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The Effect of Rapid Cooling and a Magnetic Field on the NMR Relaxations and Thermal Behavior of [*N*-(*P*-ethoxybenzylidene)-*p*-butylaniline] (EBBA)

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Rapid cooling of EBBA from the nematic phase results in a mixture of amorphous and crystalline material. The presence of these two phases are detected in the nmr relaxation data by the occurrence of two separate relaxations for reorientation of the methyl/ethyl groups in each of these phases. Aligning of the molecules in the liquid crystalline state by a magnetic field prior to crystallization gives rise to morphological changes which are manifested by a melt temperature some two degrees higher than the normal crystal melt.

[*N*-(*p*-ethoxy-benzylidene)-*p*-*n*-butylaniline] (EBBA) is a thermotropic liquid crystal whose transition from the crystal to the nematic phase occurs around room temperature. The vast majority of studies which have been undertaken on this material and liquid crystals in general have focused on the liquid crystalline state. In this communication we report on the effect of the rate of cooling and the influence of a magnetic field on the features of the spin lattice relaxation (T_1) and calorimetric data of the solid state of EBBA.

EBBA was obtained from the condensation reaction of equal molar amounts of *P*-ethoxybenzaldehyde (Eastman Kodak Chemicals) and *p*-*n*-butylaniline (Aldrich Chemical Co.) with trace amounts of acid. The EBBA

was purified by vacuum distillation. Purified EBBA was placed in 9 mm (o.d.) cylindrical pyrex nmr tubes. The tubes were not subjected to any surface treatment. The samples were heated to the isotropic melt, degassed and sealed under a 10^{-5} mm Hg vacuum. Spin-lattice relaxation times were measured by the 180-t-90 degree pulse technique,[1] at 90 mHz in a magnetic field of 21 kgauss. T_1's were obtained from plots of $[M(\infty) - M(t)]$ versus t, where $M(\infty)$ is the magnetization at infinite time between the 180 degree and 90 degree pulses and $M(t)$ the magnetization at time t between the pulses. The magnetization recovery was exponential at all temperatures examined. The T_1's of EBBA were measured in the following ways. One sample was quenched from the liquid crystalline phase to the solid phase outside the magnetic field, while another was quenched in a similar manner within the magnetic field. Both samples were rapidly quenched by immersing the samples in a liquid nitrogen bath. A third sample was cooled slowly (measurements were made at five degree intervals, waiting ten minutes between measurements for the sample to equilibrate) from the liquid–crystalline phase to the solid phase in the magnetic field. Similarly, a fourth sample was cooled slowly at 1°/minute in a Delta Design Model 5750 environmental oven (without a magnetic field) and transferred to the magnetic field for T_1 measurements. In both the quenched samples and the sample cooled slowly outside the magnetic field T_1's were measured from 140°K to 320°K, while for the sample cooled slowly in the magnet T_1's were measured during the slow cooling process. Differential scanning calorimetry (DSC) traces of the solid to liquid–crystal transition of EBBA were also obtained for samples aligned in the magnetic field, and for samples quenched outside the field.

The differences in the plot of log T_1 versus temperature for the various thermal treatments are shown in Figure 1. As in MBBA there is a low temperature minimum at 170°K for all samples, due to the reorientation of the methyl/ethyl portions of the ethoxy and n-butyl groups.[2] The minimum at 230°K, which appears as a change in slope, is observed only for the quenched samples. In addition the minimum at 170°K for the quenched samples and the sample which was slow cooled in the magnetic field is flatter than that of the sample which was cooled slowly outside of the magnetic field. Previous T_1 measurements on EBBA revealed what appeared to be similar double minima in the low temperature solid phase which were assigned to reorientation of the methyl and methylene units.[3]

Quenching MBBA from the liquid phase to the solid phase results in a metastable solid phase which exhibits new endotherms at 212°K and 217°K, and lowers the crystal melt by 1.3°K. The metastable state has a lower enthalpy and entropy of fusion and converts spontaneously with the liberation of heat to the more stable form.[4] X-ray diffraction studies of the crystalline and metastable states indicate that the metastable state is an amorphous

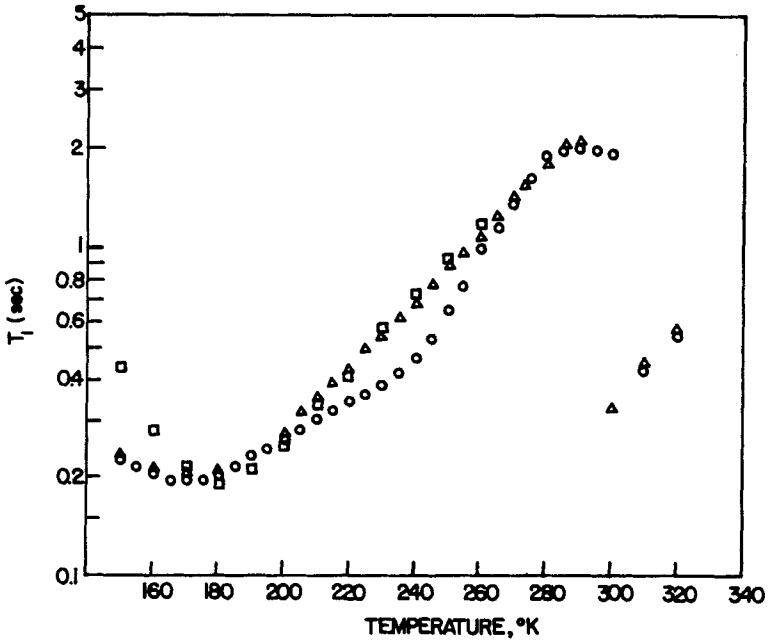

FIGURE 1 Proton spin-lattice relaxation times (T_1) versus temperature for EBBA samples, ○ quenched from the nematic phase outside the magnetic field. △ cooled slowly from the nematic phase in the field. □ cooled slowly from the nematic phase outside the field. Samples quenched inside the magnetic field give results similar to those quenched outside the field and were not included for the sake of clarity.

phase in which the molecular arrangement of the liquid-crystalline order is frozen in by the quenching process.[5] In addition, nmr proton relaxation studies on MBBA have revealed the same complex low temperature behavior in which the higher temperature minimum is only observed for the quenched samples.[2] Crystallization of MBBA in a magnetic field gives rise to a very complicated solid state structure whose thermograms show multiple transitions which are intimately related to the crystallization rate and the presence of the magnetic field during crystallization.[2] It is not surprising therefore, that in light of the similarities in chemical structure between MBBA and EBBA similar nmr relaxation and thermal behavior are observed. Since the high temperature minimum at 230°K is only observed for the quenched samples and this minimum disappears on slow cooling one can conclude that like MBBA this minimum is due to reorientation in the metastable amorphous phase. The reorientation process is the same methyl/ethyl reorientation as that observed at 170°K for the normal crystalline material. With both the 170°K and the 230°K minima resulting from similar types of reorientation in the crystalline and amorphous phases

respectively, if both reorientations begin at approximately the same temperature and that in the amorphous state is governed by a lower activation energy, the minimum of the amorphous phase will occur at a higher temperature. In addition, the second moment of the nmr adsorption line for the crystalline and amorphous phases of EBBA are identical and no transition in the second moment corresponding to the high temperature minimum is observed. This tends to support the assignments given above and it rules out the possibility that the 230°K minimum may be due to an overall tumbling of the methyl/ethyl side group.

Some evidence of the effect of the magnetic field on the solid state crystal structure of EBBA is also observed in the nmr data. For all samples crystallized in the magnetic field the low temperature minimum (at 170°K) is flatter than that of samples crystallized outside the field. This is a reflection of the anisotropies in the solid state structure which result from retention of some of the liquid-crystalline order on quenching, and from the aligning effect of the magnetic field prior to crystallization. The sharp minimum observed for the sample crystallized outside the magnetic field is characteristic of a narrow distribution of correlation times for the corresponding molecular motion, as a result of a more perfectly annealed structure. The broad minimum is therefore indicative of a wider distribution of correlation times associated with the methyl/ethyl reorientation due to the complicated morphology. In addition, the magnetization recovery for the quenched samples which contain both crystalline and amorphous phases exhibit a single exponential decay which suggests that the spin diffusion mechanism of relaxation is operative. Such a mechanism provides for the transfer of spin energy from the more rigid regions to the lattice via the freely reorienting groups. If the time of diffusion of spin energy from the rigid regions is small relative to the spin lattice relaxation time of the reorienting group, only one T_1 will be observed. It is for this reason, one does not observe a separate spin-lattice relaxation time for the amorphous component of the quenched samples.

The DSC traces are given in Figure 2. Samples which have been aligned in the magnetic field exhibit a crystal melt two degrees higher in temperature than samples not similarly aligned. The heats of fusion obtained from both traces are identical within limits of error of our measurements. The higher melting temperatures and the broadening of the endotherm for the samples which were crystallized in the magnetic field are indicative of a crystal structure which is influenced by the aligning effect of the magnetic field. In the case of MBBA the apparent shift to higher temperatures for the magnetic field aligned samples is actually due to the overlap of the normal crystal melt and the emergence of a second endotherm at a slightly higher temperature. Thermal treatment dictates the relative proportions of the two structures

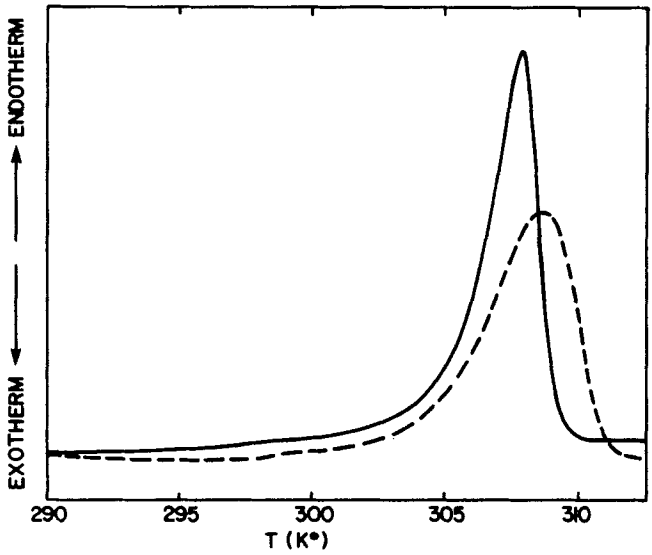

FIGURE 2 Differential scanning calorimetry traces of EBBA, ---- quenched from the nematic liquid in a 21 kgauss magnetic field, ——— quenched outside of the magnetic field.

which give rise to these transitions. Consequently, the extent of the apparent upward shift in temperature and the width of the crystal melt of the samples which were crystallized in the magnetic field is really a manifestation of the relative proportions of these two structures. Quenching the field aligned samples after melting produces the endothermic melt observed for the non-field aligned samples, indicating that the structure produced by the magnetic field is destroyed on melting.

As a consequence of the various thermal treatments it is concluded that the T_1 minimum observed at 170°K results from reorientation of the methyl/ethyl groups in the normal crystalline material. The T_1 minimum at 230°K is due to the reorientation of the same groups in the metastable amorphous phase, where the activation energy for reorientation is probably smaller than that for the same reorientation in the crystalline phase. Differential scanning calorimetry of samples which were aligned in a magnet field prior to crystallization suggests the formation of a second crystal phase whose melt temperature is a few degrees higher than the normal crystal melt.

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