Photon transmission technique for studying multiple phase transitions in a liquid crystal

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A photon transmission technique was used to monitor the multiple phase transitions in a 4-butoxyphenyl-4′-declyoxybenzoate (BOPDOB) liquid crystal. Drastic decreases in the transmitted photon intensity (I) were attributed to the sequential phase transitions in BOPDOB upon cooling. In this paper, it is assumed that the order parameter ρ is proportional to the transmitted photon intensity. The isotropic-nematic and nematic–smectic-A transitions were observed and found to be of first order. It was observed that the smectic-A–smectic-C and smectic-C–smectic-G transitions are second order. It was found that for the smectic-A–smectic-C transition, critical exponent crosses over from $\beta=0.513\pm0.006$, which is consistent with mean-field theory, to $\beta=0.35\pm0.009$, which is consistent with heliumlike behavior, as the Ginzburg criterion predicts. The critical exponent for the smectic-C–smectic-G transition was found to be $\beta=0.703\pm0.001$. Transition temperatures were established at each phase transitions and found to be 84.92 °C, 74.85 °C, 52.96 °C, and 33.03 °C for isotropic-nematic, nematic–smectic-A, smectic-A–smectic-C and, smectic-C–smectic-G transitions, respectively. [S1063-651X(99)01206-4]

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I. INTRODUCTION

Liquid crystals are composed of large asymmetric molecules. These crystals do not melt in a single step during their transitions from the anisotropic solid to an isotropic liquid state. The differences between orientational and spatial ordering of these molecules define the mesophase structures. Crystal and liquid states are seen in a variety of mesophases, which present certain symmetries. Liquid crystals are excellent systems for studying melting processes, phase transitions, and critical phenomena. As far as the phase transitions are concerned, liquid crystals have a peculiar property, i.e., unlike most other materials, which have a single-phase transition, liquid crystals may have a series of phase transitions (multiple phase transitions) in a relatively small temperature range [1]. In other words, the ordered phase makes a continous phase transition to less ordered phase at T_C that then undergoes to another phase transition at a higher temperature T_1 to an even more disordered phase. In most of the liquid crystals, the ratio T_C/T_1 is significantly smaller than one. In this sequence of transitions, the order parameter, which is defined as a quantitative measure for the alignment of the molecules in liquid crystalline phase, is associated with the phase transition at T_1. It is almost saturated at T_C and it will not dramatically affect the other order parameter, which sets in near the transition at T_C [2].

It is known that 4-butoxyphenyl-4′-declyoxybenzoate (BOPDOB) liquid crystal possesses the property of multiple phase transitions [3]. This material has the following sequence of phases upon cooling: isotropic (I), nematic (N), smectic A (SmA), smectic C (SmC), and smectic G (SmG). We present the following phase transitions [3]: I82 °C N72 °C SmA53 °C SmC40 °C SmG, which are usually observed by the polarizing microscope, which can be used to determine only the critical temperatures and mesophase textures [3]. In this paper, photon transmission technique is used to study these phase transitions upon cooling. We observed that the transmitted photon intensity I dramatically decreased at four different temperatures upon cooling. The behavior of I is attributed to the four sequential phase transitions of the BOPDOB liquid crystal. Critical temperatures, order of transitions, and critical exponents were determined during I-N, N–SmA, SmA–SmC, and SmC–SmG transitions of BOPDOB.

II. EXPERIMENTAL

The structural formula of BOPDOB, which was purchased from Soyushim Reactive Inc. (Russia), is shown in Fig. 1. The sample purity was estimated to be 99.7% by liquid chromatograpy [3]. We prepared the sample by placing the BOPDOB powder in between two glass plates, which were heated in an oven at 100 °C. *In situ* transmitted photon intensity measurements were performed using a Perkin Elmer Lambda 2 ultraviolet/visible (UV/VIS) spectrometer in the time drive mode at 750 nm. The sample is placed in the spectrometer after heating, then the isotropic liquid is left to be cooled to room temperature during UV measurements. The temperature was measured with a Cu-Sn thermocouple. The linear dependence of time on temperature was confirmed by using the calibration curve.

III. RESULTS AND DISCUSSION

The plot of transmitted photon intensity versus time for the cooling BOPDOB sample is shown in Fig. 2. It can be seen that transmitted photon intensity decreased drastically at

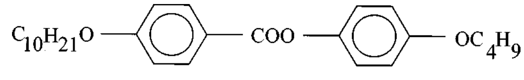

FIG. 1. The structural formula of BOPDOB.

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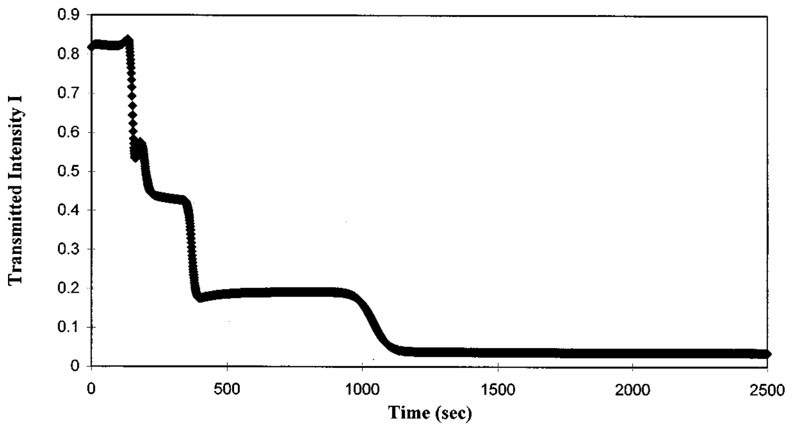

FIG. 2. Plot of transmitted photon intensity I versus time in the time drive mode at 750 nm.

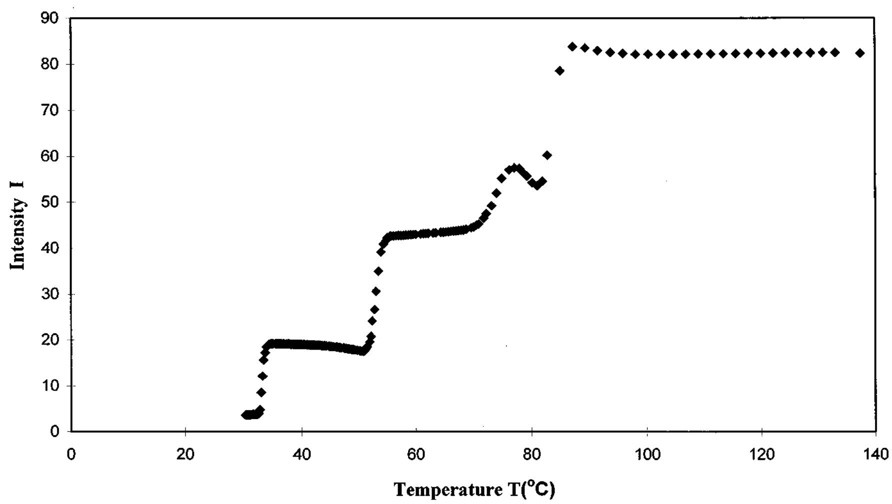

FIG. 3. Plot of transmitted intensity versus temperature.

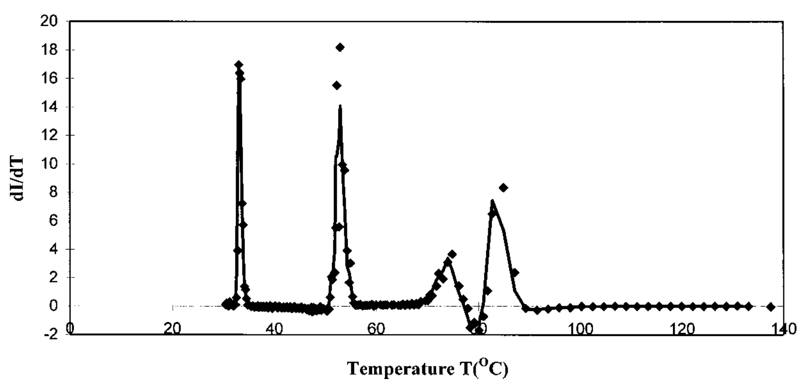

FIG. 4. Plot of the first derivative of $I(T)$ curve versus temperature.

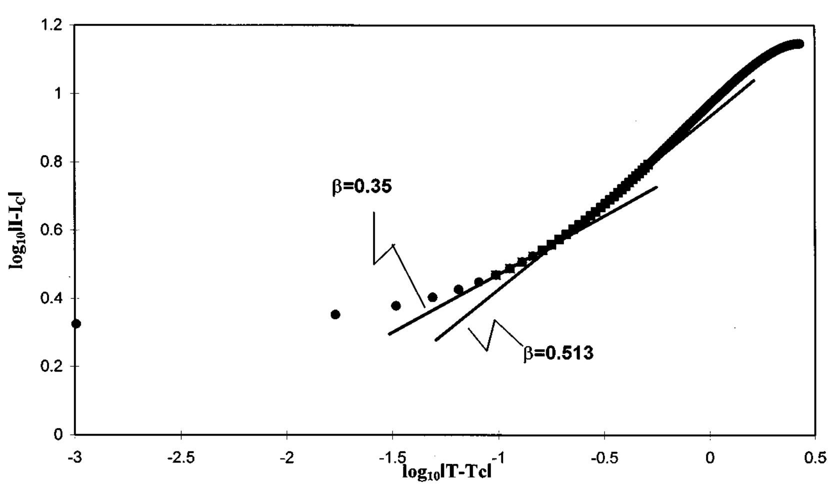

FIG. 5. Log-log plot of the intensity versus temperature for the smectic-A–smectic-C transition.

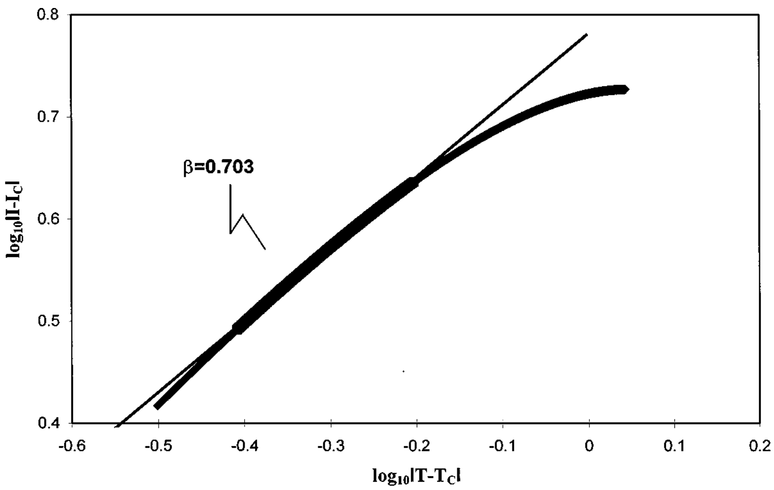

FIG. 6. Log-log plot of intensity versus temperature for the smectic-C–smectic-G transition.

four different onset temperatures, which may correspond to the phase-transition temperatures T_C. Since the molecules of the liquid crystal sample prefer to be reordered at cooling, the transmitted intensity I sequentially decreases. In other words, the intensity I is much higher for the isotropic liquid phase and decreases as the system goes into the ordered phases. As a result it can be assumed that the transmitted photon intensity I is proportional to the order parameter ρ.

In order to quantify the above results we assume that liquid crystals have some physical quantities that can be described by a power law relation above and below the critical temperature T_C during the phase transition. The order parameter ρ is given by the following relation:

$$|\rho-\rho_C|=A|T-T_C|^{\beta}, \tag{1}$$

where ρ_C is the value of ρ at T_C, β is the critical exponent, and A is a proportionality factor. Using the above assumption for the transmitted intensity I, Eq. (1) can be written as follows:

$$|I-I_C|=A'|T-T_C|^{\beta}, \tag{2}$$

where A' is a new proportionality factor and I_C is the value of at T_C. The data in Fig. 2 is replotted in Fig. 3 by using the calibration curve between time and temperature. This result can now be used to determine transition temperatures and the exponents. Transition temperatures were determined from the maxima of the first derivative of $I(T)$ curve, which are shown in Fig. 4. Transition temperatures are listed in Table I, and they are consistent with the previous measurements using optical microscopy [3].

In Fig. 3 it can be seen that the intensity I has a nearly discontinuous decrease at 84.9 °C, which indicates that the phase transition is first order. Here we intuitively conclude that the transition is from the isotropic to the nematic phase of BOPDOB, which is consistent with the Landau model of de Gennes [4]. The mean-field theories of Kobayashi [5] and Mc Millan [6] have shown that the smectic-A–nematic (SmA–N) transition can be either first or second order depending on the value of the ratio of the nematic–smectic-A transition temperature to the nematic-isotropic transition temperature (T_{AN}/T_{NI}), which is called the Mc Millan ratio. In Fig. 3 a similar discontinuous behavior of the intensity I is observed at 74.8 °C which shows that this phase transition is also first order. The Mc Millan ratio can be used to predict the nature of this phase transition. The ratio of 74.8/84.9 produces the value 0.881, which is consistent with the Mc Millan ratio of $T_{AN}/T_{NI}<0.87$. From this we conclude that the first-order phase transition at 74.8 °C is in between nematic to smectic-A phases of BOPDOB and corresponds to the transition temperature T_{AN}. These results are consistent with the theoretical models of Kobayashi and Mc Millan. In Fig. 3 the third-phase transition, which occured at 52.9 °C, shows continuous behavior. According to de Gennes's suggestion [7] the smectic-A–smectic-C (SmA–SmC) phase transition may be continuous and it can exhibit heliumlike critical behavior, which has been of considerable interest in the field of critical phenomena [8]. It has been also reported that critical exponents vary from mean field [9,10] to heliumlike behavior [11–13] or may have values in between [14–16]. The exponents in Eq. (2) can be determined from the log-log plot of the intensity I versus temperature data. Over the reduced temperature range $3\times10^{-3}<|1-T/T_{AC}|<1\times10^{-2}$ below 52.9 °C in Fig. 3, the critical exponent is found to be $\beta=0.513\pm0.006$, which is consistent with mean-field theory. However, over the reduced temperature range $1.8\times10^{-3}<|1-T/T_{AC}|<3.6\times10^{-3}$ below 52.9 °C in Fig. 3, the critical exponent is found to be $\beta=0.35\pm0.009$. This value of the exponent is consistent with heliumlike behavior. A log-log plot of the intensity versus temperature is shown in Fig. 5, which presents a quite linear behavior. Here the values of β show that this phase transition is between SmA and SmC and as a result the critical temperature at 52.9 °C should correspond to T_{AC}. The values of the exponent β crossover from mean-field exponent to helium exponent as the Ginzburg criterion predicts [17]. In the fourth and the final phase transition in Fig. 3, the critical temperature is observed and

TABLE I. Transition temperatures of BOPDOB upon cooling.

Phases	Transition temperature °C	
Isotropic-Nematic	T_{IN}	84.92
Nematic–Smectic A	T_{NA}	74.85
Smectic A–Smectic C	T_{CA}	52.96
Smectic C–Smectic G	T_{CG}	33.03

found to be 32.03 °C. Over the reduced temperature range $1.2\times10^{-2}<|1-T/T_{CG}|<1.9\times10^{-2}$, the critical exponent is measured and found to be $\beta=0.703\pm0.001$, which is greater than what is found in mean-field theory ($\beta=0.5$). In Fig. 6 the log-log plot of the intensity versus temperature is presented. The β value (0.703) predicts that this final phase transition of BOPDOB is in between Sm*C* to Sm*G* and the corresponding critical temperature is T_{CG}.

In summary, we introduced a spectroscopic technique to study multiple phase transitions upon cooling in a liquid crystal of BOPDOB by monitoring the transmitted photon intensity as a function of time. The transmitted photon intensity is assumed to be proportional to the order parameter ρ. Using this simple technique it was observed that *I*-*N* and *N*–Sm*A* transitions are of first order, and Sm*A*–Sm*C* and Sm*C*–Sm*G* transitions are continuous. The crossover from mean-field regime to heliumlike behavior was observed in the critical exponent β for the Sm*A*–Sm*C* transition.

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[1] P. G. de Gennes. *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
[2] M. J. Stephen and J. P. Straley, Rev. Mod. Phys. **46**, 618 (1974).
[3] Private communication with Soyushim Reactive Inc., Russia.
[4] P. G. de Gennes, Mol. Cryst. Liq. Cryst. **12**, 193 (1971); Phys. Lett. **30A**, 454 (1969).
[5] K. K. Kobayashi, Phys. Lett. **31A**, 125 (1971); J. Phys. Soc. Jpn. **29**, 101 (1970).
[6] W. L. Mc Millan, Phys. Rev. A **4**, 1238 (1971).
[7] P. G. de Gennes, Mol. Cryst. Liq. Cryst. **21**, 49 (1973).
[8] R. Schaetzing and J. D. Litster, in *Advances in Liquid Crystals*, edited by G. H. Brown (Academic, New York, 1979), Vol. IV, p. 147.
[9] M. Delaye and P. Keller, Phys. Rev. Lett. **37**, 1065 (1976); D. Guillon and A. Skoulious, J. Phys. (Paris), Colloq. **38**, 79 (1977); S. Meiboom and R. C. Hewitt, Phys. Rev. A **15**, 2444 (1977).
[10] C. R. Safinya, M. Kaplan, J. Als. Nielsen, R. J. Birgeneau, D. Davidov, J. D. Litster, D. L. Johnson, and M. E. Neubert, Phys. Rev. B **21**, 4149 (1980).
[11] P. J. Flanders, Appl. Phys. Lett. **28**, 571 (1976).
[12] M. Delaye, J. Phys. (Paris), Colloq. **40**, C3-350 (1979).
[13] Y. Galerne, Phys. Rev. A **24**, 2284 (1981).
[14] R. A. Wise, D. H. Smith, and J. W. Doanne, Phys. Rev. A **47**, 1366 (1973); S. Garoff and R. B. Meyer, Phys. Rev. Lett. **38**, 848 (1977).
[15] K. C. Lim and J. T. Ho, Phys. Rev. Lett. **40**, 1576 (1978); Mol. Cryst. Liq. Cryst. **58**, 245 (1980).
[16] Y. Galerne, J. Phys. (Paris), Colloq. **39**, 1371 (1978).
[17] V. L. Ginzburg, Fiz. Tverd. Tela (Leningrad) **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1960)].