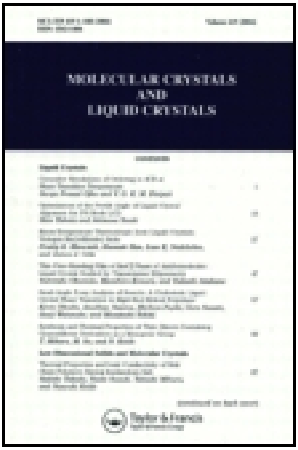

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Pressure Induced Change of The Nature of The Isotropic to Nematic Phase Transition for 4-(Trans-4-Butylcyclohexyl)Benzonitrile

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Pressure Induced Change of The Nature of The Isotropic to Nematic Phase Transition for 4-(Trans-4-Butylcyclohexyl)Benzonitrile

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Pressure-volume isotherms for 4-(trans-4-butylcylohexyl)benzonitrile were measured by means of piston-cylinder method. This substance has a monotropic nematic phase at atmospheric pressure. But over a pressure, the nature of isotropic to nematic phase transition changed from monotropic to enantiotropic phase transition. It is the first observation in P-V-T experiments that the monotropic isotropic-nematic transition changes enantiotropic under pressure.

Keywords: pressure, volume, transition, monotropic, enantiotropic, change

INTRODUCTION

Pressure studies of liquid crystalline substances have been found to show many anomalous thermodynamical behavior; for example, tricritical point, reentrant behavior, appearance of nematic phase at high pressure and change of nature of phase transition.[1] Robbrecht[2] found that the nature of the isotropic to cholesteric transition in cholesteryl methylcarbonate can be changed by pressure from monotropic to enantiotropic. In the case of the isotropic-nematic transition, Shashidhar[3] observed a similar behavior in 4-cyanophenyl 4-propoxy-2-methylcinnamate by high pressure differential thermal analysis (DTA). He has observed that the peak of DTA for the isotropic to nematic phase transition appears before nematic to solid transition peak at 138 bar. These phenomena predict that the nature of the transition changes from monotropic to enantiotropic. Such a change in the nature of transition from monotropic to enantiotropic has not yet been observed by pressure-volume-temperature measurements.

We report in this paper pressure-volume-temperature relations for 4-trans-butylcyclohexyl-4-benzonitril(4PCH) and a change of nature of transition.

EXPERIMENTAL

4PCH of electro display grade (Merck Co., Ltd.) was used as obtained without further purification. Density of this sample was measured by Lipkin-Devison type pycnometer. P-V-T relations were measured by using a piston-cylinder apparatus.[7] Variation of the pressure was detected by a manganin pressure gage mounted in the cylinder. The degree of compression of the sample was estimated by a differential transformer attached to one end of a piston. Both the analog output of the differential transformer and that of manganin pressure gage were acquisited by a microcomputer after the proper amplification and digital conversion. The microcomputer also served to control an oil pressurizing pump to compress the sample at a predetermined sequence by monitoring these signals. To avoid a multivalent effect of equation of state at phase transition, the sample was compressed in volume increments. The step of volume increment was changed in transition region. To attain equilibrium, the time interval was 3 minutes. The volume of the cylinder was about 10 cm^3. The error of measurements of pressures and volumes were within ±0.03 MPa and ±0.002%, respectively. The piston cylinder apparatus was kept in an air bath which was thermocontrolled within ±0.01K.

RESULTS AND DISCUSSION

Figure 1 shows the density curve as a function of temperature at atmospheric pressure. The density was measured in both cooling and heating cycles. It is seen from Figure 1 that the data in these two cycles fitted perfectly. The phenomenon is similar to those observed for enantiotropic liquid crystals. Figure 2 shows pressure-volume isotherms at four typical temperatures for 4PCH out of 23 runs. Plateaus for isotropic to nematic phase transition are observed: they are marked with the letter A in Figure 2. The pressure of the sample suddenly

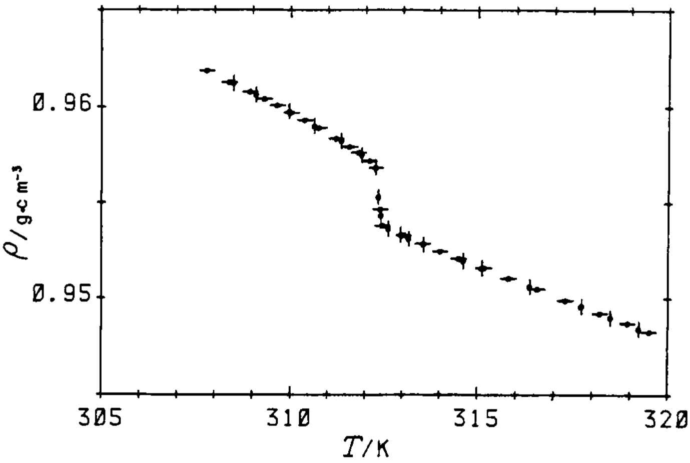

FIGURE 1 Density as a function of temperature for 4PCH. —●— is cooling cycle. ⧫ is heating cycle.

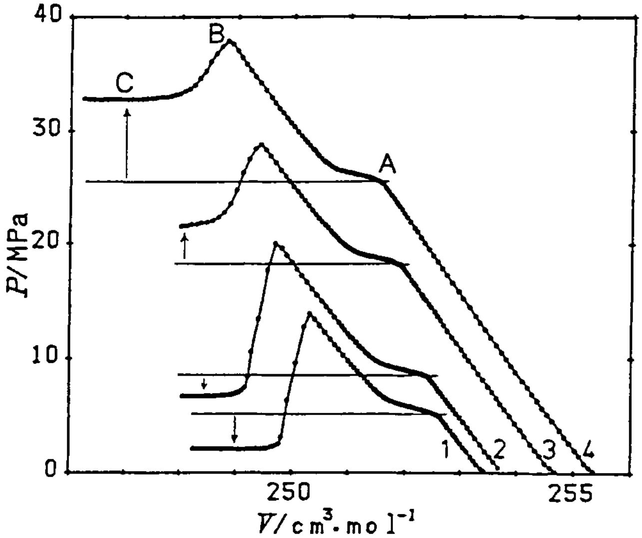

FIGURE 2 Four typical pressure-volume isotherms of 4PCH out of 23 runs. 1:313.71 K; 2:315.35 K; 3:319.78 K; 4:323.22 K. *A* is the pressure of isotropic to nematic phase transition. *B* is over pressure of nematic to solid phase transition. *C* is the pressure of nematic to solid transition.

dropped at point B: the nematic to solid phase transition occurred. The nematic to solid phase transition often occurred due to "superpressure;" this phenomenon corresponds to "supercooling" in freezing process. It starts at random pressure in each isotherm. This irregularity will be natural because this state is an unstable free energy state. The pressure of the sample is gradually decreased and kept at a constant pressure. The plateau, marked with the letter C in Figure 2, is caused by the nematic-solid coexistance equilibrium state. We could not verify the end of this transition, because the maximum measurable capacity change of our piston-cylinder apparatus is 5%, while the volume change accompanying with the nematic-solid phase transition will be approximately 7–10%. It is found in Figure 2 that the pressure of the isotropic-nematic transition is coming close to the nematic-solid transition pressure with elevation of temperature. At 317 K, the pressure of nematic-solid phase transition agrees with that of isotropic-nematic phase transition. The pressure of isotropic-nematic phase transition is higher than that of the nematic-solid transition at temperatures from 313.71 K to 317 K. However, this relation is reversed at temperatures over 317 K. These results mean that the nature of phase transition of nematic-isotropic has changed from monotropic to enantiotropic. These transition pressures are plotted in Figure 3 as a function of temperature. The isotropic-nematic transition line and the nematic-solid transition line crosses at about 12 MPa and 317 K. Clearly, the nature of the isotropic to nematic transition changed from monotropic to enantiotropic at this pressure.

Shashidhar has also observed that the change in the nature of transition at about 520 bars for trans-p-n-propoxy-α-methyl-p′-cyanophenyl cinnamate.[3] It is interest to note change of nature of phase transition for two monotropic nematic samples. Chandrasekhar *et al.* have observed induced mesophases.[4,5] They interpreted that this phenomena occurs below some value (ν) of a measure of relative barriers for the rotation of molecules and for its diffusion to an interstitial site in their theory.[4]

However, the induced mesophase is the same phenomenon as our observed enantiotropic region in the phase diagram. We observed that the monotropic region is an unstable phase in nematics. These two phenomena can be interpreted in the same mechanism. Order-disorder theory of nematics postulated that pressure induced enantiotropic nematics are always stable nematics. Figure 4 shows a phase diagram for Pople-Karasz-Chandrasekhar theory of nematics.[4,6] Dashed line, extrapolated from the enantiotropic phase appears as a monotropic phase. In this theory, a monotropic phase is an unstable phase

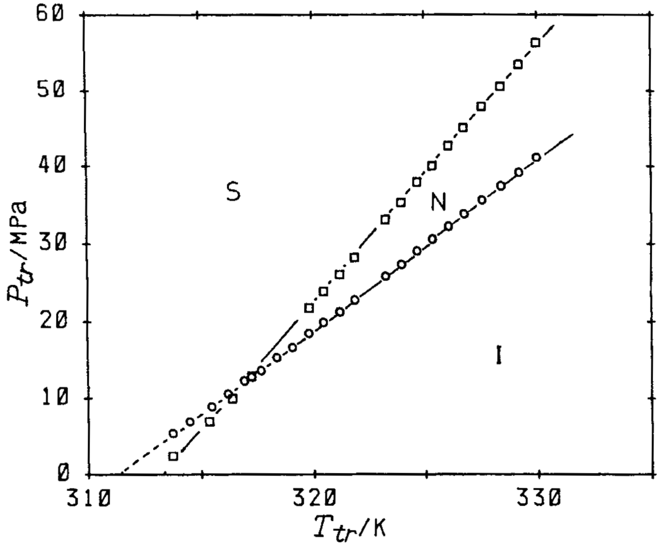

FIGURE 3 The phase diagram isotropic to nematic and nematic to solid phase transition for 4PCH. The dashed line is monotropic region of nematic to isotropic phase transition. *I* is isotropic region, *N* is nematic region and *S* is solid region.

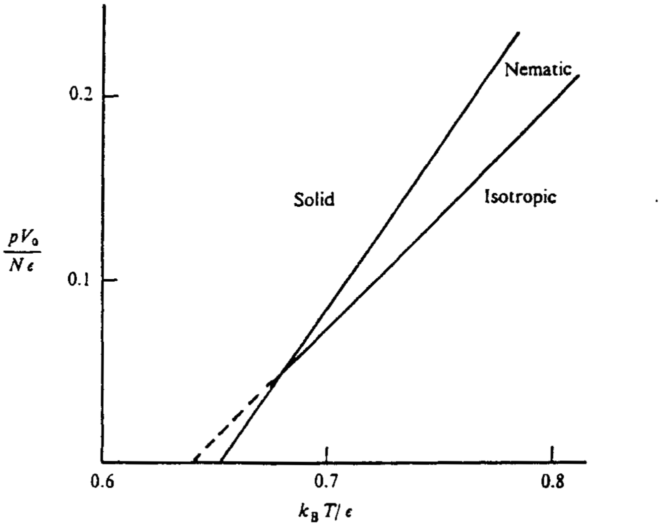

FIGURE 4 Theoretical variation of the transition temperatures with pressure $\nu = 0.95$. (After reference 6)

which is formed when the nematic-isotropic phase line crosses to the nematic-solid phase line. Hence, if solid-nematic phase line crosses to nematic-isotropic phase line, monotropic phase changes to enantiotropic phase over a pressure in the theory. Lampe and Collings observed a smectic A-nematic-isotropic triplepoint at 376K and 92MPa for dinonylazoxybenzene(9AB).[8] They did not observe monotropic nematic-smectic A phase line. They may not have been able to observe supercooling or superpressure, because nematic-smectic transition is nearly second kind phase transition. From these results, it is predicted that all monotropic nematic phases will change to enantiotropic nematic phases at high pressure.

We conclude that we have observed for the first time the nature of change of phase transition of nematics by P-V-T measurement. This phenomena is the same one as pressure induced nematics. It is predicted that all monotropic nematic phases will change to enantiotropic over a pressure decided from minimum energy of interaction ϵ and constant ν, a measure of relative barriers.

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