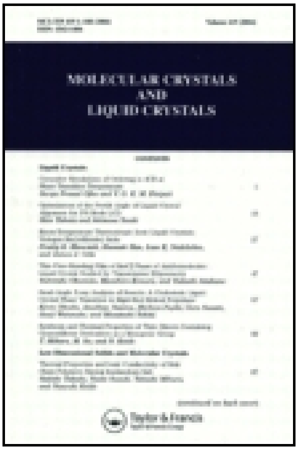

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Gas Sorption Properties in a Smectic Liquid Crystal

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Sorption behavior of CO_2 in a low molar mass liquid crystal (MLC) which exhibits a smectic mesophase has been measured by using an electromicrobalance. The sorption values at the same gas pressure are demonstrated to increase significantly at crystalline-smectic and smectic-isotropic transitions. The phase diagram of the MLC-CO_2 binary system has been measured through the use of the sorption method. The sorbed CO_2 has been shown to influence the phase behavior of the MLC. The isotropization transition of the MLC is found to be broadened by the formation of a biphasic region, which consists of a smectic and isotropic phases. The method for the determination of the compositions of the smectic and isotropic phases within the biphasic region has been offered.

Keywords: Gas sorption, liquid crystalline, biphasic region, liquid crystal

INTRODUCTION

Since low molar mass liquid crystals (MLCs) can exhibit various mesophases and have a sharp transition of them, a study of gas sorption properties in these materials are of importance for the understanding of the correlation between molecular organization and both gas diffusion and solution properties. The results are helpful in realizing the relationship between gas permeation behavior and physical structure of a polymeric membrane, especially that with liquid crystalline (LC) order.[1-6]

The sorption behavior of a nematic MLC has been investigated in a previous study.[7] The results have shown that LC order significantly affects solution and diffusion properties of a gas in the MLC. In addition, the influence of LC order on gas solubility of the MLC can be quantitatively known due to the dramatic change in sorption value that occurred at isotropization transition. The appreciable difference between the equilibrium sorption values in LC and in isotropic states also enables the MLC to exhibit sorption-desorption characteristics when the molecular states changed from one to another. One can use these characteristics to easily demonstrate that isotropization temperature of the MLC is depressed due to gas sorption.

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In this paper the sorption behavior of CO_2 in a smectic MLC is reported. We focus our attention on the influence of the sorbed CO_2 on smectic-isotropic transition. The depression of isotropization temperature and the formation of biphasic region due to CO_2 sorption are characterized and discussed. The compositions of the smectic and isotropic phases within the biphasic region have been determined by the sorption method.

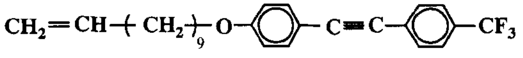
EXPERIMENTAL

Figure 1 shows the chemical structure of the MLC and its phase behavior. The detailed synthetic procedure and the characterization of the MLC will be published elsewhere.[8] The chemical structure of the MLC has been confirmed by the measurements of the NMR and Mass spectrum. A Nikon optical polarizing microscope equipped with a Mettler FP82 hot stage was used for locating phase transitions and analyzing the anisotropic textures. The type of the mesophase of the MLC was demonstrated to be Smectic E (S_E) by analyzing the anisotropic textures and the diffraction patterns of the X-ray (from a Rigaku RAD-C diffractometer).

The sorption behavior of CO_2 in the MLC was carried out on a Sartorius high pressure electromicrobalance (model S3D-P) assembly thermostatted by a mini-oven controlled to ±0.1°C. The sample was degassed prior to introducing CO_2 into the sorption chamber. The weight increase of the sorbing sample was continuously recorded as a function of time by a computer.

RESULTS AND DISCUSSION

Figure 2 shows the equilibrium concentrations of the sorbed CO_2 obtained in different phases of the MLC. The equilibrium values are found to increase significantly at the transitions of the crystalline to a smectic and the smectic to an isotropic phase. The change in sorption value at later transition is higher than that at former transition. The phenomenon is similar to the one found in the previous study on a nematic MLC[7]; this further demonstrates the significant influence of LC order on gas sorption. According to the studies by Hildebrand *et al.*,[9,10] gas solubility in a liquid can be correlated with the magnitude of the solubility parameter of a liquid. The higher the solubility parameter, the lower is the gas solubility. This fact implies that the solubility parameter in LC state is much higher than that in isotropic state, since gas sorption values are much lower in the former state than in the later. The higher solubility parameter originates obviously from the higher intermolecular cohesion due to the higher degree of order in LC phase.



K 66.0 S_E 78.6 I

FIGURE 1 Structure of the liquid crystal and its phase behavior.

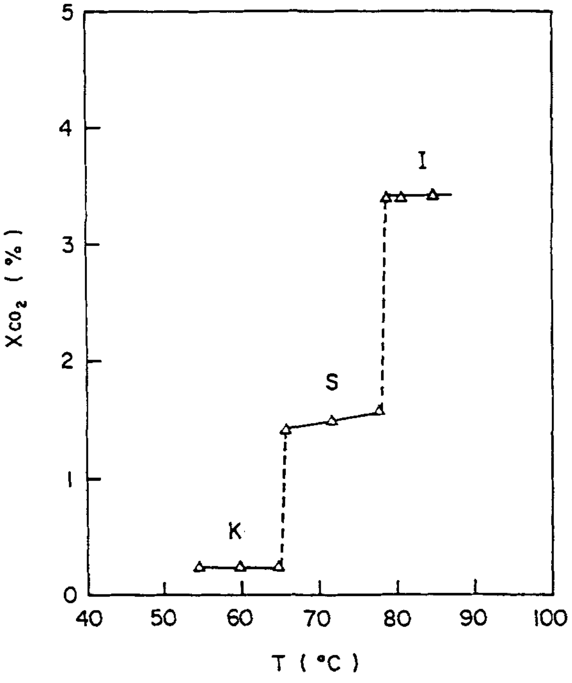


FIGURE 2 Equilibrium concentrations (mole fraction) of sorbed CO_2 at 1.2 bar in crystalline (*K*), smectic (*S*) and isotropic (*I*) states.

For easier discussion we designate the increase in sorption value of CO_2 at isotropization point as "transition sorption" S_t. At a temperature interval of 78°C to 79°C, S_t was measured as a function of the concentration of the sorbed CO_2. The results are shown in Figure 3. It is interesting to find that S_t decreases with increasing concentration and finally becomes zero. Since S_t is caused by the isotropization of LC phase, the decrease in S_t suggests a change in LC structure of the MLC in the above temperature range. The reasonable explanation is that there exists a biphasic region which is composed of a smectic and an isotropic phase at the isotropization transition. As the concentration of the sorbed CO_2 increases, the proportion of smectic phase could decrease, thus resulting in a decrease in S_t.

In order to demonstrate the assumption of the existence of a biphasic region, small temperature increments from smectic to isotropic phases were used to obtain S_t. A typical example is illustrated in Figure 4. At a specific CO_2 concentration ($X = 4.5\%$), the small rise in temperature did not cause any apparent sorption when the MLC was in smectic phase (the temperature is lower than 77.2°C). An apparent sorption, however, occurred as the temperature was raised from 77.2°C to 77.4°C. The new sorption could reach an equilibrium state after a period of time. The temperature was then raised after the equilibrium state had been attained. Several additional sorptions could be similarly found by such small temperature increments up to 78.0°C. For the temperature higher than 78.0°C, the increasing temperature did not cause any sorption behavior again; this suggests a complete isotropization of LC phase. The wide isotropization transition differed from the

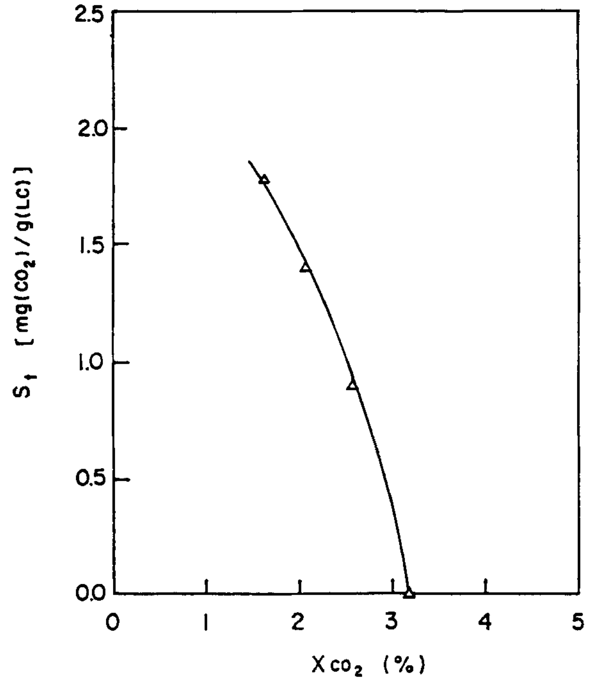


FIGURE 3 Effect of the concentration of sorbed CO_2 on the transition sorption (S_t) from smectic to isotropic.

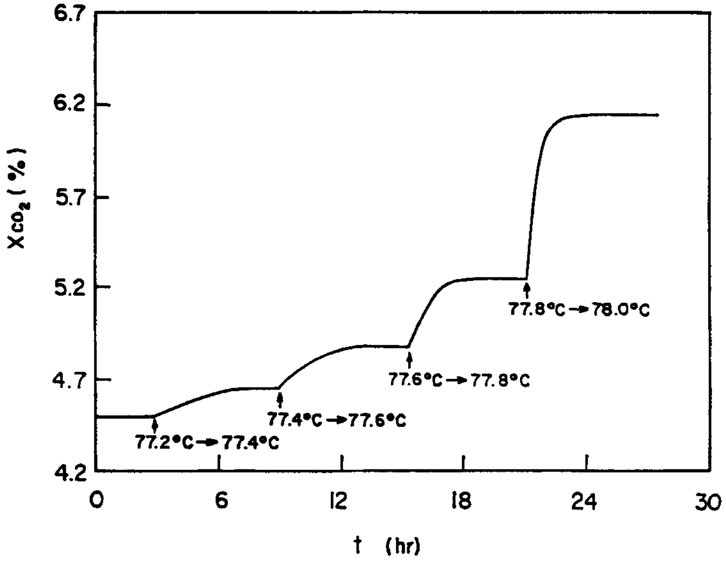


FIGURE 4 A demonstration of the existence of the biphasic region at the isotropization transition of the liquid crystal. Several equilibrium sorption states could be obtained from the indicated small temperature increments.

sharp one observed under polarizing microscope. Obviously, the isotropization transition was broadened by the formation of a biphasic region within which smectic and isotropic phases could exist simultaneously. The temperature was reduced to be in the range of smectic phase after the complete isotropization of LC phase. A desorption of the sorbed CO_2 could be found on lowering the temperature because of the lower gas solubility in smectic phase.[7] The gas pressure was then increased and the same procedure was repeated to obtain the sorption properties at higher concentration of the sorbed CO_2.

Figure 5 shows the phase diagram of the MLC-CO_2 binary system. The boundary temperatures of the biphasic region is shown to be linearly depressed. The slope of the incipient temperature (T_s) of biphase versus the mole fraction of the sorbed CO_2 is found to be more negative than that of the complete isotropization temperature (T_c) of biphase. Biphasic region is therefore broadened as the concentration of the sorbed CO_2 increases. The depression of isotropization transition and the formation of biphase were also reported for the binary systems consisting of organic solvents and nematic MLCs[11,12] or organic solvents and main-chain LC polymers.[13,14] This demonstrates that the sorbed CO_2 can act as the same role as an organic solvent to affect the phase behavior of a MLC.

A distinct advantage of the sorption method for observing biphase behavior is to be capable of determining the compositions of smectic and isotropic phases within the biphasic region. This is achieved by the procedure as has been used in

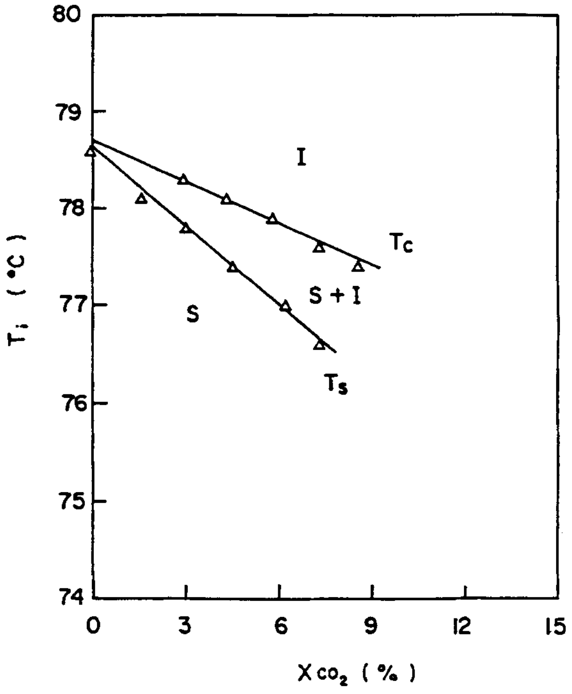


FIGURE 5 Phase diagram of the MLC-CO_2 binary system. In the temperature range T_s to T_c the smectic (S) and isotropic (I) phases coexist.

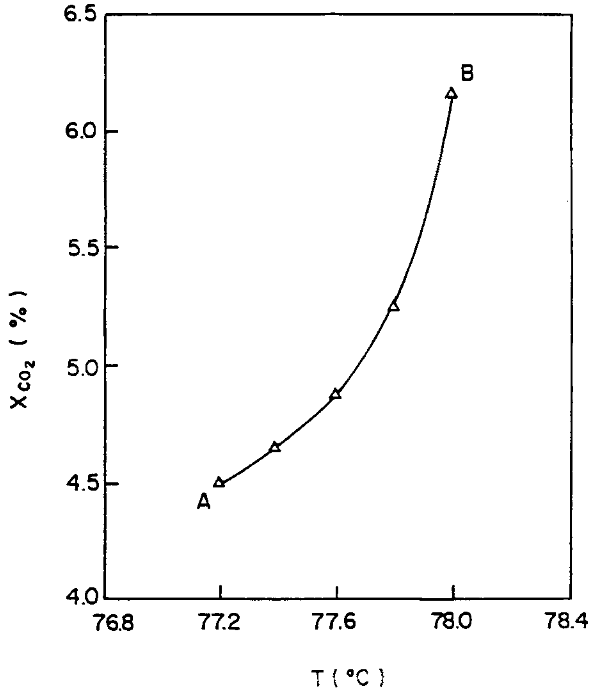


FIGURE 6 Equilibrium concentration of sorbed CO_2 within biphasic region as the temperature changes from the incipient point (A) to the complete isotropization point (B) of the biphase.

Figure 4. The total transition sorption (S_{tt}) from incipient temperature T_s to complete isotropization temperature T_c can represent the sorption value that the proportion of isotropic phase changes from 0% to 100%. Thus, once the intermediate transition sorption value (S_{ti}) between T_s and T_c is obtained, the proportion of isotropic phase within the biphasic region can be calculated by the value S_{ti}/S_{tt}, and the proportion of smectic phase by $(1 - S_{ti}/S_{tt})$. Figure 6 shows a typical change in the concentration of the sorbed CO_2 as the temperature increases from T_s (point A) to T_c (point B). The curve indicates that the change in concentration is more pronounced at a temperature range near T_c. This means that most of the smectic phase undergoes isotropization in this temperature range. The behavior could be attributed to the plasticizing effect of the sorbed CO_2, since the higher sorbed concentration near T_c would further destabilize the LC phase due to the intermolecular interaction of the sorbed CO_2 with the MLC.

In conclusion, the present study demonstrates that a smectic liquid crystalline phase can seriously lower the gas solubility of a MLC. The sorbed gas could play a role as a nonmesogenic solute to cause the formation of a biphasic region, of which boundary temperatures are depressed by increasing concentration of the sorbed gas. The compositions of the smectic and isotropic phases within the biphasic region can be determined by the sorption method. Most of the LC molecules are shown to exist in the form of smectic state in the incipient region of the biphase. They undergo isotropization in a temperature range near complete clearing point.

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