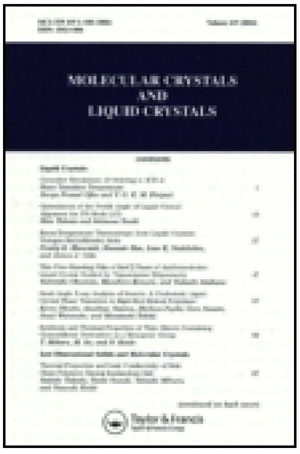

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

An Investigation of Polymorphism in N-(P-Butoxybenzylidene)-p-Propylaniline

W. W. Walker [a]

[a] Department of Physics and Astronomy, The University of Alabama, University, Alabama, 35486

Version of record first published: 20 Apr 2011.

Mol. Cryst. Liq. Cryst. 102 (Letters), pp. 129-132
0140-6566/84/1025-0129$18.50/0

AN INVESTIGATION OF POLYMORPHISM IN N-(p-BUTOXYBENZYLIDENE)-p-PROPYLANILINE

W. W. WALKER
Department of Physics and Astronomy, The University of Alabama, University, Alabama 35486

(Received for Publication June 6, 1984)

ABSTRACT: Experimental data are reported on phase transitions of N-(p-butoxybenzylidene)-p-propylaniline (40.3) using the techniques of differential scanning calorimetry and positron annihilation. These data reveal the existence of metastable solid phases in 40.3 which has been fast cooled from the nematic.

A number of studies[1,2] of the solid forms of the N-(p-alkoxybenzylidene)-p-alkylanilines obtained by abrupt cooling from the mesophase has revealed the existence of a multiplicity of low temperature states. Some of these states have been described as metastable while others are referred to as glassy. The most extensively studied of these compounds is MBBA, abbreviated as 10.4 in the nO.m notation where n and m denote the lengths of the terminal alkyl chains. Most of these investigations have utilized such techniques as thermal analysis, infra-red absorption, Raman spectroscopy, and neutron diffraction. This paper presents experimental data for 40.3 using differential scanning calorimetry and positron lifetime measurements. No previous solid phase studies of 40.3 are known to have been published. Use of the positron lifetime technique for the examination of benzylideneanilines which have been fast cooled from the nematic has been reported for only two cases: 10.4[3,4] and 30.5[5].

The sample of 40.3 was obtained from Eastman Organic Chemicals and used without further purification. Eastman quoted a nematic range of 53°C to 82°C for this compound. Thermal measurements utilized a Perkin-Elmer DSC-1B. The positron lifetime measurements were made with a conventional apparatus which has been described previously[6]. Samples described as being fast cooled from the nematic were immersed in liquid nitrogen while enclosed in heat-sealed plastic bags.

Figure 1 shows a typical DSC heating thermogram obtained for a fast-cooled sample of 40.3 using a heating rate of ten degrees per minute. Although the DSC measurements started at -100°C, that portion of the trace for temperatures below about 10°C is not shown since no endotherms or exotherms were observed in that region. The thermogram for a slow-cooled sample was much simpler, showing only the last two endotherms of Figure 1 (at 53°C and 82°C), corresponding to the solid-nematic and the nematic-isotropic liquid transitions, respectively. It is seen from Figure 1 that a fast-cooled sample exhibits a multiplicity of endotherms below the melting point. It was found that the temperatures at which these endotherms occur as well as their relative sizes depend on the length of time that the sample was held at the low temperature and on the heating rate employed. This type of behavior indicates a complicated solid-state morphology in the fast-cooled sample. It is apparent from the DSC data that 40.3 can exhibit several metastable solid phases, possibly separately or in combination, and the particular result obtained is dependent on sample treatment.

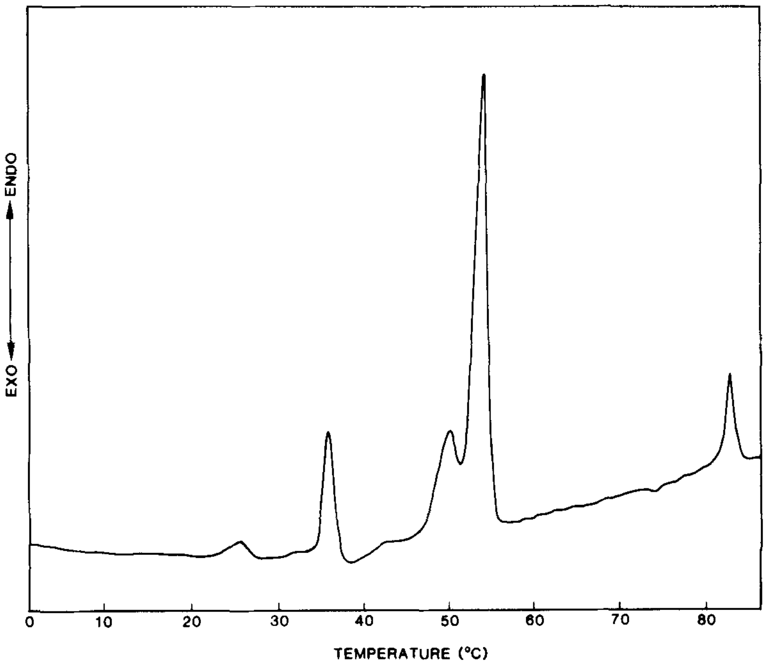

Figure 1. DSC heating thermogram for fast-cooled sample

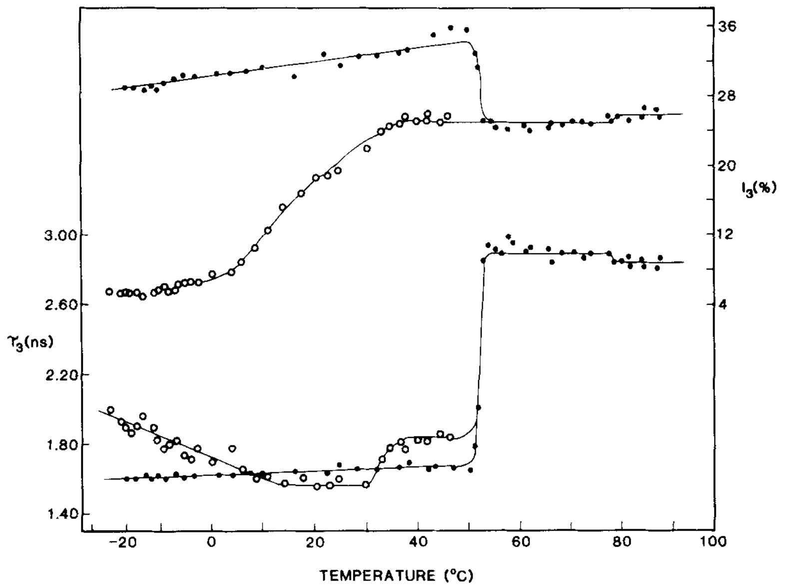

Figure 2. Positron lifetime data: open circles for fast-cooled sample, solid circles for slow-cooled sample.

The positron lifetime results are given in Figure 2. Since heating rates employed in these measurements are quite slow and since the transition temperatures of the metastable states are highly dependent on the rate of warming, it was not possible to obtain close agreement with the DSC measurements. The positron data were analyzed into three components using the computer program "Positronfit"[7], with τ_3 and I_3 representing the lifetime and the intensity of the longest-lived component. I_3 is considered to be a measure of the amount of triplet positronium (Ps) formed while τ_3 is the effective lifetime of triplet Ps in that medium. The τ_3 value for the stable solid obtained by slow cooling is approximately constant at $\sim$1.6 ns at all temperatures investigated. I_3 for this case exhibits a small temperature effect, increasing linearly from $\sim$ 29% to $\sim$ 35% over the seventy degree range for which the solid was studied. However, in agreement with the DSC results, the behavior of both τ_3 and I_3 was much more complex for the fast-cooled sample. The positron data indicate several distinct changes in the structure of the sample as it warms from -22°C. τ_3 for this sample has values both above and below the value which was obtained for the slow-cooled sample. I_3 is relatively small (~5%) for the fast-cooled sample at the lower temperatures, but it increases rapidly with increasing temperature above ~4°C.

These positron results for 40.3 differ in an important way from the results obtained for two other benzylideneanilines (10.4 and 30.5) previously studied in this laboratory[3,5]. I_3 is smaller for the fast-cooled sample of 40.3, just opposite from the behavior in the other two cases. This indicates that metastable states formed in 40.3 are less conducive to Ps formation.

Another way in which fast-cooled samples of 40.3 differ from 10.4 and 30.5 is in the absence of an exotherm in the DSC heating thermogram. This result indicates that the metastable solid phases of 40.3 do not undergo spontaneous recrystallization upon warming.

The positron data, which correspond to an extremely slow warming of the fast-cooled sample, suggest that possibly three different metastable phases are formed. The metastable solid phase (K_1) present at -22°C appears to be changing gradually with increasing temperature into a second solid phase (K_2) in the temperature interval ending near 17°C. Phase K_2 exists between ~17°C and ~30°C, at which temperature it begins to be converted into a third metastable solid form (K_3). The conversion into K_3 is completed near 38°C and K_3 exists until the melting point is reached. Clearly, additional techniques need to be applied to substantiate this interpretation and to further identify the nature of the solid phases.

One further observation is that the transition from nematic to isotropic liquid is marked by a small increase in I_3 and a small decrease in τ_3. This agrees with the behavior previously observed for 30.5[5]. The smallness of the effects here emphasizes the fact that the positron probe senses a very similar electronic environment in the nematic and isotropic liquid phases.

REFERENCES

1. N. Kirov, M.P. Fontana, and F. Cavatorta, Mol. Cryst. Liq. Cryst. 54, 207 (1979).
2. V.K. Dolganov, M. Gal, N. Kroo, L. Rosta, and E.F. Sheka, Mol. Cryst. Liq. Cryst. Lett. 92, 281 (1984).
3. W.W. Walker, Appl. Phys. 16, 433 (1978).
4. S.R.S. Kafle and P.C. Jain, Positron Annihilation, Ed. by P.C. Jain and R.M. Singru, South Asian Publishers (New Delhi) 1980, p. 247.
5. W.W. Walker, Adv. Chem. Ser. 175 (1979), Ch. 2.
6. W.W. Walker and E.L. Mueller, Appl. Phys. 3, 155 (1974).
7. P. Kirkegaard and M. Eldrup, Comp. Phys. Commun. 7, 401 (1974).