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D. Armitage [a b] & F. P. Price [a]

[a] Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, 01002

[b] Department of Biophysics, Boston University Medical Center, Boston, MA, 02118

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Volumetric Behavior of Liquid Crystal N-*p*-Cyanobenzylidene-*p*-Octyloxyaniline†

D. ARMITAGE‡ and F. P. PRICE§

Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01002

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Using a differential dilatometer technique, we have measured the volume changes associated with the liquid crystal phase transitions in *n*-*p*-cyanobenzylidene-*p*-octyloxyaniline (CBOOA). A volume discontinuity is not observed at the smectic A to nematic transition, and we conclude that it is less than 10^{-5} ml/g. The volume behavior in a range $\pm 15°C$ about the nematic–isotropic transition has been studied. The critical exponent derived from this data is consistent with the mean field theory of the isotropic phase.

INTRODUCTION

There is considerable interest in the phase transition smectic A to nematic in the liquid crystal *n*-*p*-cyanobenzylidene-*p*-octyloxyaniline (CBOOA),[1–6] which is virtually a second order transition. We have developed a precision recording dilatometric system to measure changes in volume association with phase transitions.[7] Changes in the order parameter of a liquid crystal phase are reflected in small, but observable changes in volume. Results of the application of this technique to the phase transitions in CBOOA are presented here.

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‡ Present address: Department of Biophysics, Boston University Medical Center, Boston, MA 02118.

§ With regret the untimely death of Professor F. P. Price is noted.

APPARATUS

This is described in detail elsewhere.[7] Briefly, the technique is based on the classical mercury capillary method, which has already been used in a volumetric study of CBOOA.[3] We have added a concentric capacitor transducer around the capillary to electronically detect mercury height changes. A further sophistication is the addition of a second dilatometer containing a reference material which is connected in opposition to the sample dilatometer so as to form a differential dilatometer system.[7] The electronic circuitry is manipulated to cancel a linear component of expansion and permit the recording of nonlinear volume change as the temperature is swept through the transition region. For a 3 ml sample, precision in volume change is better than $1:10^5$.

Temperature adjustment is achieved by manually setting a constant power input to the oil bath which is contained in a strip silvered glass Dewar. The temperature is set to drift slowly through the region of interest. Sample and reference dilatometer cells are immersed in the oil bath where temperature gradients are eliminated by magnetic stirring. The bath temperature is measured with a thermocouple and recorded along with the volume. Precision in temperature is better than 0.02°C. The thermal time constant of the dilatometer is 1 min. This introduces a temperature gradient in the sample proportional to sweep rate value of 0.02°C at a rate of 1°C/hr.

SAMPLE PREPARATION

Eastman supplied the CBOOA, which was further purified by a low temperature recrystallization from methanol and several recrystallizations from *n*-heptane. The sample purity as estimated from a DSC thermogram of the solid crystal melting transition is better than $1:10^3$. The transition temperatures and widths listed in Table I confirm that the purity of our sample is comparable with published data.[1–6]

The glass cell of the dilatometer is silane treated (Dow–Corning XZ-2300) to give perpendicular sample alignment promoting large domain size in the liquid crystal phase. However, the shape of the cell precludes the possibility of a single domain sample. In the smectic phase the sample is translucent and the domain size is seen to be several mm. There is evidence that the domain size has an influence on the transition behavior.[3]

A sample weighing 3 g is inserted into the dilatometer cell in the liquid phase under vacuum, cooled to solidification, and sealed with mercury.[7] A suitable reference material, sulfolane ($C_4H_8O_2S$), is loaded into the reference dilatometer in the same way. The reference should have a similar expansion

TABLE I

CBOOA transition enthalpy and volume with related proper

Transition	T^a (°C)	Width (°C)	Enthalpy H (cal/g)		Specific[a] Volume (ml/g)	Volu v (10^{-4}
Crystal–Smectic	73.1	<0.9	19.2	18.7[c]	0.9362	672
Smectic–Nematic	83.3	<3	<0.02	0.04[d]	1.011	<0.1
Nematic–Isotropic	107.9	0.15	0.37	0.50[d]	1.034	16.5

[a] Specific volume and temperature prior to transition.
[b] Ref. 5 experimental value.
[c] Ref. 1.
[d] Ref. 4.
[e] Ref. 3.
* Not listed due to lack of lower limit on v and H.

coefficient and thermal diffusivity to that of the sample and these properties should be independent of temperature.[7]

EXPERIMENTAL RESULTS

DSC thermograms are taken after the dilatometer experiments, with samples extracted from the dilatometer, to check that there has been no change in the transition temperature. Figure 1 is such a thermogram of the smectic to nematic transition. A careful check of the DSC baseline is necessary, before and after the sample run, in order to measure the small increase of heat capacity with temperature. The dashed line is an estimate of background heat capacity derived from an extrapolation of the lower temperature region. A well defined peak identifies the smectic to nematic transition point. Interpolating the heat capacity in the conventional manner to extract the area under the peak gives the transition heat listed in Table I. Judging from liquid crystal transitions in general[8] this is an overestimate due to pretransition increase of heat capacity. It is better to run the DSC at its slowest rate of 0.31°C/min in order to minimize the contribution of heat capacity; the remaining transition heats quoted in Table I correspond to this condition. Our figure for the nematic–isotropic transition enthalpy is low. This is because pretransition effects are eliminated. If we include pretransition enthalpy over a range of 2°C, the total transition enthalpy becomes 0.57 c/g. At rates below 1.25°C/min the smectic to nematic transition is difficult to measure due to

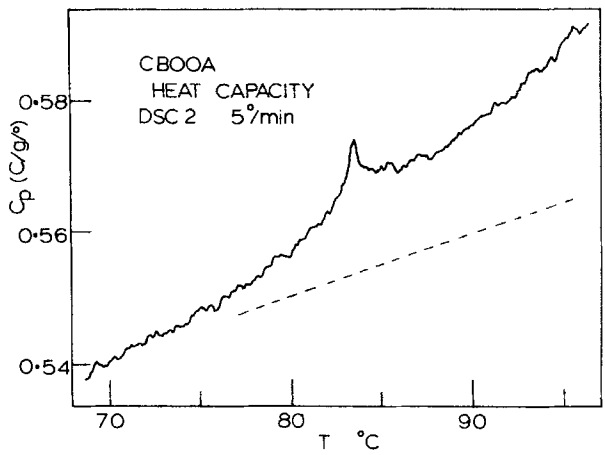

FIGURE 1 DSC thermogram of CBOOA through the smectic to nematic transition. Scale is cal/g/°C; sample weight is 16 mg; sweep 5°/min; sensitivity 0.1 mcal/sec.

sensitivity limitations. The transition widths are upper limits since the dynamic methods overestimate in proportion to the transition heat and sweep rate.

Figure 2 is a differential dilatometer recording showing the nonlinear volume change as the temperature is swept at 3°C/hr through the smectic to nematic transition region. Also shown is a plot of the nonlinear volume change from smectic to isotropic. The nematic to isotropic volume discontinuity has been left blank. There is no indication of a volume discontinuity at the smectic to nematic transition. This transition region has been examined at increasing and decreasing rates in the range 0.5 to 7°C/hr; a discontinuity is not observed. This means that the volume discontinuity at the transition is less than $1:10^5$. Visually the transition takes place over a range of temperature 82 to 84°C when the sample changes from translucent to opaque yellow. The nonlinear temperature scale is a consequence of the constant power input to the thermal bath.

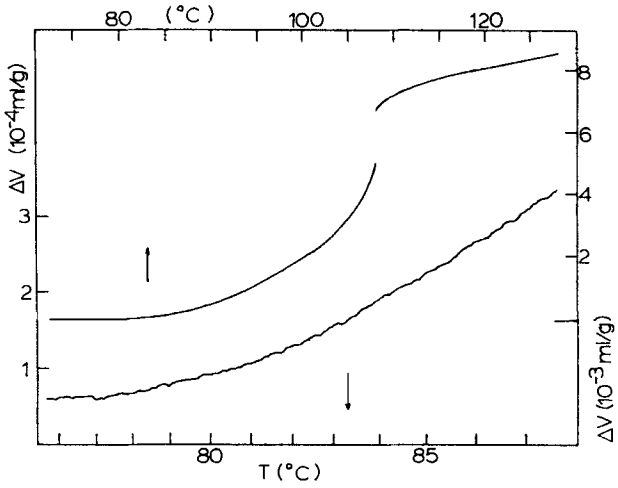

FIGURE 2 Differential dilatometer recording of smectic to nematic transition in CBOOA (lower and left scales). Plot of nonlinear component of volume change smectic to isotropic (upper and right scale). Arrow indicates smectic–nematic transition temperature.

The pretransition volume changes associated with the nematic to isotropic transition are measured over a temperature range ± 15°C about the transition point. Figure 3 is a differential dilatometer record of nonlinear volume change in the isotropic phase. Balancing adjustments are made[7] to give an almost constant recorder output in the range 15 to 20°C above the transition point. A zero shift in the recorder, shown by the vertical dashed line, is made with negligible error at these slow chart speeds. The transition to the nematic (N) phase is sharply defined and has been indicated by a horizontal dashed

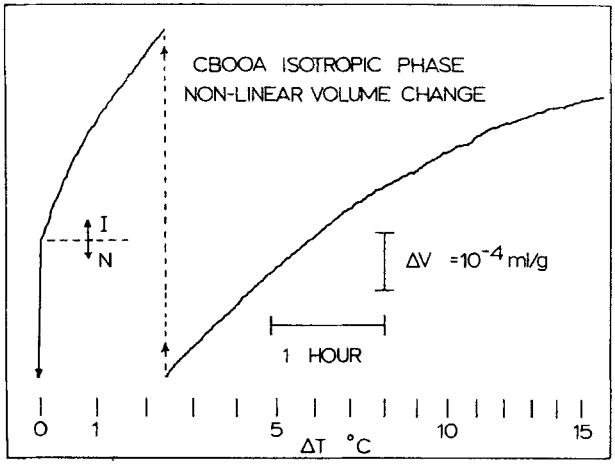

FIGURE 3 Differential dilatometer recording of CBOOA isotropic pretransition region.

line. Nucleation of the nematic on the glass wall of the dilatometer is also observed at this point.

The transducer capacitance of the sample dilatometer is now disconnected and it therefore follows[7] that the previously cancelled component of expansion can now be recorded. Thus complete expansion data is available.

The procedure is repeated for the pretransition region in the nematic phase. The volume discontinuity at the transition is measured in a slow run through the transition at about 0.5°C/hr.

The solid crystal to smectic volume change is outside the volume range of the 0.5 mm diameter capillary tube used in the experiment. It is possible to change to a larger capillary,[7] but since we are not specially interested in this transition it is sufficient to derive the transition volume by weighing the mercury removed from the top of the dilatometer as a function of temperature. This procedure is also required to get the specific volume data in Table I. The specific volume at 25°C is 0.9179 ml/g by calibration of the dilatometer cell with mercury.

DATA ANALYSIS

The data shown in Figure 2 fit the expression $\Delta V = 1.78 \times 10^{-6}(T - 75.5)^{2.04}$ ml/g in the range 75.5 to 88°C with rms deviation 4×10^{-6} ml/g. This means that the transition region is associated with an almost uniformly increasing expansion $744 + 3.63(T - 75.5)^{1.04} \times 10^{-6}$ ml/g/°C where the background expansion has been included. We note that smectic disordering has a weak effect on expansion.

The functional form of the isotropic pretransition behavior in the mean field approximation[9,10] has been derived for expansion.[11] We use the following integrated form which introduces negligible error: $\Delta V = A\Delta T + E(\Delta T + D)^{1-\alpha} - ED^{1-\alpha}$, where, as in Figure 3, ΔT is the temperature difference and ΔV the differential volume measured from the observed transition point; α is a critical exponent appropriate to a second order transition with a predicted value 0.5 in mean field theory; D represents the temperature difference between first order and hypothetical second order transition points, a value of about 0.5°C being expected. The major component of linear expansion is automatically subtracted in the differential technique; however, a small arbitrary component A must be retained in the analysis since the true background expansion cannot be measured directly.[12] The parameter A is combined with the measured component of cancelled expansion derived from the reference dilatometer to give the total background linear expansion B.

An optimization weighted in favor of small ΔT is adopted. Data points are taken at °C intervals of 0.1 up to 1, 0.5 up to 5, and 1 up to 15°C. The sum of the percent errors is minimized in a mean square procedure which varies α in steps of 0.1 while scanning D values. This gives the parameters shown in Table II.

TABLE II

CBOOA pretransition parameters fitting the expression: $\Delta V = B\Delta T + E((\Delta T + D)^{1-\alpha} - D^{1-\alpha})$

Phase	α	D (°C)	E (10^{-4} ml/g)	Background (B) (10^{-4} ml/g)	Error (rms %)
Smectic				7.44	
Nematic	0.4	0.10	12.9	6.11	1.3
Nematic	0.5	0.17	14.3	6.96	1.2
Nematic	0.6	0.23	17.2	7.5	1.5
Isotropic	0.3	0.21	4.79	6.48	0.88
Isotropic	0.4	0.32	4.97	6.98	0.78
Isotropic	0.5	0.42	5.66	7.28	0.85

We find a shallow minimum in both cases, giving optimum values: nematic, $\alpha = 0.5$, $D = 0.17$ °C; isotropic, $\alpha = 0.4$, $D = 0.32$. It is interesting to note that the background (B) term is the same in both phases. If these parameters are physically significant, then the background should be almost the same in both phases. Similarly, B should be slightly less than the limiting smectic expansion 7.44×10^{-4} ml/g.

If we subtract the initial 4 points in the analysis so that a first order transition is simulated at $\Delta T = 0.4$°C, then the parameters shift significantly. For the nematic the optimum values become $\alpha = 0.9$ and $D' = 1.2$°C, and in the

isotropic $\alpha = 0.3$, $D' = 0.53°C$. Note that because of the shift along the ΔT axis $D = D' - 0.4°C$. These parameters are very sensitive to data close to the transition, where, of course, the physical properties are changing most rapidly.

CONCLUSION

The smectic A–nematic transition in CBOOA is dominated by continuous processes. Upper limits to the volume and enthalpy discontinuities are given in Table I. A calculated $dT/dP = Tv/H$ is not tabulated because of the lack of lower limits for v and H. The upper limits of v and H give $dT/dP = 4.2°K/kBar$; however, the agreement with the experimental value may be fortuitous. Agreement between experimental and calculated values of dT/dP to within 10% is expected in the other transitions, particularly the crystal–smectic.

An earlier study[3] of the transition volume of the smectic A–nematic in CBOOA, using conventional dilatometry, gave a lower limit of 3×10^{-5} ml/g. The conventional dilatometric method is very sensitive to temperature stability and measurement; e.g. a sample with expansion coefficient 8×10^{-4} ml/g/°C demands temperature control and precision $\pm 0.01°C$ for a precision $\pm 8 \times 10^{-6}$ ml/g in specific volume. The differential system described here eliminates to first order this temperature error. A further limitation of mercury capillary dilatometry is due to the sticking effect of mercury in the capillary and fluctuations in the meniscus which reduce the precision in mercury height measurement. Our method of continuously recording the mercury height allows this effect to be averaged out. The scanning dilatometer has the disadvantage of introducing a temperature gradient in the sample. However, this is only 0.02°C at a sweep rate of 1°C/hr. A density discontinuity of 4×10^{-5} ml/g at the focal conic to blue phase transition in the cholesteryl esters has been observed using this technique.[7] We cite this as evidence that very small discontinuities are distinguished by this instrument. Thus it is difficult to attribute our non-observance of a discontinuity in CBOOA to instrument deficiencies.

Over the range 75–83°C the pretransition volume increase is $\Delta V = 10^{-4}$ ml/g as shown in Figure 2. The single domain sample used in Ref. 3 could have a smaller pretransition effect and, consequently, a larger discontinuity at the transition.

The density behavior around the nematic–isotropic transition is similar to the well-known nematogen MBBA.[12] However, the parameter reported here is closer to the mean field value (0.5). We have also made measurements on MBBA and find our data in good agreement with Ref. 12. The α parameters we derive for MBBA are nearly the same as for CBOOA. It should be

appreciated that small differences in data comparisons can generate large discrepancies in parameters such as α. MBBA and other nematogen and cholesteric data will be published separately.

Our assumption that the theory[9,10] holds 15°C into the isotropic phase is verified by magnetic birefringence measurements.[13]

Specific heat measurements[14] of the isotropic phase of MBBA favor $\alpha = 0.52$, suggesting a similar value for the expansion data. Here the parameters are also very sensitive to data close to the transition.

A semi-empirical theory[15] that $\alpha = 0.5$ in the nematic phase is verified here.

It is interesting to note that the pretransition volume changes in a range ± 15°C about the nematic–isotropic transition are more than a factor 3 greater than the volume discontinuity at the transition.

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References

1. W. L. McMillan, *Phys. Rev.*, **A7**, 1419 (1973).
2. K. C. Chu and W. L. McMillan, *Phys. Rev.*, **A11**, 1059 (1975).
3. S. Torza and P. E. Cladis, *Phys. Rev. Lett.*, **32**, 1406 (1974).
4. D. Djurek, J. Baturic-Rubcic, and K. Franulovic, *Phys. Rev. Lett.*, **33**, 1126 (1974).
5. W. J. Lin, P. H. Keyes, and W. B. Daniels, *Phys. Lett.*, **49A**, 453 (1974).
6. H. Birecki, R. Schaetzing, F. Rondelez, and J. D. Litster, *Phys. Rev. Lett.*, **36**, 1376 (1976).
7. D. Armitage and F. P. Price, *J. Appl. Phys.*, **47**, 2735 (1976).
8. E. M. Barrall II and J. F. Johnson, *Liquid Crystals and Plastic Crystals* (vol. 2), eds. G. W. Gray and P. A. Winsor (Ellis Horwood, 1974), p. 258.
9. P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford, 1974).
10. M. J. Stephen and J. P. Strayley, *Rev. Mod. Phys.*, **46**, 617 (1974).
11. H. Imura and K. Okano, *Chem. Phys. Lett.*, **17**, 111 (1972).
12. M. J. Press and A. S. Arrott, *Phys. Rev.*, **A8**, 1459 (1973).
13. J. C. Filippini and Y. Poggi, *J. de Physique*, **37**, L17 (1976).
14. G. Koren, *Phys. Rev.*, **A13**, 1177 (1976).
15. H. Gruler and F. Jones, *J. de Physique*, **C1**, 53 (1975).