Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Effect of Cooling Rate and Magnetic Field on the NMR Relaxation and Thermal Behavior of [N- (p-methoxybenzylidene) -p-n-butylaniline] (MBBA)

Michael Froix [a] & John Pochan [b]
[a] Celanese Research Corp., Summit, New Jersey, 07901
[b] Xerox Corp., Rochester, New York, 14580
Version of record first published: 28 Mar 2007.

To cite this article: Michael Froix & John Pochan (1978): The Effect of Cooling Rate and Magnetic Field on the NMR Relaxation and Thermal Behavior of [N- (p-methoxybenzylidene) -p-n- butylaniline] (MBBA), Molecular Crystals and Liquid Crystals, 46:3-4, 147-156

To link to this article: http://dx.doi.org/10.1080/00268947808083719

Mol. Cryst. Liq. Cryst., 1978, Vol. 46, pp. 147–156

Printed in Holland

The Effect of Cooling Rate and Magnetic Field on the NMR Relaxation and Thermal Behavior of [*N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline] (MBBA)

MICHAEL FROIX

Celanese Research Corp., Summit, New Jersey 07901

and

JOHN POCHAN

Xerox Corp., Rochester, New York 14580

(*Received January 5, 1978*)

NMR relaxation time measurements and the dsc thermal behavior of the solid state of MBBA have been examined as a function of cooling rate and aligning magnetic field. The results indicate a complicated solid state morphology as a result of these effects. Aside from the normal crystal structure, anisotropies are introduced by the aligned magnetic field and the liquid-crystalline structure that is retained on quenching to the amorphous metastable state. These anisotropies are reflected in the occurance of additional endotherms in the thermal data, and by separate relaxations for methyl reorientation in the normal crystal and the metastable amorphous material in the nmr data. The activation energies for methyl reorientation are determined.

INTRODUCTION

[*N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline] (MBBA) is a thermotropic liquid crystal whose transition from the crystal to the nematic phase occurs around room temperature. Much of the literature concerning this material and the effect of aligning fields on thermotropic liquid crystals in general have been confined to the liquid crystalline phases.[1-6] However, a recent report has shown that quenching MBBA from the liquid crystalline phase can produce a metastable solid phase which exhibits additional endotherms

below room temperature, and a crystal melt 1.3°K lower than that of the normal crystal. The metastable state also has a lower enthalpy and entropy of fusion, and converts spontaneously with the liberation of heat to the stable crystalline form.[7] X-ray diffraction studies confirmed the amorphous nature of the metastable state. It further illustrated that the molecular arrangement of the liquid-crystalline phase is frozen in by the quenching process and as a result the anisotropy of the liquid crystal phase is retained in the metastable state.[8] In an earlier communication on a nuclear magnetic resonance (nmr) relaxation study of a similar nematic liquid crystal, [*N*-(*p*-ethoxy-benzylidene)-*p*-*n*-butylaniline] (EBBA), multiple relaxations were observed in the solid state.[9] Subsequent re-examination of the solid state by nmr and differential scanning calorimetry (dsc) techniques has shown that rapid quenching from the nematic phase gives rise to the formation of a mixture of crystalline and metastable amorphous material. Both of these phases exhibit minima, in the spin-lattice relaxation plots, for reorientation of the methyl/ethyl portions of the ethoxy and *n*-butyl groups. DSC further established that EBBA samples which were crystallized in a magnetic field exhibited a melting point some two degrees higher than the normal melt.[10] The effects of the rate of cooling and an aligning magnetic field seems to be crucial to the solid state structure and consequently to the molecular reorientational processes and thermal behavior of these molecules.

In the light of the structural changes, brought about by quenching to the low temperature phase of MBBA[7,8] and the effect of quenching and an aligning magnetic field on the solid state of EBBA,[10] it was felt that similar perturbations in the solid state properties of other liquid crystals should be realized if prepared in a similar fashion. As a result the nmr relaxation and dsc thermal behavior of MBBA samples were examined as a function of cooling rate. In addition the effects of the aligning magnetic field on the low temperature relaxations and the thermal behavior have been scrutinized in detail. Attempts are also made to show that some of the features observed here are general for all thermotropic liquid crystals.

EXPERIMENTAL

MBBA was obtained from Eastman Kodak Chemical Company. It was purified by vacuum distillation. NMR samples were prepared by placing MBBA in 10 mm (od) tubes and heating to the isotropic melt under vacuum. The tubes were degassed and sealed under a vacuum of $\sim 10^{-5}$ mm Hg. NMR spin-lattice relaxation times (T_1) were measured by the 180-t-90 degree pulse technique at 90 mhz in a magnetic field of 21 kgauss. All T_1s were obtained from plots of $[M(\infty) - M(t)]$ versus t. The magnetization recovery in all

cases was exponential and could be described by one time constant. $T_1 s$ were measured as a function of temperature on MBBA samples which were prepared by four different procedures. Method I involved quenching the sample from the nematic phase to liquid nitrogen temperatures outside the magnetic field. The sample was then placed in the sample coil, and $T_1 s$ were measured from 150°K to 320°K. In Method II MBBA samples were quenched from the nematic phase to liquid nitrogen temperatures in the magnetic field. $T_1 s$ were again measured from 150°K to 320°K. Method III required cooling the sample slowly from the nematic phase to the low temperature solid phase in the magnetic field. Slow cooling was accomplished by beginning at 320°K lowering the temperature in five degree intervals, waiting ten minutes for the sample to come to thermal equilibrium before measuring T_1. Method IV involved cooling the sample from 320°K to 200°K in a Delta design environmental oven at the rate of 1°K/minute. On reaching 200°K the sample was quenched to liquid nitrogen temperatures and transferred to the magnetic field. $T_1 s$ of this sample were measured from 150°K to 320°K. Plots of T_1 versus temperature for MBBA prepared by all methods are given in Figure 1.

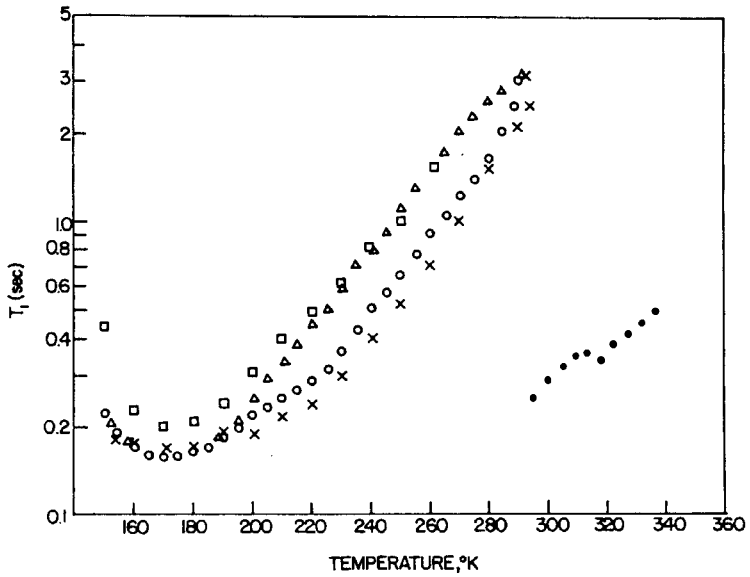

FIGURE 1 Plots of T_1 versus temperature for MBBA samples. × —Sample quenched from the nematic phase to liquid N_2 temperatures outside the magnetic field. ○—Sample quenched from the nematic phase to liquid N_2 in the magnetic field. △—Sample cooled slowly from 320°K lowering the temperature in five degree intervals, waiting ten minutes for the sample to come to thermal equilibrium. □—Sample cooled from 320°K to 200°K at the rate of 1°/minute outside the magnetic field, then quenched to liquid N_2 temperatures and transferred to the magnetic field. The closed circles represent the temperature region above the crystal melt.

DSC traces of MBBA were obtained in the following manner. Samples were quenched from the nematic phase to liquid nitrogen temperatures in the same magnetic field in which the nmr experiments were carried out. Other samples were cooled to liquid nitrogen temperatures from the nematic phase in the magnetic field at the rate of 10°/minute. Another sample was cooled to liquid nitrogen temperatures from the isotropic melt, in the magnetic field at a rate of 1°/minute. All samples were transferred from the magnetic field via a liquid nitrogen bath to the calorimeter and scanned upward in temperature through the crystal melt, and in some cases to the isotropic melt. After the initial scans the samples were quenched to the low temperature crystalline phase in the calorimeter and scanned again (in some cases several times) to determine the thermal behavior of the material when crystallized without the influence of the magnetic field. All dsc data were obtained on a Perkin-Elmer DSC II. The thermal data of MBBA is given in Figure 2.

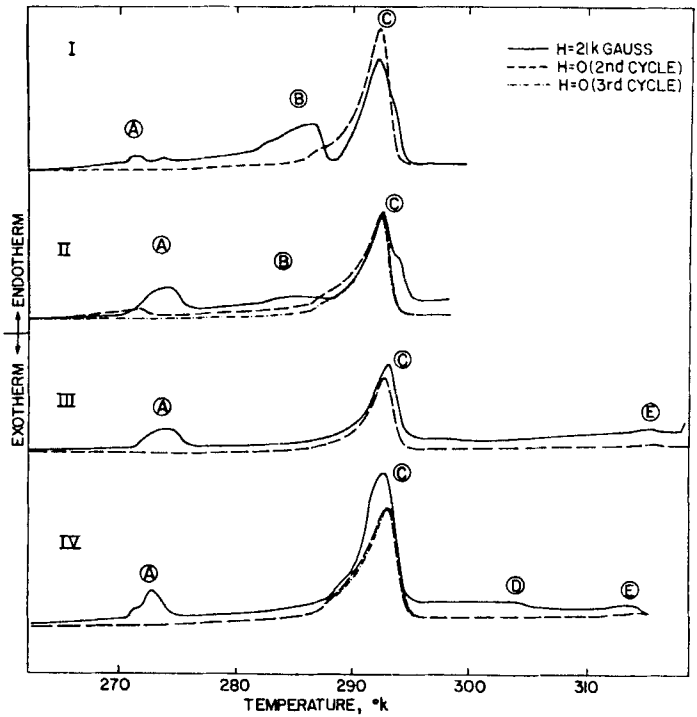

FIGURE 2 Differential scanning calorimetry traces of MBBA. I and II—Samples quenched in the 21 kgauss magnetic field from the nematic phase to liquid N_2 temperatures. III—Sample cooled from the nematic phase to liquid N_2 at the rate of 10°/minute in the magnetic field. IV—Sample slow cooled from the isotropic melt to liquid N_2 at the rate of 1°/minute in the magentic field. ---Represents the second scan after melting the field aligned sample and quenching to liquid N_2 in the calorimeter. ——·—Represents a third scan.

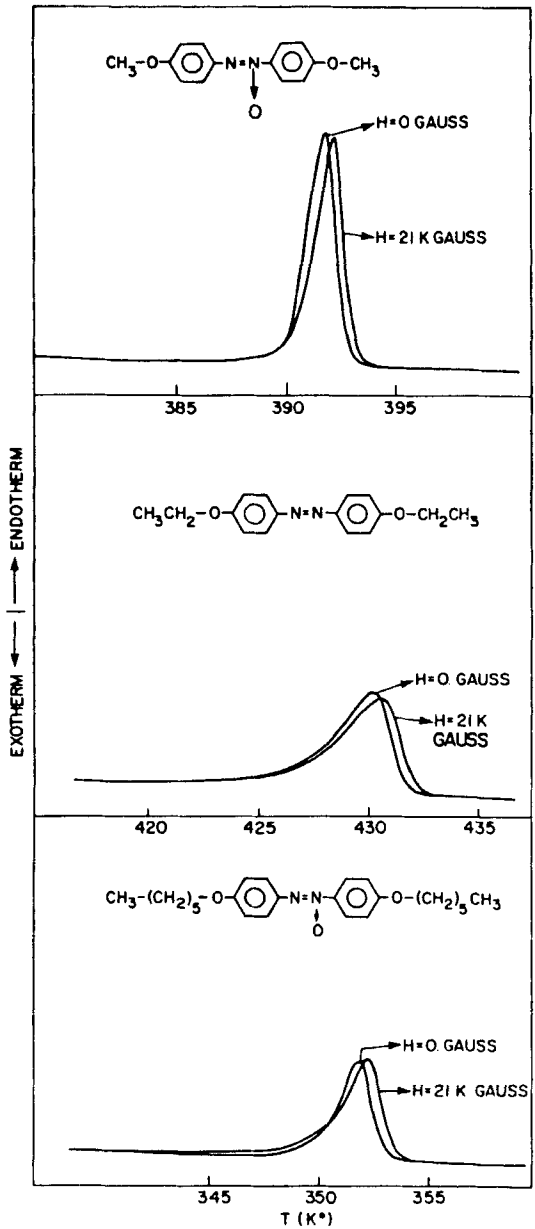

FIGURE 3 Differential scanning calorimeter traces of PAA, BHAB and ADP samples aligned in the nematic phase by a 21 kgauss magnetic field prior to crystallization and samples crystallized by quenching in the calorimeter.

Para-azoxyanisole (PAA), Bishexyloxy-azoxybenzene (BHAB), and 4,4'-azodiphenetole (ADP) were obtained from Eastman Kodak Chemical Company. These materials were recrystallized from ethanol. To examine the effects of crystallization in a magnetic field on the structure of the crystalline phase, PAA, BHAB and ADP were quenched from their isotropic melts to the solid crystalline phase in the 21 k gauss magnetic field. Samples were transferred to the calorimeter and scanned upward through the crystalline melt to the liquid crystalline phase. The samples were quenched to the solid phase in the calorimeter and scanned again. DSC traces after melting the field aligned samples were identical to those obtained from the recrystallized material. These results are given in Figure 3.

RESULTS AND DISCUSSION

It has previously been shown that quenching EBBA from the liquid crystalline state produces a mixture of the normal crystalline material and an amorphous metastable phase. The coexistence of these phases gives rise to double minimum in T_1, of which the low temperature (170°K) minimum is shown to result from the normal crystalline material while the 230°K relaxation arises from the amorphous phase. The T_1 plots of MBBA (Figure 1) are very similar to those of EBBA. The MBBA samples which were slow cooled either in or out of the magnetic field show only the low temperature minimum at 170°K while the quenched samples exhibit minima at 170°K and 230°K. Applying similar arguments to MBBA the minimum at 170°K must be due to reorientation of the methyl group in the normal crystalline material. The minimum at 230°K is also only observed in the quenched samples and it reinforces the conclusion that this minimum results from a similar methyl reorientation in the metastable amorphous state.[10] The possibility has been examined that the double minimum results from anisotropic reorientation of the methyl group. One may postulate that the low temperature minimum may be due to reorientation of the methyl group about its symmetry axis while the high temperature relaxation results from the overall tumbling of this group. The disappearance of the 230°K minimum on slow cooling and the absence of a change in the second moment of the absorption line corresponding to the high temperature minimum, lends less support to this argument than the assignments given above. In addition the dsc[7] and x-ray[8] data which demonstrate the coexistence of morphologically different environments in the quenched samples further reinforces the assignments.

It is also worthy to note that, like EBBA,[10] the sample which was slow cooled in the magnetic field exhibits a low temperature minimum which is as broad as that of the quenched samples. This was taken as evidence that the aligning effect of the magnetic field introduces additional motional aniso-

tropies in the solid state materials leading to a broader distribition of correlation times for the reorientational process and a less perfectly annealed structure than the sample slowly cooled outside the field. The activation energy for methyl reorientation was determined from the straight line portion of the plot of log T_1 versus temperature. From the low temperature minimum of the slow cooled sample a value of 3.1 kcal/mole is obtained, in good agreement with the value for EBBA. If the reorientation of the methyl group in both the amorphous and crystalline material begin at approximately the same temperature and the activation energy for such reorientation in the amorphous phase is lower than that of the crystalline material, one would expect the T_1 minimum for the amorphous phase to be observed at a somewhat higher temperature.

In measuring T_1s of the quenched samples from 150°K upwards the results follow those given in Figure 1. If at some point above 240°K one reverses the direction and measures T_1 while decreasing the temperature of the sample, the T_1 plot in the downward direction follows that of the slowly cooled sample. This supports the earlier observation that the metastable form converts spontaneously with the liberation of heat to the stable form.[7] It also suggests that the endotherms observed at 212°K[7] may be due to the glass transition of the metastable state. Above the glass transition the molecules posses sufficient motional freedom to allow them to reorient to the normal crystalline structure. At any temperature above the glass transition therefore, if sufficient time is allowed for the molecules to reorient, reversal of the measuring direction on a quenched sample will result in T_1s which follow those of the slowly cooled sample.

In addition to the differences in the crystallization behavior as a result of changes in the cooling rate, further changes due to crystallization of MBBA in the magnetic field are also observed in the dsc data, see Figure 2. The thermal response of the field aligned samples can be divided into five regions. All samples which have been crystallized in the magnetic field show a double endotherm at 271°K and 273°K (region A). Samples quenched from the nematic phase to liquid nitrogen temperatures in the magnetic field also show a broad asymmetric endotherm centered at 287°K (region B). The intensities of A and B appear to be inversely related. For the quenched samples the intensity of B is greater than that of A, while for the slowly cooled samples the intensity of A is larger than B. On the second heating cycle after scanning through the crystal melt (region C), the isotropic melt (region E) and quenching to liquid nitrogen temperatures in the DSC, region A disappears. At the same time region B is reduced and appears only as a low temperature tail on the crystal melt endotherm (region C). This suggests that the endotherms of region A result from a transition in the material as a result of aligning in the magnetic field.

Region C, the endotherm at approximately 293.3°K is the normal crystal melt of the unaligned sample. There is almost always a shift to higher temperature for the magnetic field aligned samples.[10] In some cases the endotherm for the magnetic field aligned samples is broken into a doublet. Quenching in the magnetic field seems to bring out the additional lesser intense endotherm at approximately 294.5°K while slow or intermediate cooling does not show this peak. The additional endotherm at 294.5°K is therefore associated with a magnetic field aligned phase whose structure is somewhat different from the normal crystalline phase ($mp \sim 293.3$°K). The presence of the normal and magnetic field aligned phases in any sample and their relative proportions determine the extent of the apparent upward shift in temperature of the crystal melt for samples crystallized in a magnetic field. Crystallizing MBBA in a magnetic field therefore, appears to produce variations in crystal structures of differing stability. When crystallization is produced by quenching in the magnetic field, the heat of fusion that is given up at the crystallization temperature is removed fast enough so that randomization of the magnetically ordered structure does not occur. Most of the ordered structure remains intact because the surroundings are at a lower temperature than the molecules which are crystallizing and the heat given off is rapidly removed by the surroundings. On the other hand, in slow cooling, the temperature of the surroundings is approximately equal to that of the forming crystals. The time for the transfer of the heat given up at fusion is therefore long compared to that of the quenched sample. As a result, some thermalization of the magnetic field aligned structure takes place. This results in a more imperfect field oriented structure having a melting temperature a fraction of a degree lower than the normal melt. Such evidence supports the arguments presented above that the field ordered crystal melt is dependent on the cooling rate of the samples. Samples which were slow cooled in the magnetic field do not show the high temperature endotherm of region C. There also appears to be a further correlation between the endotherms of regions A and C. From a comparison of the endotherms in these regions it appears that in the slowly cooled sample, (cooling rate 1°/min.) the high temperature peak of region A is more intense than its low temperature counterpart. On the other hand, for the quenched sample both peaks of region A appear to be of equal intensity and shifted to slightly higher temperature. At the same time the high temperature peak of region C is well defined. The existence of endotherms in these regions are interrelated because they both result from alignment by the magnetic field. However, their intensities and temperature positions are determined by the cooling rate of the sample.

Above the crystal melt there is evidence of residual ordering in the field aligned samples. Such ordering gives rise to an increase in the heat capacity

in the liquid crystalline phase (region D) of the field aligned sample. The order is only destroyed by passing through the isotropic melt (region E). As a matter of fact the magnetic field ordered samples always have a higher heat capacity, over the temperature range scanned, than the normal crystal. This seems to imply that the mixture of morphologies obtained in such samples exhibits an overall increase in anisotropies giving the appearance of increased motional freedom. There is, however, one exception to the residual order in the liquid crystalline state of the magnetic field aligned sample. The thermograms (in I of Figure 1) which do not show the residual order above the crystal melt also have the more intense B region and the less intense A region. Since the intensities of these regions appear to be related to the cooling rate and the degree of thermalization possible on crystal formation, it appears that the more rapidly quenched sample exhibit the greater intensity endotherm at 287°K and the smaller degree of residual ordering above the crystal melt. The degree of residual ordering above the crystal melt may therefore be subject to the existence of the structure which is observed to melt at region B.

As a result of the effects observed for MBBA samples which were magnetic field aligned in the liquid crystalline phase prior to crystallization, several high temperature nematics were subjected to the same field aligned crystallization. The results of PAA, BHAB and ADP are given in Figure 3. The samples which were crystallized in the magnetic field all show higher melting temperatures than the non-alighed samples. The heat of fusion obtained from both traces are identical within limits of error of our measurements. The results are consistent with those of EBBA,[10] and MBBA and demonstrate that the magnetic field effects appear to be general for nematic liquid crystals.

SUMMARY

When a thermotropic liquid crystal is placed in a magnetic field the molecules align themselves in a direction parallel to the applied field. The field required to align the molecules is fairly small. From the relationship $T = \gamma/\Delta\chi H^2$, where T is the time required to align the molecules parallel to the applied field, γ is the torsional viscosity and $\Delta\chi$ is the anisotropy of the magnetic susceptibility one can estimate the field required for a particular T. Taking $\Delta\chi \sim 10^{-7}$ (cgs) and $\gamma \sim 0.1$ poise, for an aligning time of 1.0 second a field of 1.0 kgauss is required.[12] A magnetic field of 21 kgauss is therefore larger than the critical field required to align the molecules. The presence of such a field on the liquid-crystalline phase prior to crystallization has profound effects on the structure of the solid state material. The magnetic field aligned samples of MBBA exhibit endotherms at 271, 273, 287 and 294°K in addition

to the normal crystal melt. The intensities of these additional endotherms appear to be interrelated and together with the residual order observed in the liquid-crystalline state for the field aligned samples they all seem to be influenced by the rate of cooling of the sample from the liquid crystalline phase of the solid state. The magnetic field aligned samples consist of an intricate solid state morphology. Aside from the normal crystal structure, additional anisotropies are introduced by the aligning magnetic field and the liquid-crystalline structure that is retained in the metastable state on quenching. These anisotropies are also reflected in the nmr relaxation measurements where separate relaxations are observed for methyl reorientation in the normal crystal and the metastable amorphous state. Activation energies for methyl reorientation in the normal crystal are about 3.1 kcal/mole. For the metastable material the value appears to be lower, giving rise to a T_1 minimum some 60°K higher in temperature than that of the normal crystal. The dsc transition at 212°K appears to be associated with the glass transition of the metastable material above which the molecules can reorient themselves spontaneously to form the normal crystal structure.

References

1. *Liquid Crystals*, (Eds., G. Brown, G. Dienes, and M. Labes), Gordon and Breach Science Publishers, New York, N.Y., 1966.
2. G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, New York, N.Y., 1962.
3. G. H. Brown, J. W. Doane, and V. D. Neff, *Critical Reviews in Solid State*, **1**, 303 (1970).
4. R. D. Spence, H. A. Moses, and P. F. Jain, *J. Chem. Phys.*, **21**, 389, (1953).
5. J. C. Powell, W. D. Phillips, L. R. Melby, and M. Ponai, *J. Chem. Phys.*, **43**, 3442 (1965).
6. F. A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, N.Y., 1969.
7. J. Mayer, T. Waluga, and J. A. Janik, *Chem. Phys. Lett.*, **41A**, 102 (1972).
9. S. D. Goren, C. Korn, S. B. Marks, and R. Potashnik, *Chem. Phys. Lett.*, **24**, 249 (1974).
10. M. F. Froix, J. M. Pochan, and J. Yanus, to be published.
11. J. O. Kessler and J. E. Lydon, *Liq. Cryst. and Ordered Fluids*, **2**, 331 (1973).
12. J. Pirs, P. Ukleja, and J. W. Doane, *Solid State Chem.*, **19**, 877 (1976).