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Phase transition behavior of hydrogen bonded liquid crystal $(6BA)_2$-$(BPy)_x$ as studied by ^{2}H NMR

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Abstract The thermal properties and the orientational order of hydrogen-bonded liquid crystals $(6BA)_2$-$(BPy)_{0.4}$ and $(6BA)_2$-$(BPy)_{0.3}$ (6BA: 4-n-hexylbenzoicacid, BPy: 4,4'-bipyridine) were investigated by DSC and ^{2}H NMR. On cooling, isotropic liquid - liquid crystal phase transition temperatures were $T_C = 409$ and 405 K for $(6BA)_2$-$(BPy)_{0.4}$ and $(6BA)_2$-$(BPy)_{0.3}$, respectively. Thermal anomalies in the liquid crystal phase were observed at $T_{LC1} = 402$ and $T_{LC2} = 375$ K for $(6BA)_2$-$(BPy)_{0.4}$ and at $T_{LC1} = 398$ and $T_{LC2} = 375$ K for $(6BA)_2$-$(BPy)_{0.3}$. For $(6BA)_2$-$(BPy)_{0.4}$, only the smectic component was created above T_{LC1}. In addition, the nematic component was created below T_{LC1}. The nematic component gradually changed to the smectic component with decreasing temperature and only the smectic component was observed below T_{LC2}. For $(6BA)_2$-$(BPy)_{0.3}$, only the nematic component was created above T_{LC2}. The phase transition from the nematic phase to the smectic phase took place at around T_{LC2}.

Keywords Liquid crystal · Hydrogen bond · Quadrupole interaction · ^{2}H NMR

1 Introduction

The thermotropic hydrogen-bonded liquid crystal 4-n-hexylbenzoicacid (6BA), in which 6BA molecules form a cyclic dimer $(6BA)_2$ by two hydrogen bonds between carboxylic acids (Chart 1a), exhibits a nematic liquid crystal phase in the temperature range between
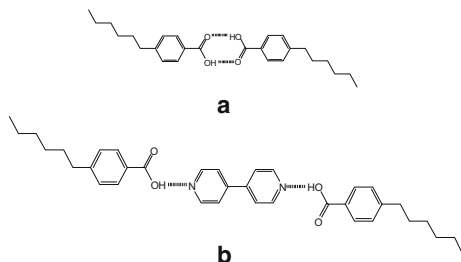

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Chart 1 Structures of cyclic
dimer $(6BA)_2$ (**a**) and
$(6BA)_2$-$(BPy)_1$ (**b**)

371 and 380 K [1–3]. The thermotropic hydrogen-bonded liquid crystal $(6BA)_2$-$(BPy)_1$, in which 4,4'-bipyridine (BPy) is incorporated into $(6BA)_2$ (Chart 1b), can be obtained by mixing 6BA and BPy at a molar ratio of 2:1 [4]. $(6BA)_2$-$(BPy)_1$ exhibits a smectic liquid crystal phase in the temperature range between 368 and 427 K [4, 5]. The investigation of phase behavior and local structure in the liquid crystal $(6BA)_2$-$(BPy)_x$ $(0 < x < 1)$, which is the mixture of nematic $(6BA)_2$ and smectic $(6BA)_2$-$(BPy)_1$, is important to understand the properties of self-assembled supramolecular liquid crystals. Previously, the phase behavior and molecular orientational order of $(6BA)_2$-$(BPy)_{0.5}$, in which the ratio of $(6BA)_2$ and $(6BA)_2$-$(BPy)_1$ is 1:1, were investigated by thermal analysis and ^2H NMR spectroscopy [5]. From the transition enthalpy value and temperature dependence of the orientational order parameter, $(6BA)_2$-$(BPy)_{0.5}$ was found to be a smectic liquid crystal. In addition, a liquid crystal – liquid crystal phase transition was observed. However, the liquid crystal state of $(6BA)_2$-$(BPy)_x$ in excessive nematic $(6BA)_2$ has not been investigated.

^2H NMR spectroscopy is very sensitive to the orientational order of molecules and the dynamics of molecules in the liquid crystal phase [6]. The ^2H NMR spectrum is also sensitive to the strength and direction of a hydrogen bond since the electric field gradient at deuteron is strongly affected by the hydrogen bond [7].

In the present work, the temperature range of the liquid crystal phase and the orientational order of molecules in the liquid crystal phase of $(6BA)_2$-$(BPy)_{0.4}$ and $(6BA)_2$-$(BPy)_{0.3}$ were investigated by ^2H NMR and differential scanning calorimetry (DSC) in order to clarify the effects of excessive nematic $(6BA)_2$ on the mixed liquid crystal state. The cooling process was observed in order to investigate the well-blended state of $(6BA)_2$ and $(6BA)_2$-$(BPy)_1$. For the ^2H NMR measurement, 6BA-d, whose COOH group was deuterated, was used.

2 Experimental

2.1 Sample preparation and identification

6BA-d, in which hydrogen of the COOH group is deuterated, was obtained by recrystallization from deuterated ethanol (99.8 atom% D). $(6BA-d)_2$-$(BPy)_x$ was prepared from dry pyridine solution containing an appropriate amount of 6BA-d and BPy. The ratio x was determined by elementary analysis of H, C and O.

2.2 DSC

DSC was performed using a Rigaku Thermo Plus EVO DSC 8230. DSC measurements were performed between 300 and 450 K. The results of the second cooling process were used to determine the thermal parameters.
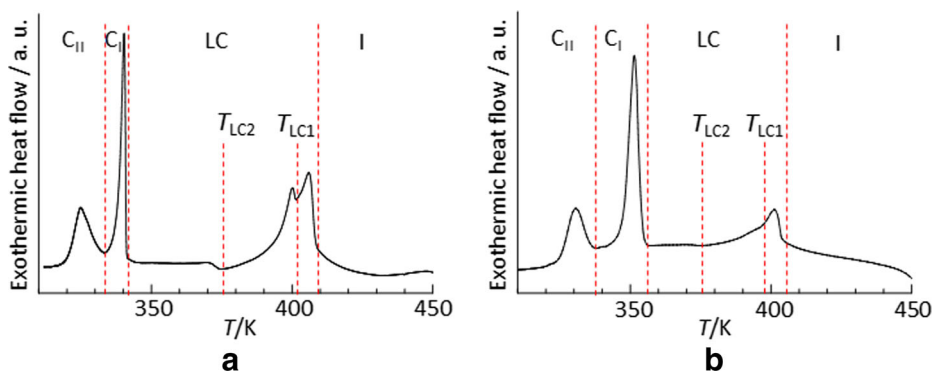
Fig. 1 DSC thermodiagram of x=0.4 (**a**) and 0.3 (**b**) during cooling

2.3 ^{2}H NMR

^{2}H NMR was measured using a JEOL ECA-300 spectrometer at 45.282 MHz. The ^{2}H NMR broadline spectra were measured using a quadrupole echo sequence $(90°)_x - \tau - (90°)_y - \tau - t_{acq}$, where τ and t_{acq} are the interval of the first and second pulses and acquisition time, respectively. The 90° pulse width and τ were 2.5 and 20 μs, respectively.

3 Results and discussion

Figure 1 shows the DSC thermodiagram of x = 0.4 and 0.3 during the cooling process. The temperatures of the isotropic liquid (I) - liquid crystal (LC) phase transition, the LC - crystal (C_I) phase transition, and the crystal (C_I) - crystal (C_{II}) phase transition were determined as 409, 342, and 333 K for x = 0.4 and 405, 356, and 338 K for x = 0.3, respectively. Two exothermal peaks were observed in the LC phase at $T_{LC1} = 402$ and $T_{LC2} = 375$ K for x = 0.4. For x = 0.3, weak thermal anomalies were observed at $T_{LC1} = 398$ and $T_{LC2} = 375$ K in the LC phase.

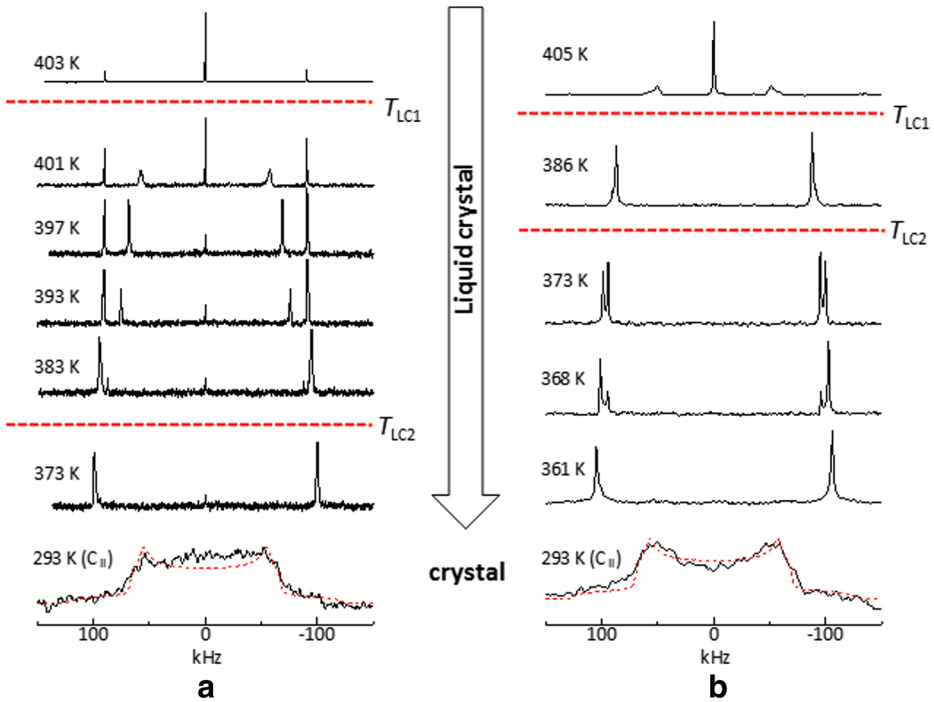Figure 2 shows static ^{2}H NMR spectra in the liquid crystal phase and crystal phase during the cooling process for x = 0.4 and 0.3.

Above T_{LC1}, two sharp peaks of the quadrupole splitting due to the orientational order of LC molecules and the central sharp peak corresponding to the isotropic liquid component were observed for both samples.

For x = 0.4, two pairs of the quadrupole splitting were observed in the temperature range between T_{LC1} and T_{LC2}. Below 400 K, the intensity of the two outside peaks increased as the intensity of the inside peaks decreased with decreasing temperature. Below T_{LC2}, only one quadrupole splitting doublet was observed.

For x = 0.3, the isotropic liquid component disappeared at T_{LC1}. Two pairs of the quadrupole splitting were observed below T_{LC2}. The intensity of the two outside peaks increased as the intensity of the inside peaks decreased with decreasing temperature and the inside peaks disappeared at around 363 K.

In the crystal phase, the line shape of the ^{2}H NMR spectrum indicates a rigid deuterium powder pattern. The quadrupole coupling constant (e^2qQ/h) and asymmetry parameter (η) were estimated as 163 kHz and 0.1, and 170 kHz and 0.1 for x = 0.4 and 0.3, respectively from the line shape analysis of the spectrum at 293 K.

Fig. 2 Static ^{2}H NMR spectrum in the liquid crystal phase and crystal phase for (6BA-d)$_2$(BPy)$_{0.4}$ (**a**) and (6BA-d)$_2$(BPy)$_{0.3}$ (**b**) on cooling. *Broken lines* in the spectra at 293 K show calculated powder pattern using $e^2qQ/h = 163$ kHz and $\eta = 0.1$ (**a**) and $e^2qQ/h = 170$ kHz and $\eta = 0.1$ (**b**)

From the quadrupole splitting width of the ^{2}H NMR spectra dν in the liquid crystal phase, the order parameter S was calculated using [6]

$$S = \frac{2}{3}\frac{h}{e^2qQ}\mathrm{d}\nu. \tag{1}$$

The e^2qQ/h values of the crystal phase were used for the calculation. Figure 3 shows the variation of S of x = 0.4 with respect to reduced temperature $\tau = (T - T_{\rm c}) / T_{\rm c}$, where $T_{\rm c}$ is the isotropic liquid - liquid crystal phase transition temperature.

For a comparison, S of x = 0 and 0.5 are also shown [3, 5]. S of the nematic liquid crystal (6BA)$_2$ decreased largely from 0.75 to 0.42 as τ approached 0 [3]. On the other hand, S of the smectic liquid crystal (6BA)$_2$-(BPy)$_x$ (x $\geq$ 0.5) decreased gradually from $ca.$ 0.85 as τ increased and was higher than 0.7 even at around $\tau = 0$ [5]. The temperature variation of S of x = 0.4 was similar to that of x $\geq$ 0.5 above $T_{\rm LC1}$. Therefore, the smectic component is created above $T_{\rm LC1}$ for x = 0.4. The additional component that appeared below $T_{\rm LC1}$ is the nematic phase since S of this component showed a similar temperature variation as (6BA)$_2$. The maximum abundance ratio of 0.46 for the nematic component in the liquid crystal phase was obtained at around 400 K from the spectral intensity of the ^{2}H NMR spectrum. The amount of the nematic component decreased with decreasing temperature and only the smectic component was observed below $T_{\rm LC2}$ (Fig. 2a).

Figure 4 shows the temperature dependence of S for x = 0.3. S decreased largely with increasing τ in the temperature range between $T_{\rm LC2}$ and $T_{\rm c}$ for x = 0.3. This result suggests

Fig. 3 Temperature variation of order parameter S for $(6BA)_2(BPy)_x$. Transverse axis on the top of figure shows temperature of $(6BA)_2(BPy)_{0.4}$
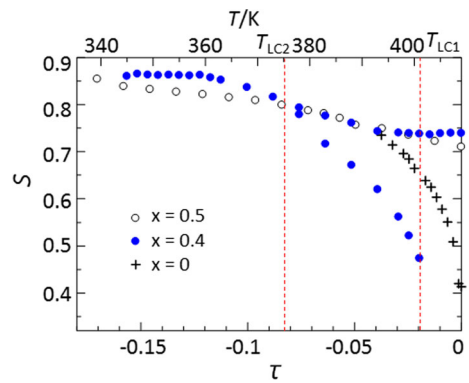
Fig. 4 Temperature dependence of order parameter S for $(6BA)_2(BPy)_{0.3}$
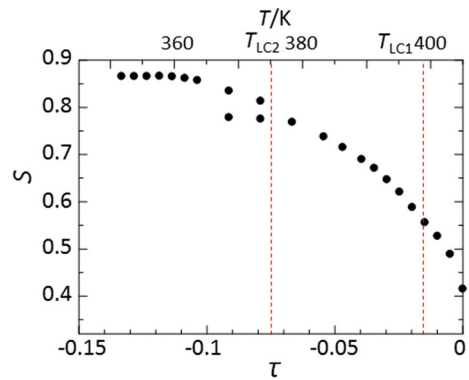
that x $=$ 0.3 forms a nematic phase in this temperature range. Below T_{LC2}, the large S value of about 0.85 indicates that a smectic phase is formed. The gradual transition from the nematic phase to the smectic phase was observed in the temperature range between 375 and 365 K, assessed from the change in intensity of two quadrupole splitting doublets in Fig. 2b.

$(6BA)_2$-$(BPy)_{0.5}$, in which the ratio of nematic $(6BA)_2$ and smectic $(6BA)_2$-$(BPy)_1$ is 1:1, shows only the smectic phase [5]. On the other hand, the additional nematic component appeared in the temperature range between T_{LC1} and T_{LC2} for $(6BA)_2$-$(BPy)_{0.4}$ which includes excessive nematic $(6BA)_2$. For $(6BA)_2$-$(BPy)_{0.3}$ including more $(6BA)_2$, only the nematic phase was created above T_{LC2} and a nematic – smectic phase transition took place at around T_{LC2}.

4 Conclusion

The influence of excessive nematic $(6BA)_2$ upon the mixed liquid crystal state of $(6BA)_2$-$(BPy)_x$ was investigated using $(6BA)_2$-$(BPy)_{0.4}$ and $(6BA)_2$-$(BPy)_{0.3}$. Although the smectic component was formed at first, an additional nematic component appeared below T_{LC1} for $(6BA)_2$-$(BPy)_{0.4}$. The transition from the nematic phase to the smectic phase took place gradually with decreasing temperature and only the smectic component was observed below T_{LC2}. For $(6BA)_2$-$(BPy)_{0.3}$, the nematic phase was formed at first. The nematic - smectic phase transition took place at around T_{LC2}.

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