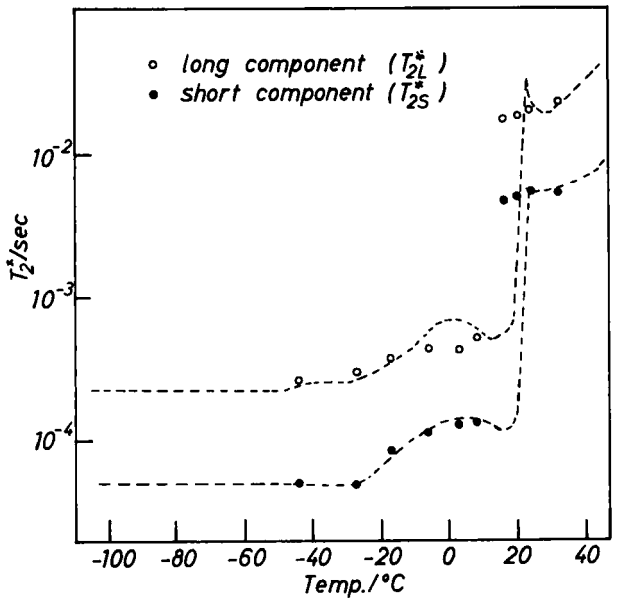

FIGURE 5 T_2^* values as a function of temperature on the cooling process in MBBA. The dotted lines represent the data for the warming process reported in Figure 4.

CONCLUSIONS

The proton spin-spin relaxation time of MBBA was obtained by a modified Carr–Purcell method in the temperature range from −110 to 65°C.

Two discrete spin-spin relaxation times (T_{2L}^* and T_{2S}^*) were observed in either solid or nematic phase of MBBA. It is concluded that these two relaxations arise from two groups with different mobility in a MBBA molecule.

With increasing temperature, T^*_{2L} and T^*_{2S} decreased in the temperature range from 0 to 15°C on the warming process and this anomalous phenomenon is interpreted as an indication of the structural change toward a closer molecular packing, in accordance with the previous x-ray data reported by Lydon *et al.*[5]

In the nematic region, T^*_{2L} initially decreased sharply in the temperature range from 20 to 25°C and then increased gradually, while T^*_{2S} increased monotonically with increasing temperature. The decrease of T^*_{2L} (20–25°C) is explained by the increase of restriction on the mobility of the methoxy and butyl groups due to the alignment of the two phenyl rings along the applied magnetic field.

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