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Studies on the Nematic-Isotropic Phase Transition of 4-Methoxybenzylidene 4-*n*-butylaniline (MBBA)

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The isothermao compressibilities (K_T) and the thermal expansion coefficients (α_P) of 4-methoxybenzylidene 4-*n*-butylaniline (MBBA) were measured in the temperature range of 307.15–323.15 K up to 140 bar. The isothermal compressibility and the thermal expansion coefficient were fitted to the equations of the form as $K_T = K_T^\circ + W|T - T_c^*|^{-\gamma}$ and $\alpha_P + Z'|T - T_c^*|^{-\alpha}$ in both above and below the phase transition points, and 1.18 ($T < T_c^*$), 1.31 ($T > T_c^*$) for the critical exponent γ and 0.59 ($T < T_c^*$), 0.53 ($T > T_c^*$) for α were found. The pretransitional phenomena in both the nematic phase and also in the isotropic phase were observed. By the Clausius–Clapeyron equation, the transition enthalpy ($\Delta H_{\text{N-I}} = 0.92$ J/cm^3) and the transition entropy ($\Delta S_{\text{N-I}} = 0.72$ J/mole.K) accompanied by the nematic–isotropic phase transition were obtained, and the specific heat (C_P) was calculated from the experimental results of K_T and α_P using the method proposed by Chin and Neff.

INTRODUCTION

Thermotropic liquid crystals take a state of the mesophase between the crystal and the isotropic phase, and have common structural features as elongated and "rod like molecules." The studies of the nematic-isotropic (N-I) phase transitions were the subjects of several investigators.[1–5] The Maier–Saupe theory[6] predicts that this phase transition is of the first order, but it could not predict the pretransitional phenomena observed in the isotropic phase.

On the other hand, some papers reported about the anomalies in the physical properties of the liquid crystals (e.g., the specific heat,[7,8] the light scattering intensity,[9,10] the thermal expansion coefficient[2,3] and the relaxation time for the order fluctuation[11]) and the pretransitional phenomena in both above and below the N-I phase transition points. These observations were well explained by the Landau-model theory proposed by de Gennes[12,13] phenomenologically. In this theory, the pseudocritical temperature (T_c^*) is very near the critical temperature (T_c), and the transition enthalpy ($\Delta H_{\text{N-I}}$) has very low values (about 1 J/cm^3), and the N-I phase transition seemed to be "almost second order" or sometimes "weakly first order,"[13] and the order of this phase transition, the first or the second, is still obscure.

Recently, on the basis of the Landau-model theory of de Gennes, the anomaly of K_T near the N-I phase transition point was reported by Bendler.[14] The adiabatic compressibility of *p*-azoxyanisole (PAA) are studied by Hoyer and Nolle[15] using ultrasonic pulsed-signal method, and the anomalous increase near the transition point was found. Also, Zawisza and Stecki[4] reported K_T's of MBBA at several constant temperatures, but, unfortunately, their experimental results contained little information to understand the behavior of the N-I phase transition. In general, it is well known that the volumatric study is one of the important methods to determinations of the P–V–T relations of the liquid crystals near the phase transition temperature point are of interest.

In this paper, we report about the isothermal compressibilities and the thermal expansion coefficients of MBBA near the N-I phase transition point in the temperature range of 307.15–323.15 K and the pressure up to 140 bar. We accounted for the temperature dependence of K_T and α_P near the phase transition point on the basis of the Landau-model theory of de Gennes. Also, we estimated the specific heat (C_P) from the experimental results of these quantities by using the method proposed by Chin and Neff,[16] and from the Clausius-Clapeyron equation, the transition enthalpy ($\Delta H_{\text{N-I}}$) and entropy ($\Delta S_{\text{N-I}}$) accompanied by the N-I phase transition were obtained.

EXPERIMENTAL

MBBA was prepared by refluxing of equimolar amounts of 4-methoxybenzaldehyde and 4-*n*-butylaniline in the presence of a small amount of absolute ethanol, according to the procedure of Kelker and Schurle.[17] The products were purified by several distillations under vacuum until the N-I phase transition temperatures were fixed. The N-I phase transition temperature of MBBA was measured using a modified Gray's apparatus[18] (i.e., polarizing microscope equiped with a heating stage). Table I shows that these phase transition temperatures were comparable with the other literature values.[1–4,23]

A detailed description of apparatus used in this work is shown in Figure 1, and the procedures used for determining P–V–T relations of liquid crystals were described elsewhere.[19,20] The volume can be read to the amount of 1×10^{-4} cm^3, and the pressure can be read to the order of 10^{-1} bar. The difference of the bath temperature is measured by the Beckmann thermometer.

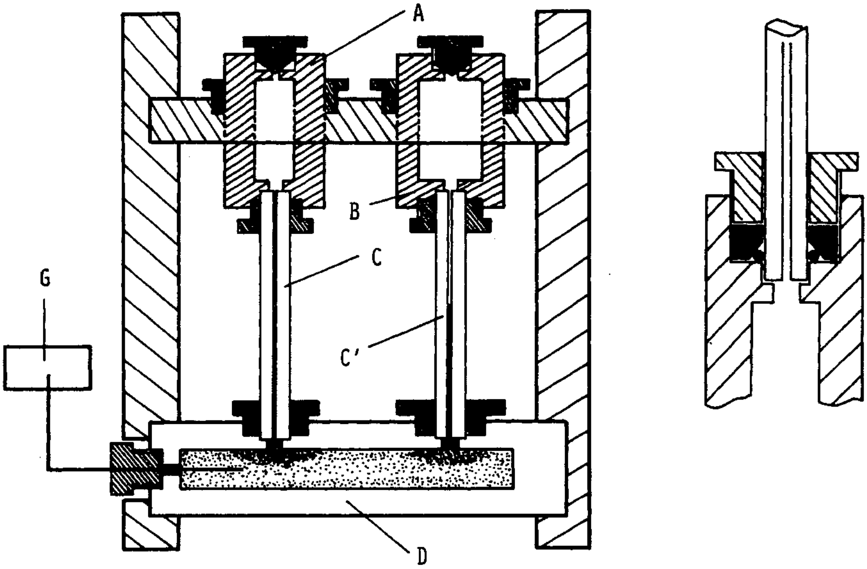

FIGURE 1 Apparatus for P-V-T relation measurement of liquid crystal; A: Sample cell, B: Reference cell, C and C': Pylex capillary tube, D: Mercury container, G: Pressure generator. An equal pressure is transmitted by mercury to A and B.

RESULTS AND DISCUSSION

The N-I phase transition temperature of MBBA obtained from this work was listed in Table I. From these results, we assumed that our sample suffices to be used for determining the P-V-T relations of MBBA.

A part of the P-V relations of MBBA in the vicinity of the N-I phase transition point at constant temperatures are shown in Figure 2. The isothermal compressibilities were obtained from the gradients of these graphs.

TABLE I

The comparison of the nematic-isotropic phase transition temperature (K), T_c, under atmosphere.

R. Chang[1]	316.28, 318.16
M. J. Press[2]	317.80
Our results	317.91
Y. Poggi[22]	318.20
B. Chu[3]	319.21, 319.37
A. C. Zawisza[4]	319.75
A. Demat[5]	319.85

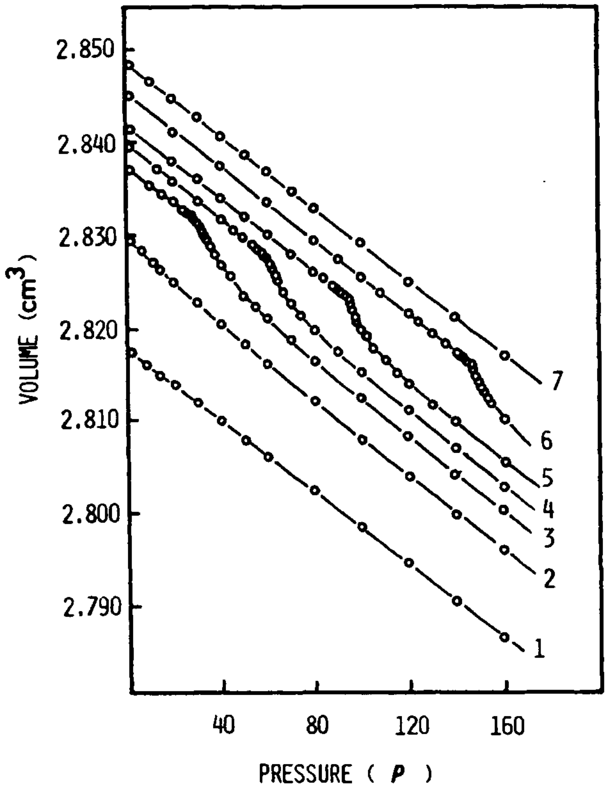

FIGURE 2 Pressure-volume relations for MBBA at various temperatures; 1:312.25, 2:316.83, 3:318.24, 4:319.06, 5:320.05, 6:321.82, 7:323.77 K.

Figure 3 shows the plots of K_T against the pressure in the vicinity of the N-I phase transition point. In this figure, the value of K_T at the critical pressure (P_c) does not not seem to converge. If we assumed that K_T near the range of P_c can be expanded as follows[21]

$$\frac{K_T}{K_T^\circ} = \begin{cases} \zeta(+\theta)^{\mu}(1 + \cdots)(P > P_c) \\ \zeta'(-\theta)^{\mu'}(1 + \cdots)(P < P_c) \\ \theta = \dfrac{P - P_c}{P_c} \end{cases} \tag{1}$$

where K_T° is the background isothermal compressibility of fluid, μ and μ' the critical exponents, ζ and ζ' the constants. The value of μ or μ' will be obtained by plotting log K_T against log $|P - P_c|$. But it is impossible to determine directly the value of P_c from the P-V relations, then owing to determine the

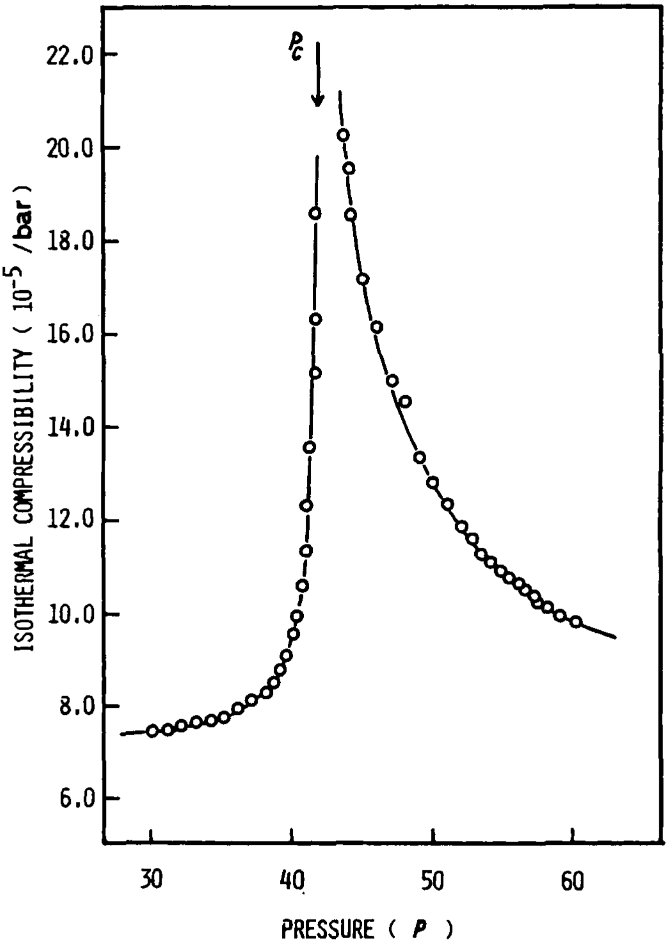

FIGURE 3 Isothermal compressibility-pressure relation for MBBA at 318.55 K.

value of P_c, we assumed that the values of μ and μ' in Eq. (1) are equal. By choosing as $P_c = 41.8$ bar for each phase, two straight lines with the same slope are obtained as shown in Figure 4, and the value of the critical exponent was found to be $\frac{1}{3}$ in this case. From this experiment, the value of K_T at $P_c = 41.8$ bar which correspond to the critical pressure of this phase transition (which is shown by an arrow in Figure 3) has not the finite value.

Figure 5 shows the plot of the value of K_T^{-1} against P. As is shown in this figure, the value of K_T^{-1} suddenly decreases as the pressure is approached to P_c. In general, the relation between the isothermal compressibility and the correlation length (ξ) near the critical point is expressed as $K_T \propto \xi^{-2}$.[17]

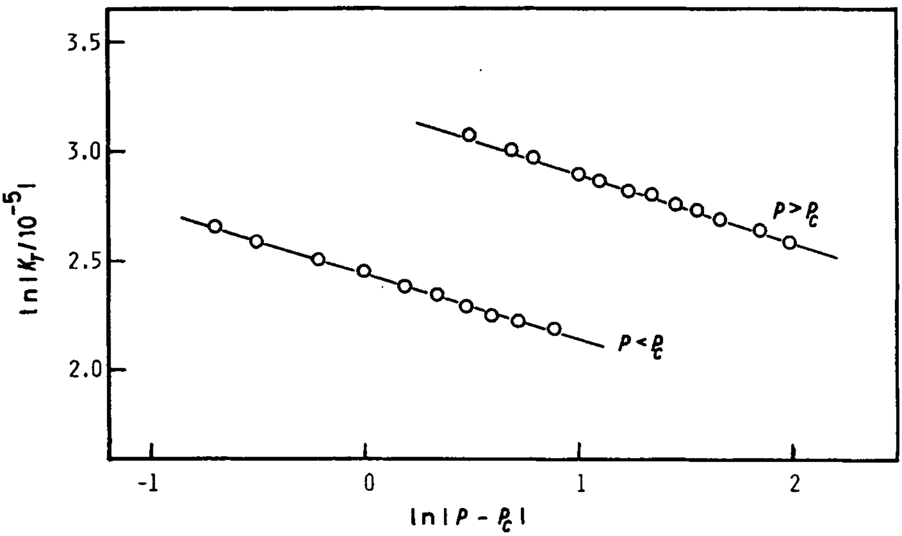

FIGURE 4 ln K_T − ln|P − P_c| relations for MBBA at 318.55 K. The same slope is obtained if we chose P_c = 52.8 bar.

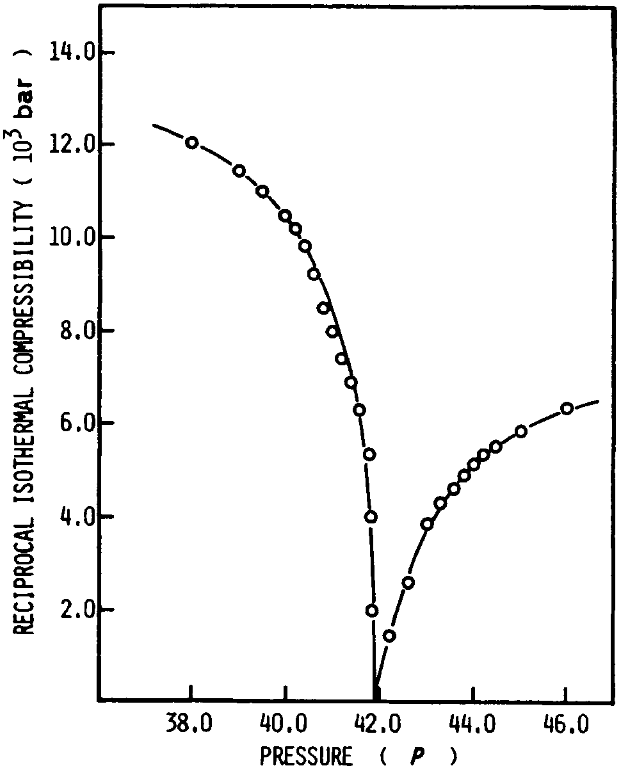

FIGURE 5 Reciprocal isothermal compressibility-pressure relation for MBBA at 318.55 K

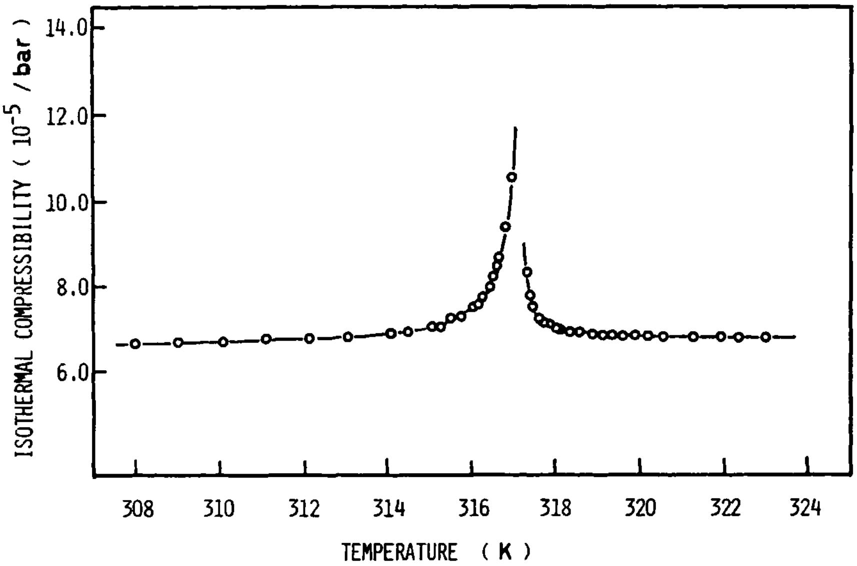

FIGURE 6 Isothermal compressibility-temperature relations for MBBA near the nematic-isotropic phase transition point under 1 bar. The solid line in the nematic phase represents $K_T = \{6.62 + 1.02(317.41 - T)^{-1.18}\} \times 10^{-5}$/bar, and in the isotropic phase represents $K_T = \{6.79 + 0.23(T - 317.19)^{-1.31}\} \times 10^{-5}$/bar.

Therefore, the divergence of K_T at P_c (see Figure 3) is caused by the sudden increasing in the correlation length of liquid crystal molecules as the phase transition point is approached from above P_c, and the order and density fluctuations increase.

The plot of K_T at $P = 1$ bar as a function of temperature is shown in Figure 6. On the basis of the Landau model theory of de Gennes, the increments in K_T were fitted to the empirical equation of Bendler as follows[14]

$$K_T = K_T^\circ + W|T - T_c^*|^{-\gamma} \tag{2}$$

where K_T° is the background isothermal compressibility of the fluid, W a constant, and γ the critical exponent. The behavior in the vicinity of the N-I phase transition point can be understood from the magnitude of W and γ. K_T's were fitted to Eq. (2) by a least-square method in both above and below the N-I phase transition points. Values of T_c^* and γ were specified to determine K_T° and W; by choosing proper values of T_c^* and γ, the values of the four parameters (K_T°, T_c^*, W and γ) were determined so as to minimize the standard deviation for the experimental and calculated data. The results were

$$K_T = \{6.62 + 1.02(317.41 - T)^{-1.18}\} \times 10^{-5}\text{/bar} \tag{3}$$

$$T_c^* = 317.41\text{ K} \quad \text{and} \quad \gamma = 1.18$$

in the nematic phase and

$$K_T = \{6.79 + 0.23(T - 317.19)^{-1.31}\} \times 10^{-5}/\text{bar} \tag{4}$$

$$T_c^* = 317.19\text{K} \quad \text{and} \quad \gamma = 1.31$$

in the isotropic phase.

The solid lines in Figure 6 are those of Eqs. (3) and (4). From these results (see Figure 6), we found that the experimental results of K_T in both phases can be well reproduced by Eq. (2). As are shown in Eqs. (3) and (4), the value of K_T° in the nematic phase at $P = 1$ bar was not larger than that in the isotropic phase. Also the results of γ for both phases were 1.18 and 1.13 for $T < T_c^*$ and $T > T_c^*$, and the coefficient W for the nematic phase is several times as large as that of the isotropic phase. These results mean that K_T in the nematic phase diverges more broadly than that in the isotropic phase as the phase transition point is approached to T_c. This behavior may be

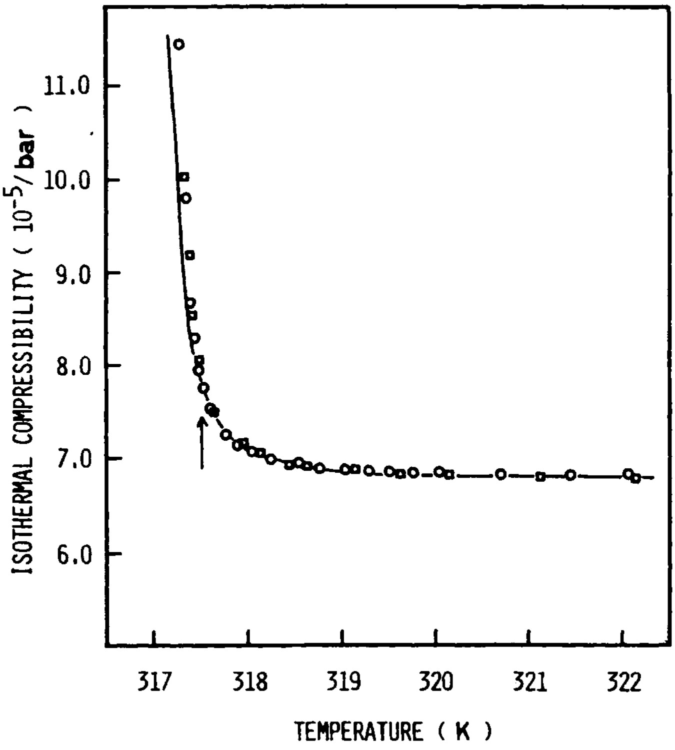

FIGURE 7 Isothermal compressibility-temperature relations for MBBA above the nematic -isotropic phase transition point under 1 bar. The solid line represents $K_T = \{6.69 + 0.36 (T - 317.19)^{-1}\} \times 10^{-5}$/bar. The open circles represent experimental results, and the squares represent $K_T = \{6.79 + 0.23(T - 317.19)^{-1.31}\} \times 10^{-5}$/bar.

caused by the order and density fluctuations, and the rapid increase of the correlation length in the vicinity of the N-I phase transition point. From Figure 6, we observed the anomalies of K_T, or the pretransitional phenomena above and below the N-I phase transition point. The former indicates the existence of the orientational arrangement of the liquid crystal molecules even above the N-I phase transition point.

Our results of K_T in the isotropic phase were fitted to the empirical equation of Bendler as $K_T = K_T^\circ + W'(T - T_c^*)^{-1}$. The results were

$$K_T = \{6.69 + 0.36(T - 317.19)^{-1}\} \times 10^{-5}/\text{bar} \tag{5}$$

$$T_c^* = 317.19\ \text{K} \quad \text{and} \quad \gamma = 1$$

Figure 7 shows the result of Eq. (5). As is shown in this figure, good agreements between the results of Eqs. (4) and (5) were found in the higher temperature range than $T = 317.50$ K (which is shown by an arrow in Figure 7), but the deviations between these results were observed in the lower temperature range; i.e., the Bendler empirical equation has smaller value than the experimental K_T at the same temperature in this range. This is caused by the fact that the value of γ postulated by Bendler is smaller than that obtained from this work ($\gamma = 1$ for Bendler's theory and $\gamma = 1.31$ for this work).

Figure 8 shows the volume-temperature relation of MBBA under atmosphere in the vicinity of the N-I phase transition point, and α_P was obtained from the gradient of this graph. Figure 9 shows plots of α_P as a function of temperature. In this figure, our result was compared with that reported by Press and Arrott,[2] and by Chu *et al.*[3] As is shown in Figure 9, the behavior in this work showed qualitatively a good agreement with the others except for the value of the critical temperature. Also, the value of α_P at T_c does not seem to converge, and the pretransitional phenomena in the nematic and the isotropic phase was observed. This behavior is also reported by some investigators.[1-3,11]

The volume change of MBBA in the pretransition region depends on the order parameter Q of the liquid crystal in ordered state,[1] and the relation between Q and T for this state may be expected that $Q = Q_N + A'(T_c^* - T)^{\nu}$,[12] here Q_N is the value of the order parameter at the inflection point of the free energy $-Q$ curve for $T = T_c^*$. If the density change is proportional to the order parameter then

$$\left\{\frac{1}{V(\mathrm{d}V/\mathrm{d}T)} - \alpha_P^\circ\right\} \propto \left(-\frac{\mathrm{d}Q}{\mathrm{d}T}\right) = A'(T_c^* - T)^{\nu-1} \tag{6}$$

and

$$\Delta\alpha_P = B(T_c^* - T)^{-\alpha} \tag{7}$$

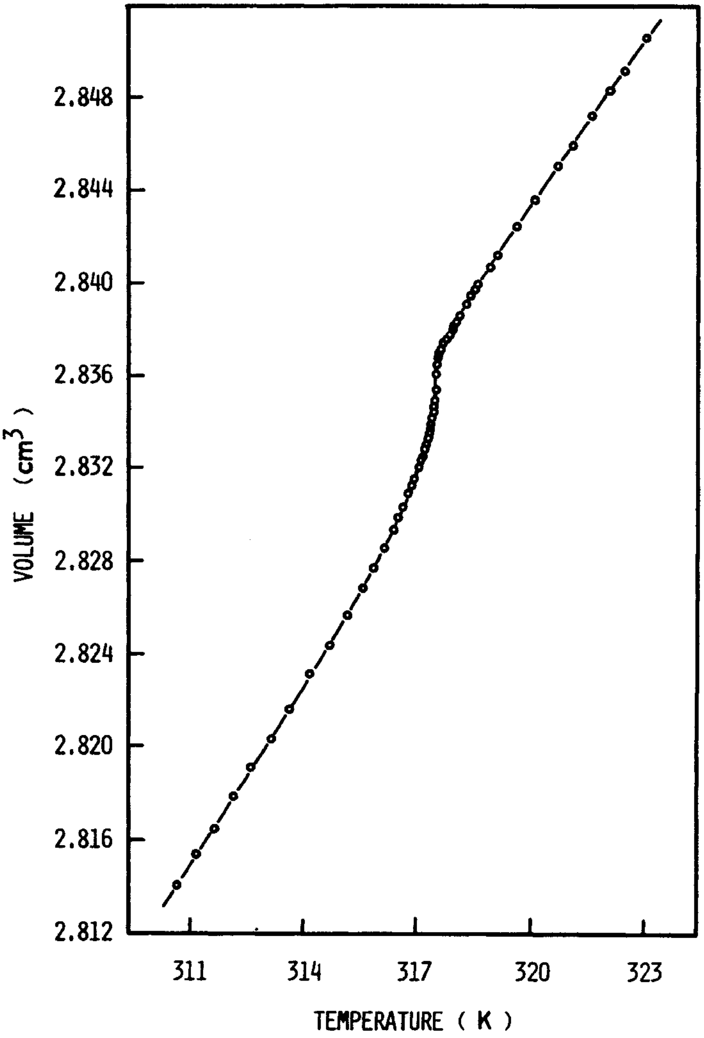

FIGURE 8 Volume-temperature relation for MBBA under atmosphere.

where $B = A' \cdot \nu$, and $\alpha = 1 - \nu$. On the basis of Eq. (7), these data for α_p were fitted to an equation of the form

$$\alpha_p = \alpha_p^\circ + B|T - T_c^*|^{-\alpha} \tag{8}$$

where α_p° is the background thermal expansion coefficient of the fluid, B the constant, and α the critical exponent for α_p. We can understand the behavior of α_p near the N-I phase transition point from the magnitude of B and α.

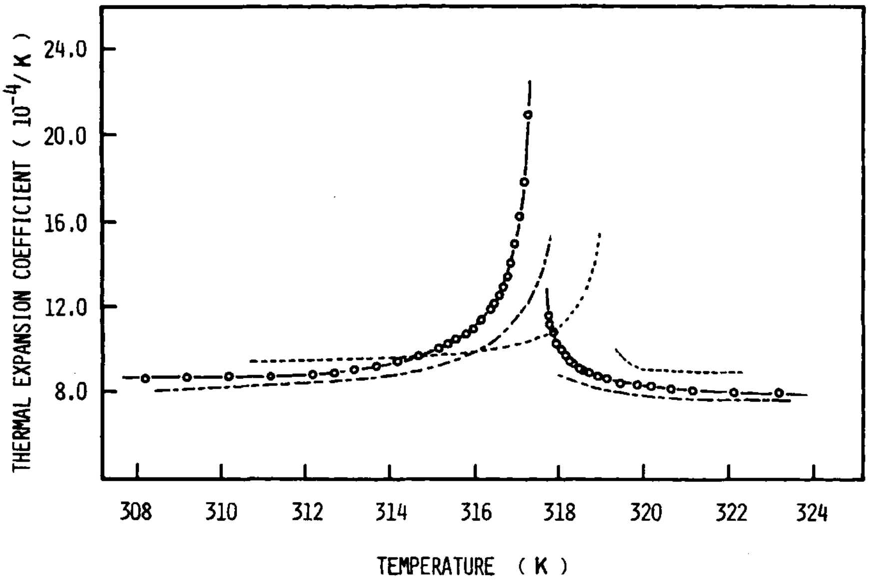

FIGURE 9 Thermal expansion coefficients-temperature relations for MBBA near the nematic-isotropic phase transition point under atmosphere. The open circles represent the experimental datas, and the solid line in the nematic phase represents $\alpha_P = \{7.34 + 5.46\,(317.45 - T)^{-0.59}\} \times 10^{-4}/\mathrm{K}$, and in the isotropic phase represents $\alpha_P = \{7.22 + 1.97\,(T - 317.50)^{-0.53}\} \times 10^{-4}/\mathrm{K}$. The dashed line is the fit of Chu[4], and the dot-dashed line is the fit of Press and Arrott.[3]

The four parameters included in Eq. (8) were determined by the same method described in Eq. (2). The results were

$$\alpha_P = \{7.34 + 5.46(317.45 - T)^{-0.59}\} \times 10^{-4}/\mathrm{K} \tag{9}$$

$$T_c^* = 317.45\ \mathrm{K} \quad \text{and} \quad \alpha = 0.59$$

in the nematic phase, and

$$\alpha_P = \{7.22 + 1.97(T - 317.50)^{-0.53}\} \times 10^{-4}/\mathrm{K} \tag{10}$$

$$T_c^* = 317.50\ \mathrm{K} \quad \text{and} \quad \alpha = 0.53$$

in the isotropic phase, and the results of these equations were expressed by the solid line in Figure 9. By comparing with Eqs. (9) and (10), α_P° in the nematic phase was not smaller than that in the isotropic phase. Although α took the values of 0.59 and 0.53 for $T < T_c^*$ and $T > T_c^*$, the coefficient B for the nematic phase was several times as large as that for the isotropic phase. This means that α_P in the nematic phase diverge more broadly than that in the isotropic phase.

It is well known that the thermal expansion coefficient, $\alpha_P(T)$, the correlation length, $\xi(T)$, and the specific heat, $C_P(T)$, have the same critical exponents.[7,21] Imura and Okano[8] reported that the critical exponent of α_P and C_P in the isotropic phase is equal to 0.5, and the value of 0.67 and 0.50 was also reported in the nematic phase.[2] In this work, α was found to be 0.59 for $T < T_c^*$ and 0.53 for $T > T_c^*$, and is a good agreement with that of $\alpha =$ 0.59 for $T < T_c^*$ and $\alpha = 0.54$ for $T > T_c^*$ by Gurali and Chu.[3] Press and Arrott[2] reported that $\alpha = 0.59$ for $T < T_c^*$ and $\alpha = 0.21$ for $T > T_c^*$. On the other hand, Bendler[14] reported that if the anomaly in α_P of the isotropic phase is totally due to K_T (i.e., if the thermal pressure coefficient, $\gamma_V = (\partial P/\partial T)_V$, suffers no increment), then from the relation as $\Delta\alpha_P \sim \gamma_V \Delta K_T$, the critical exponent, α, should be found to be 1. Furthermore, our results of α_P

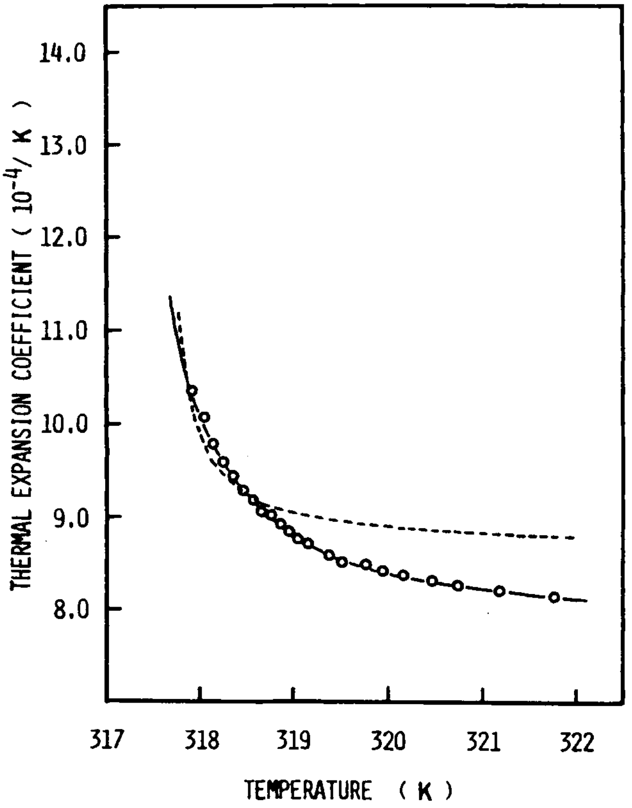

FIGURE 10 Thermal expansion coefficient-temperature relations for MBBA above the nematic-isotropic phase transition point under atmosphere. The solid line represents $\alpha_P = \{7.22 + 1.97(T - 317.50)^{-0.53}\} \times 10^{-4}$/K, and the dashed line represents $\alpha_P = \{8.65 + 0.57 (T - 317.50)^{-1}\} \times 10^{-4}$/K.

for the isotropic phase were fitted to the empirical equation of Bendler as $\alpha_P = \alpha_P^\circ + C(T - T_c^*)^{-1}$.[14] The result was

$$\alpha_P = \{8.65 + 0.57(T - 317.50)^{-1}\} \times 10^{-4}/\mathrm{K} \tag{11}$$

$$T_c^* = 317.50\ \mathrm{K} \quad \text{and} \quad \alpha = 1$$

and are shown in Figure 10. The solid line shows the result of Eq. (10), and the open circles are the experimental data, and the dashed line expresses the result of Eq. (11). As is shown in Figure 10, the result of Eq. (11) did not show a good agreement with the experimental data. From this fact, we considered that the empirical equation of Bendler described above is not a good equation to reproduce the experimental results of α_P in the isotropic region, and also it is questionable whether the assumption of Bendler is reasonable or not.

After the correction for the increment by the thermal expansion, the volume change, ΔV, which was obtained from the V-T relation, was plotted against the temperature, and is shown in Figure 11. In the measurement of the V-T relation, we also observed the two phase region near the N-I phase transition point. The temperatures T_B and T_P for the beginning and the end of the two

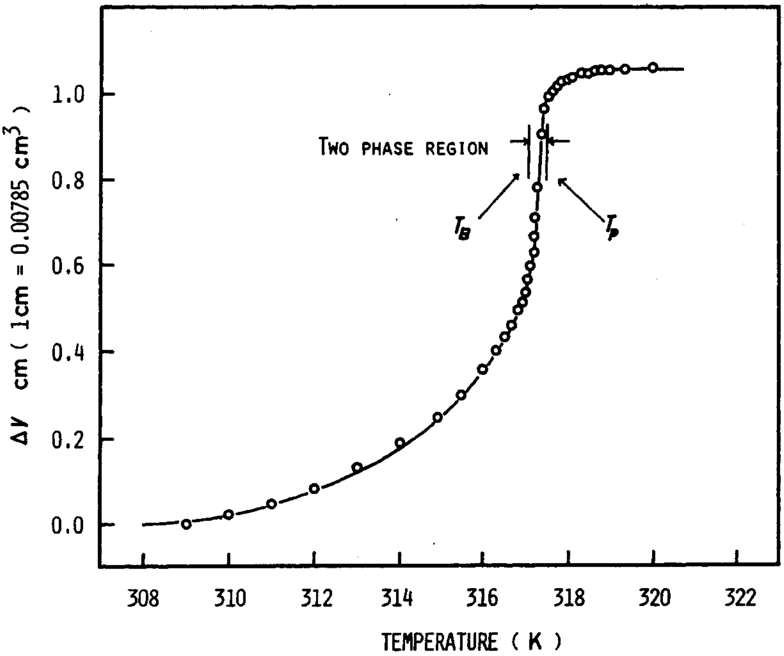

FIGURE 11 Volume change (ΔV)-temperature relation for MBBA under atmosphere near the nematic-isotropic phase transition point.

phase region are also indicated in this figure. T_B is the temperature at which the nematic phase begins to change partially into the isotropic phase, and T_P is the temperature at which the nematic phase is completely converted into the isotropic phase. Because of the coexistence of this two phase region, we cannot directly measure the critical temperature T_c. $|T_P - T_B|$ is the temperature range of the two phase region, and the temperature range is varied by the effect of impurities in the material. However, it is doubtful whether the two phase region could be eliminated entirely by removal of the impurities in the material, or not. In this work, T_P and T_B were 317.62 K and 317.26 K, and then $T_P - T_B = 0.36$ K shows a good agreement with the result found by Press and Arrott (about 0.3 K),[2] and by Chang (0.44 K).[1] If the N-I phase transition is of the second order, T_P and T_B must be equal, and these temperatures correspond to the critical temperature. In order to discuss the magnitude of $|T_c - T_c^*|$, we compared T_P with T_c^* for the nematic phase and T_B with T_c^* for the isotropic phase. The pseudocritical temperature was closed to the limiting temperature, T_P or T_B, in one phase region. $|T_P - T_c^*|$ or $|T_B - T_c^*|$ is about 0.1–0.2 K in our case, and about 0.3 K as reported by Press and Arrott.[2] From de Gennes theory[12,13] or the light scattering studies,[9,11] $|T_c - T_c^*|$ yields a value of about 1 K, and recently, Gulari and Chu[3] reported that it was virtually zero. From these results, $|T_c - T_c^*| \simeq 1$ K would be too large.

The volume change, $\Delta V/V$, accompanied by the N-I phase transition can be obtained from the volume difference between the beginning and the end point of the two phase region, was found as $\Delta V/V = 0.11\,\%$, and shows a good agreement with other results.[3,5] The effect of pressure on the N-I phase transition temperature can also be deduced from the P–V curves described above. We obtained $(\mathrm{d}P_c/\mathrm{d}T)_{\mathrm{N\text{-}I}} = 26.4$ bar/K from the slope of the critical pressure-temperature linear relation. Using the Clausius–Clapeyron equation, $\Delta H_{\mathrm{N\text{-}I}}$ accompanied by the N-I phase transition yielded a value of 0.92 J/cm^3, while $\Delta S_{\mathrm{N\text{-}I}}$ was 0.72 J/mole K. $\Delta H_{\mathrm{N\text{-}I}}$ for MBBA reported by Zawisza[4] was 1.1 J/cm^3, which is nearly in agreement with our result. But, Stinson and Lister[11] reported 1.6 J/cm^3 from the light scattering study, and calculated value of 1.42 J/cm J/cm^3 by Poggi.[22] These results are larger than ours. This may be caused by the fact that T_c, which is obtained by the de Gennes theory, was overestimated than that directly measured, as with this work.

The specific heat for MBBA in the vicinity of the N-I phase transition point was obtained by using the method proposed by Chin and Neff,[16] and is plotted as a function of temperature in Figure 12. Curve B represents the results of this work, and curve A of Hirakawa.[23] In this theory, since the fluctuation effect was not taken into account, it is only possible to discuss qualitatively the behavior of C_P in the vicinity of the N-I phase transition point. As is shown in Figure 12, the anomaly in C_P was observed in the vicinity of the phase transition point, and the value of C_P at the phase transition point seemed to diverge.

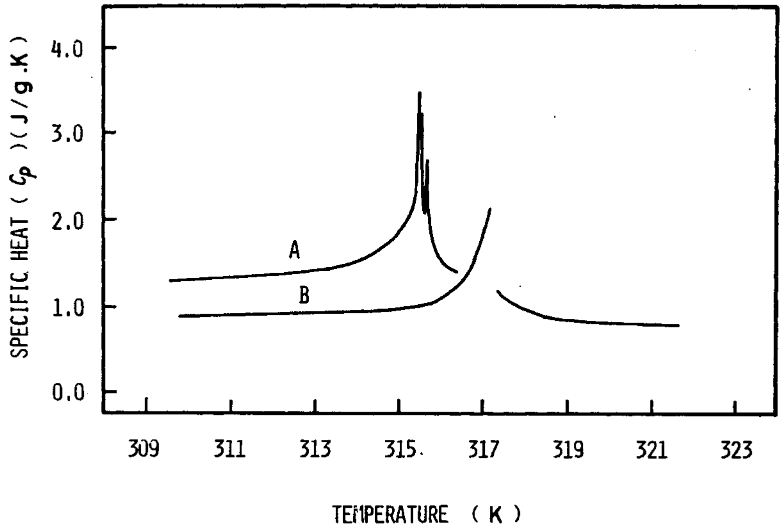

FIGURE 12 Specific heat (C_p)-temperature relations for MBBA near the nematic–isotropic phase transition point. Curve A represents the result of Hirakawa,[23] and curve B represents the experimental data.

The result of Hirakawa is somewhat larger than ours, but we considered that the two results show the similar behavior qualitatively.

CONCLUSIONS

The anomalies in K_T, α_P and C_P were observed in the nematic and the isotropic phase, and the values of these quantities seemed to diverge at the N-I phase transition point. We could interprete these results by the order and density fluctuations on the basis of the Landau model–de Gennes theory. Also, we observed the pretransitional phenomena in both the nematic and the isotropic phase. From these results, it became evident that there is an orientational effect of the liquid crystal molecules in the isotropic phase near the N-I phase transition point. Moreover, the volume change, $\Delta V/V$, the transition enthalpy $\Delta H_{\text{N-I}}$, and the transition entropy, $\Delta S_{\text{N-I}}$, accompanied with the N-I phase transition were very small; e.g., $\Delta \mathrm{S}_{\text{N-I}}$ was 0.72 J/mole. K, and $\Delta V/V$ was 0.11%, and the pseudocritical temperature, T_c^*, was closed to the limiting temperature T_P and T_B in one phase region. From these data, it may be considered that the N-I phase transition is "almost second order" or "weakly first order" as is well known.[13]

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