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The effect of *N*-(4-*n*-butyl benzilidine) 4-amino 2,2,6,6-tetramethyl piperidine 1-oxide on the nematic-to-isotropic phase transition of 4-*n*-pentyl-4′-cyanobiphenyl

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Abstract

The nematic-to-isotropic phase transitions of 'pure' 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and nine mixtures of the radical *N*-(4-*n*-butyl benzilidine) 4-amino 2,2,6,6-tetramethyl piperidine 1-oxide (BBTMPO) at very low mole fractions in 5CB were investigated by a 'visual' method and the coexistence lines of the phase diagram obtained were found to be virtually linear as quadratic least-squares fits had only slightly higher correlation coefficients than the linear ones. Thus theoretically predicted curvature in the coexistence lines remains unobserved experimentally. The result for one of the mixtures was confirmed by two methods: the density approach and an EPR method that made use of a setup which allows the control of the temperature of the sample to ±0.01 °C. In the EPR study BBTMPO acted as both probe and impurity, thereby eliminating the effect of the addition of a probe to the mixture that is being investigated. The agreement between the results of the EPR, density and visual measurements was very good. The study shows that BBTMPO is a suitable EPR probe and that a nitroxide probe need not be deuterated for investigating the two-phase region of an impure liquid crystal.

Keywords: Nematic solvent; Radical solute; Phase diagram; Density; EPR

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1. Introduction

It is now established [1] that, with few exceptions [2,3], the presence of a solute impurity in a nematogenic liquid crystal depresses its nematic-to-isotropic transition temperature $\vartheta_{\rm ni}$ and, as expected from the first-order nature of the transition, leads to a nematic–isotropic two-phase region, bounded by $\vartheta_{\rm n}$, the temperature at which the isotropic phase first appears, and $\vartheta_{\rm i}$, the temperature at which the nematic phase just disappears. The phase diagram shown in Fig. 1 is typically obtained for a nonmesomorphic solute/nematogenic solvent mixture at moderately low solute mole fractions ($0.01 < x_2 < 0.06$) where $\Theta^* = \Theta/\Theta_{\rm ni}$ (that is, $\Theta^*_{\rm n} = \Theta_{\rm n}/\Theta_{\rm ni}$ and $\Theta^*_{\rm i} = \Theta_{\rm i}/\Theta_{\rm ni}$) is a reduced temperature and $\Theta = \vartheta + 273.15$. The boundary lines for such a phase diagram have been found to be virtually linear [4–8] although several theoretical studies [9–11] predict or hint at a slight curvature. $\beta_{\rm n}$ and $\beta_{\rm i,}$ the moduli of the slopes of the nematic and isotropic boundary lines, respectively, reflect the solute's ability to destabilize the nematic phase.

The various methods for obtaining the β values for systems of volatile quasi-spherical solutes or alkanes in nematic solvents have been outlined recently [1] and, for the sake of cohesion, those used in this study are briefly outlined in Section 2. The solute mole fractions used in these studies were higher than 0.01 as lower mole fractions would have had high uncertainties because the solute was a liquid (sometimes a volatile liquid) and its mass was calculated from its volume, measured in a microliter syringe, and density, each with an appreciable uncertainty. In this study the nitroxide radical solute, *N*-(4-*n*-butyl benzilidine) 4-amino 2,2,6,6-tetramethyl piperidine 1-oxide (BBTMPO) (structure **I**), is a solid and the nematic solvent is 4-*n*-pentyl-4′-cyanobiphenyl (5CB) (structure **II**).

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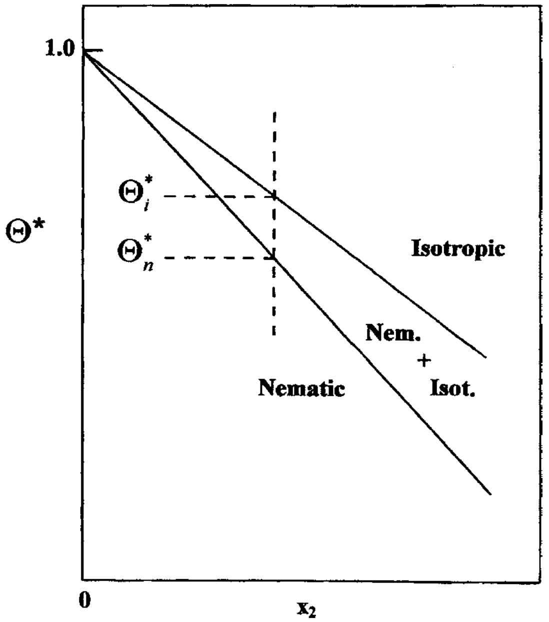
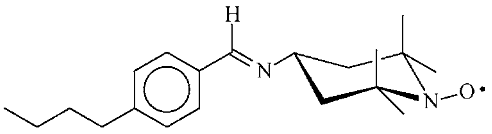


Fig. 1. Typical reduced temperature (Θ^*)—solute mole fraction (x_2) diagram for mixtures of nonmesomorphic solutes at low solute mole fractions ($0.01 < x_2 < 0.06$) in nematogenic solvents.

Since both 5CB and BBTMPO can be directly weighed it was possible to carry out this study on mixtures of more accurately known compositions down to a BBTMPO mole fraction of 1.5×10^{-4}. The aims of this paper are: (a) to apply the visual, density and electron paramagnetic resonance (EPR) methods to obtain β_n and β_i for a system that is different from those previously studied [4–7], (b) to see if theoretically predicted curvature in the boundary lines can be detected and (c) to test the feasibility of using an undeuterated probe to study the two-phase region of an impure liquid crystal.



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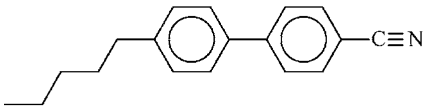

II

The radical BBTMPO was synthesized by Hwang et al. [12], has a melting point of 81.5–82 °C and is adequately soluble in 5CB at room temperature. The BBTMPO molecule is rod-like, has a high degree of rigidity and its rotational motion has been shown to be anisotropic in normal liquids [12]. The nature of the motion of BBTMPO in liquid crystals is discussed elsewhere [13].

The visual method [4,6,8,14] was used to obtain the phase diagram for 5CB–BBTMPO binary mixtures with BBTMPO mole fractions between 1.49×10^{-4} and 2.80×10^{-3}. An electron paramagnetic resonance approach [15] was used to check the boundaries of the two-phase region for a mixture with a BBTMPO mole fraction of 9.89×10^{-4}. The use of BBTMPO has the added advantage of being both the solute impurity and the nitroxide probe. The density approach [1,8] was also used to check the boundaries of the two-phase region for a mixture with a BBTMPO mole fraction of 9.76×10^{-4} and to estimate β_n and β_i for the 5CB–BBTMPO system The results of the EPR and density approaches agree with those of the visual method at the same concentrations.

2. Experimental

The liquid crystal solvent 5CB was purchased from F. Hoffmann-La Roche (Switzerland) and used as received. By dilution of a stock solution of BBTMPO in 5CB with ‘pure’ 5CB, nine solutions with BBTMPO mole fractions between 1.49×10^{-4} and 2.80×10^{-3} were prepared. Each solution was prepared from the original stock solution to avoid additive errors in successive dilutions. Each of these solutions and a sample of ‘pure’ 5CB were transferred to narrow thoroughly cleaned and dried tubes such that their heights in the tubes were in excess of 3 cm to allow the observation of the onset of the isotropic phase (a clear solution) and the disappearance of the nematic phase (a turbid solution) on very slow heating (in steps of less than 0.01 °C and allowing at least 20 min between the heating steps to ensure equilibration and phase separation). The temperature control of the insulated water bath was achieved using an RCS Lauda thermostated circulation system assisted by a Fisher Circulator Model 73 placed inside the bath. The temperature of the bath was controlled to better than ±0.005 °C and the mercury-in-glass thermometer used is one of a series of *Precision A* thermometers (manufactured in Germany) with a 10 °C scale extending over a mercury thread that is 45 cm long and with a smallest unit of 0.01 °C that, with the aid of a magnifying glass, may be read to the nearest 0.001 °C. The necessary stem correction was added to the thermometer reading. The results from this visual experiment are given in Table 1.

The measurements of density were made using an Anton Paar digital precision density system (a DMA 602 measuring cell and a DMA 60 density meter). A 0.7 cm^3 hollow U-shaped glass tube filled with a liquid is induced to vibrate at its natural frequency and a period (τ) whose square is a linear function of the density (ρ) of the fluid (i.e., $\tau^2 = A + \rho B$). To calculate the density of a liquid at a particular temperature its τ needs to be measured, and both A and B need to be known at the same temperature. A and B were calculated at each temperature used in this study from measurements of τ, for the reference fluids air and de-ionized

Table 1
The Temperatures in °C at the onset of the isotropic phase (ϑ_n) and the disappearance of the nematic phase (ϑ_i) for 'pure' 5CB and mixtures with different mole fractions (x_2) of BBTMPO in 5CB

ϑ_i[a] (°C)	ϑ_n[a] (°C)	x_2 ($\times10^{-4}$)
35.013	34.983	0.0000
34.965	34.921	1.4889
34.893	34.831	3.4801
34.837	34.753	4.4503
34.803	34.703	6.2326
34.778	34.668	7.0564
34.658[b,c]	34.523[b,c]	9.8890
34.533	34.423	13.192
34.399	34.213	18.182
34.118	33.822	27.996

[a] The temperatures are reported as read by the mercury-in-glass thermometer, after the stem correction. The temperature control is around ±0.005 °C.

[b] The EPR experiment gives 34.51 °C for ϑ_n and 34.69 °C for ϑ_i.

[c] The density experiment for a 5CB–BBTMPO mixture with a BBTMPO mole fraction of 9.7594×10^{-4} gives 34.51 °C for ϑ_n and 34.67 °C for ϑ_i.

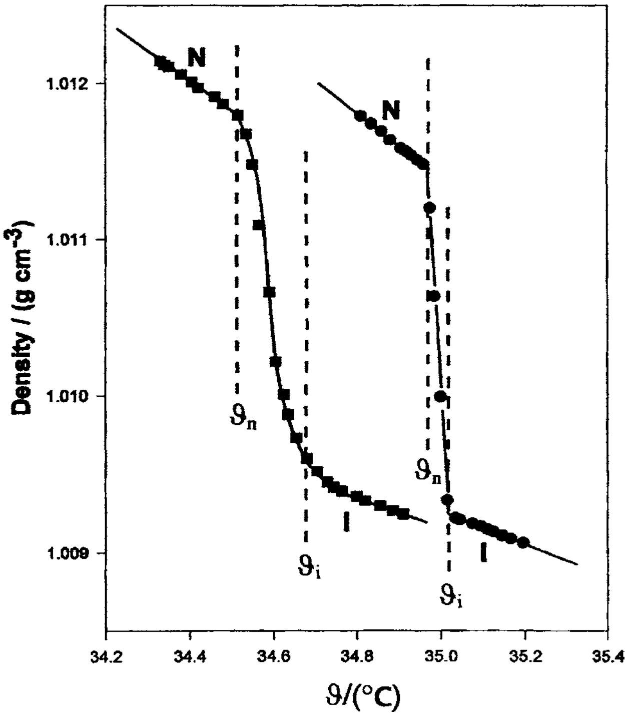

Fig. 2. The variation of density with temperature across the nematic-to-isotropic transition for pure 5CB (●) and for a mixture of BBTMPO, at a mole fraction of 9.7593×10^{-4}, in 5CB (■). The dashed lines in each system indicate the boundary of the nematic–isotropic two-phase region.

distilled water, at very close temperature intervals, over all the ranges of temperatures studied. The temperature of the fluid in the U-shaped glass tube was controlled to within ±0.01 K using an RCS Lauda thermostating circulation system and kept constant until a constant value of τ was reached. To ensure that equilibrium is reached by the liquid crystal systems τ was read only after it has been observed to be constant for at least 20 min. The temperature was raised in steps of less than 0.05 K in the vicinity of the transition temperature. Under the conditions used [16] the precision of the density values is 1.0×10^{-5} g cm^{-3}. The variation of density with temperature was measured in the vicinity of the nematic-to-isotropic transition for pure 5CB and a 5CB–BBTMPO mixture with a BBTMPO mole fraction of 9.7×10^{-4}. The results are illustrated in Fig. 2.

EPR spectra were taken in a heating cycle for a mixture of BBTMPO in 5CB at a mole fraction of 9.889×10^{-4} at various temperatures in the vicinity of its nematic-to-isotropic phase transition as determined from the visual experiment. Silicone oil circulating from an RC6 Lauda temperature controller into an especially designed brass jacket [17,18] around the EPR tube had its temperature controlled to within ±0.01 °C and measured using a mercury-in-glass thermometer immersed in the circulator bath and having a scale readable to 0.001 °C. The temperature was raised in steps of 0.05 °C or less. After the temperature reached a constant value at least 20 min was allowed to elapse before the spectrum was taken to ensure equilibration of the sample. The EPR spectra were taken using a Varian E-102 spectrometer operating at 9.155 GHz centered at 3256 G. The magnetic field was measured using a Varian NMR Gaussmeter with an accuracy of 10 mG. The microwave frequency was measured using a model 5342A HP microwave frequency counter. The spectra were recorded using a scan time of 2 min over a 50 G scan range. A number of these spectra on either side of the nematic–isotropic two-phase region are shown in Fig. 3.

3. Results and discussion

The accuracies of the solute concentrations in the BBTMPO–5CB mixtures are higher than those for liquid solutes [4,6–8] added using a microliter syringe (with a delivery error of at least 5%). Even when such mixtures are placed in tubes with vacuum tight stoppers some of the solute vaporizes into the space above the mixture. This improved accuracy in solute concentrations allowed measurements at solute concentrations that are more than one order of magnitude lower than the solute concentrations used in the past [4–8].

Visually a finite two-phase region with the isotropic phase appearing at 34.983 °C and the nematic phase disappearing completely at 35.013 °C was observed for 'pure' 5CB. This is attributed to impurities either intrinsic to the synthesis of 5CB or introduced during experimental handling. Best least-squares fits for ϑ_n versus x_2 and ϑ_i versus x_2 intersected at $x_2 \approx -1.7 \times 10^{-4}$ and ϑ (taken as ϑ_{ni}) $= 35.0765$ °C. From Θ_{ni} ($\Theta_{ni} = \vartheta_{ni} + 273.15$ K), Θ_n^* and Θ_i^* values for all the mixtures were calculated. Linear least-squares fits for Θ_n^* versus x_2 ($\Theta_n^* = 0.99963 - 1.33476x_2$) and Θ_i^* versus x_2 ($\Theta_i^* = 0.99974 - 1.04866x_2$) had correlation coefficients of 0.9987 and 0.9974, respectively. Accordingly β_n and β_i are

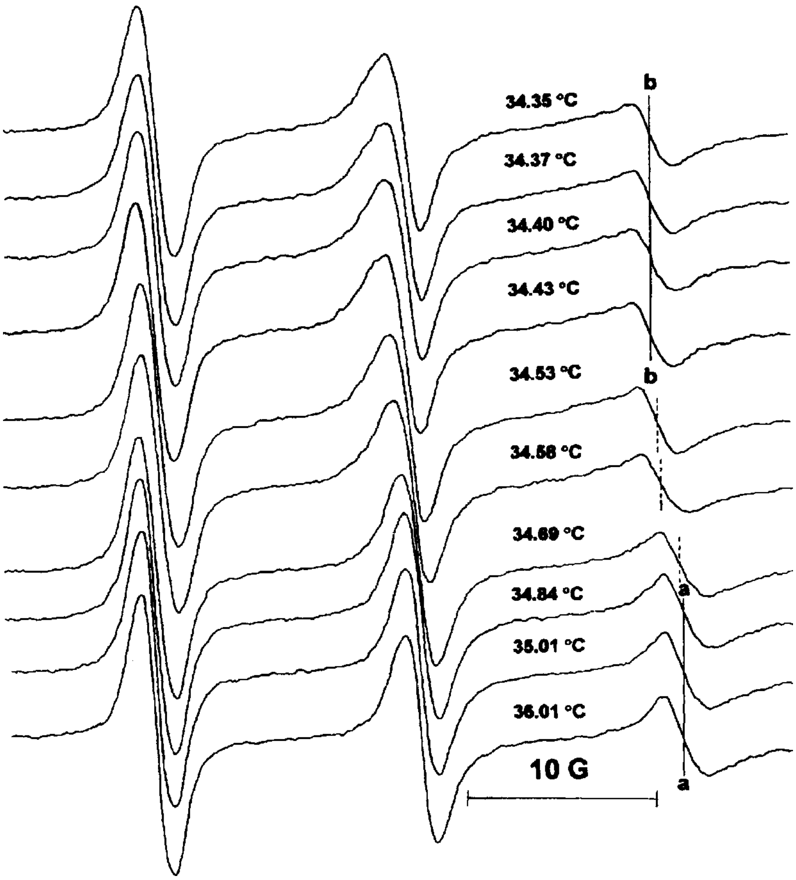

Fig. 3. Representative EPR spectra for BBTMPO at a mole fraction of 9.889×10^{-4} in 5CB at selected temperatures in the vicinity of the nematic-to-isotropic transition temperature. Lines 'bb' and 'aa', respectively, show the positions for the centers of the high-field line for the nematic and isotropic phases respectively. The dashed lines reflect the gradual increase in the high-field splitting as the amount of the isotropic phase increases along the temperature range of the two-phase region.

1.335 and 1.049, respectively. A correlation coefficient of 0.9992 was obtained for quadratic least-squares fits for $\Theta_{\rm n}^*$ versus x_2 ($\Theta_{\rm n}^* = 0.99968 - 1.47260x_2 + 49.25319x_2^2$) and for $\Theta_{\rm i}^*$ versus x_2 ($\Theta_i^* = 0.99982 - 1.24501x_2 + 71.10329x_2^2$) and accordingly $\beta_{\rm n}$ and $\beta_{\rm i}$ are given by

$$\beta_{\rm n} = -\frac{{\rm d}\Theta_{\rm n}^*}{{\rm d}x_2} = 1.47260 - 98.50639x_2 \tag{1}$$

$$\beta_{\rm i} = -\frac{{\rm d}\Theta_{\rm i}^*}{{\rm d}x_2} = 1.24501 - 142.20657x_2 \tag{2}$$

That a linear fit seems as good as the quadratic fit is probably due to the narrow range of mole fractions studied. This very slight improvement in the correlation coefficient of the quadratic fit over the linear fits hints at, but is not large enough to allow a firm statement on, curvature in the coexistence lines.

According to Eqs. (1) and (2) as the amount of BBTMPO added to 5CB increases, BBTMPO becomes less effective, on a mole fraction basis, in disrupting the nematic order of 5CB. If this curvature for the coexistence lines is real, it corresponds to the type of curvature arrived at by Dowell [11] from a lattice model for semi-flexible chain solutes in solvent molecules composed of rigid cores and semi-flexible tails. Unlike the solutes considered by Dowell [11], the BBTMPO solute molecule (structure **I**) has a rigid core and a short semi-flexible tail. 5CB has a length-to-breadth ratio of 2.8 [6] while BBTMPO has a length-to-breadth ratio close to 2.4 (Hwang et al. [12] approximated the shape of BBTMPO to a prolate spheroid with $a = 8$ Å and $b = 3.3$ Å). The system used in our experimental study involves a more rigid solute than that considered in the theoretical study by Dowell [11]. If the curvature in the coexistence lines obtained in this study is real, then the similarity to the results of Dowell [11] may be attributable to the restrictions, assumptions and approximations of the lattice model which imparts a high degree of rigidity on the semi-flexible chain solute. That this may the case can be seen in the very large $\beta_{\rm n}^{\infty}$ (=2.9) and $\beta_{\rm i}^{\infty}$ (=1.7) values (the ∞ in superscript refers to limiting values as x_2 approaches zero) that the model [11] predicts relative to the results of this study ($\beta_{\rm n}^{\infty} = 1.47$ and $\beta_{\rm i}^{\infty} = 1.25$) and earlier experimental results which gave β values in the range 0.25–1.41 for quasi-spherical [4,6,19,20] solutes and in the range 0.35–1.15 for *n*-alkane [4,14,19,20] solutes. That the β values for BBTMPO are higher than those for *n*-alkanes and higher or comparable to

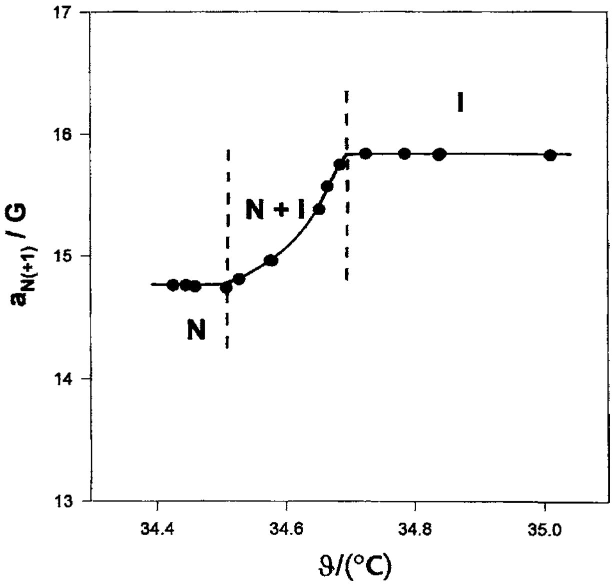

Fig. 4. The variation with temperature of the high-field splitting in the nematic and isotropic phases and along the nematic-to-isotropic phase transition (bounded by the dashed lines) for a mixture of BBTMPO in 5CB at a mole fraction of 9.889×10^{-4}.

those for quasi-spheres indicates that the piperidinyl ring in BBTMPO rotates freely around the single CN bond thereby making the molecule globular rather than rod-like.

An estimate of β_n and β_i was also obtained from the variation of the density in the vicinity of the nematic-to-isotropic transition of 'pure' 5CB and a mixture of BBTMPO at a mole fraction of 9.7594×10^{-4} in 5CB. The results (see Fig. 2) give a two-phase region extending over 0.16 °C (from 34.51 °C (ϑ_n) to 34.67 °C (ϑ_i)) for the BBTMPO–5CB mixture and over 0.05 °C (from 34.97 to 35.02 °C) for 'pure' 5CB. Assuming a linear phase diagram and ϑ_{ni} values of 34.97 °C for the coexistence line on the nematic side and 35.02 °C for the coexistence line on the isotropic side of the phase diagram, β_n and β_i estimates of 1.530 and 1.164, respectively, were obtained.

The EPR spectra for the mixture with a BBTMPO mole fraction of 9.8890×10^{-4} are shown in Fig. 3. Because of the large inhomogeneous broadening of the hydrogen atoms in BBTMPO, its EPR spectra (see Fig. 3) do not exhibit the high- and low-field doublets observed when deuterated nitroxide probes are used [15,21]. Nevertheless using the variation in the high-field splitting from its value in the nematic phase to its value in the isotropic phase along the two-phase region (see Figs. 3 and 4) we were able to pinpoint the temperatures for the onset of the isotropic phase (34.51 °C) and the disappearance of the nematic phase (34.69 °C).

4. Conclusion

The phase diagram for mixtures of BBTMPO at very low mole fractions (ranging from 1.5×10^{-4} to 2.8×10^{-4}) in 5CB was obtained from visual measurements. In agreement with similar earlier studies the addition of BBTMPO lowered the nematic-to-isotropic transition temperature of 5CB and brought about a region where the nematic and isotropic phases co-exist. Although the results hint at a slight curvature in the coexistence lines that has been theoretically predicted [11] such curvature cannot be accepted as it indicates that at higher concentration BBTMPO would start to stabilize the nematic phase rather than disrupt it. In fact according to Eqs. (1) and (2) Θ_n^* starts to increase for x_2 greater than 0.015 and Θ_i^* starts to increase for x_2 greater than 0.009. It is probable that the coexistence lines are curved at only low x_2 values and should not be fitted with one equation for all the x_2 values.

The results from the EPR study on a mixture with a BBTMPO mole fraction of 9.8890×10^{-4} and from density measurements on a mixture with a BBTMPO mole fraction of 9.7594×10^{-4} agree with the results of the visual study at these concentrations (see footnote to Table 1). The extents of the two-phase region obtained from the visual, density and EPR studies are in good agreement; they are 0.14, 0.16 and 0.18 °C, respectively. The agreement of the results of the EPR measurements with the visual and density measurements demonstrate the possibility of using BBTMPO as a new radical for EPR and shows that it, and possibly other undeuterated nitroxide probes, can be used to investigate the two-phase region in impure liquid crystals even though, unlike deuterated nitroxide probes [15,21], their low- and high-field lines are not sharp enough to show a doublet in that region.

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