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Liquid Crystals

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Synthesis and variable-temperature FTIR study of five chiral liquid crystals induced by intermolecular hydrogen bonding

Yanqing Tian^a; Fengyu Su^b; Yingying Zhao^a; Xuyang Luo^a; Xinyi Tang^a; Xiaoguang Zhao^b; Enle Zhou^b

^a Department of Chemistry, Jilin University, Changchun, P.R. China ^b Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, P.R. China

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according to a known procedure [10]. 4-Hydroxy-4'-stilbazole was prepared according to [3]. The compound MBSB was obtained by stirring a mixture of (*S*)-2-chloro-3-methylbutanoic acid (2.0 g, 13.2 mmol), 4-hydroxy-4'-stilbazole (1.50 g, 7.6 mmol), DCC (3.0 g, 14.5 mmol) and a small amount of DMAP in DMF at room temperature for two days, and purified by column chromatography on silica gel (CH₂Cl₂ as the eluent, *R_f* = 0.30). It was further recrystallized twice from cyclohexane. The yield was 31 per cent, melting point 60–61 °C. ¹H NMR (400 MHz) for MBSB (CDCl₃, ppm): 8.58 (2 H, d, *J* = 6.0 Hz) and 7.36 (2 H, d, *J* = 6.0 Hz) (pyridyl), 7.56 (2 H, d, *J* = 8.4 Hz) and 7.15 (2 H, d, *J* = 8.4 Hz) (phenyl), 7.28 (1 H, d, *J* = 16 Hz) and 6.98 (1 H, d, *J* = 16 Hz) (*trans*-CH=CH-), 4.33 (1 H, t, *J* = 6.8 Hz) (-C*HCl-), 2.48 (1 H, m) (-CH(CH₃)₂), 1.17 (6 H, d, *J* = 6.4 Hz) (-CH(CH₃)₂). Elemental analysis: Calculated for C₁₈H₁₈ClNO₂: C, 68.46; H, 5.74; N, 4.44. Found: C, 68.66; H, 5.83; N, 4.30 per cent. The mixtures (1:1 molar ratio) of proton acceptor and donors were obtained by slowly evaporating the THF solutions under reduced pressure [3].

The textures of the mesophases were characterized by polarized optical microscopy (Zeiss Jena optical microscope) in conjunction with a heating stage from HunJiang

in China. DSC measurements were conducted using a Perkin-Elmer DSC7 with a heating rate of 5 °C min⁻¹. Infrared spectra at different temperatures were obtained using a Nicolet-5DX FTIR spectrometer equipped with a hot stage, at a heating rate of 5 °C min⁻¹ from room temperature to 160 °C, with a maximal resolution of 2 cm⁻¹ over the entire range. The samples were placed in a cell consisting of two KBr pellets without any surface treatment. Samples were heated to 15 °C above the melting point and then cooled to room temperature prior to making the infrared measurements. ¹H NMR spectra were obtained using a Unity 400NMR instrument operating at 400 MHz and solutions in CDCl₃. Elemental analyses were obtained with a Perkin-Elmer 240C microanalyser.

3. Results and discussion

The phase transitions of the hydrogen bonded 1:1 complexes were studied by DSC and polarized optical microscopy. All the phases were enantiotropic. The table gives the transition temperatures and enthalpies for the chiral stilbazole (MBSB), the 4-alkoxybenzoic acids (*n*BA) and their 1:1 complexes. These results are also illustrated in figure 1.

From figure 1, we can see that the phase transition

The phases, transition temperatures (°C) and enthalpies (kJ mol⁻¹) in parentheses for MBSB, *n*BA and their 1:1 complexes.

Compounds	$[\alpha]_D^{25}$	Phase behaviour
MBSB	+ 4.75 (<i>c</i> = 0.421)	Cr 60 I
4BA		Cr 147 N 160 I
5BA		Cr 125 N 152 I
6BA		Cr 108 N 153 I
7BA		Cr 92 S 100 N 146 I
8BA		Cr 102 S 108 N 148 I
4BA:MBSB	+ 4.53 (<i>c</i> = 0.386)	Cr $\frac{114.6}{(35.77)}$ S _C [*] $\frac{122.5}{(0.66)}$ S _A $\frac{132.8}{(1.15)}$ N ^{**} $\frac{134}{(1.15)}$ I
5BA:MBSB	+ 4.44 (<i>c</i> = 0.445)	Cr ₁ $\frac{85.0}{(30.38)}$ Cr ₂ $\frac{95.3}{(30.38)}$ S _C [*] $\frac{107.3}{(—)}$ S _A $\frac{125.0}{(5.19)}$ N [*] $\frac{128.0}{(5.19)}$ I
6BA:MBSB	3.90 (<i>c</i> = 0.449)	Cr $\frac{93.0}{(23.31)}$ S _C [*] $\frac{108.8}{(—)}$ S _A $\frac{125.0}{(5.14)}$ N [*] $\frac{132.4}{(5.14)}$ I
7BA:MBSB	+ 3.75 (<i>c</i> = 0.402)	Cr ₁ $\frac{74.9}{(22.64)}$ Cr ₂ $\frac{84.4}{(12.30)}$ S _C [*] $\frac{107.8}{(—)}$ S _A $\frac{132.0}{(6.30)}$ I
8BA:MBSB	+ 3.85 (<i>c</i> = 0.520)	Cr $\frac{91.0}{(22.44)}$ S _C [*] $\frac{108.8}{(—)}$ S _A $\frac{135.1}{(7.82)}$ I

Cr: crystalline state; S: smectic phase; I: isotropic phase; N: nematic phase; (—) very small; α: value from optical microscopy; $[\alpha]_D^{25}$ was determined for CHCl₃ solutions.

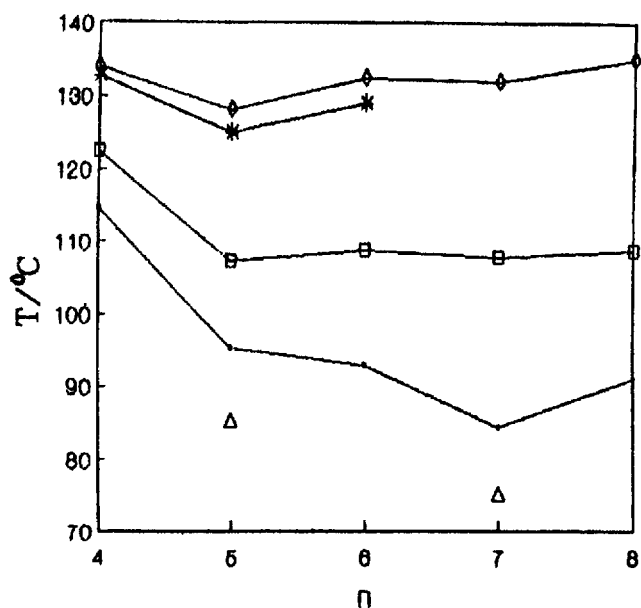


Figure 1. The variation of phase transition temperatures with increasing length of the alkoxy chains for the 1:1 complexes. Δ C_n-Cr₂; \bullet Cr-S_C^{*}; \square S_C^{*}-S_A; * S_A-N^{*}; \diamond N^{*} or S_A-I transition.

temperatures of these complexes, from the mesophase to the isotropic phase exhibit an even-odd effect, and that they are very different from those for both the proton donors and the proton acceptor. That is say, the 1:1 complex with the intermolecular hydrogen bonding behaves as a single component.

The 1:1 complexes of 4BA:MBSB, 5BA:MBSB, 6BA:MBSB show chiral smectic C phases, smectic A phases and chiral nematic phases. When n is longer (larger or equal to 7), the chiral nematic phase disappears. Under the microscope we can see the textures of the S_C^{*} phases (finger print texture), the S_A phases (simple fan shaped texture), and the N^{*} phases (schlieren texture), both on the heating and on the cooling sequence. Figure 2 illustrates the finger print texture (with faint pitchlines across the fan-shaped regions) of 4BA:MBSB at 118°C (S_C^{*} phase).

The existence of intermolecular hydrogen bonds can be identified by IR spectroscopy. As an example, figure 3 shows the IR spectra (at room temperature) of 8BA, MBSB and 8BA:MBSB. From the spectra of 8BA (see figure 3(a)), the broad band of the OH group of the carboxylic acid centred at 3000 cm⁻¹, the bands at 2560 and 2670 cm⁻¹ which are considered to be due to Fermi resonances [8, 11] and the carbonyl band at 1682 cm⁻¹ which is associated with the dimer of 8BA are seen. The spectrum (see figure 3(b)) of MBSB has a carbonyl band at 1757 cm⁻¹. The bands centred at 3000 cm⁻¹, 2560 cm⁻¹ and 2670 cm⁻¹ disappear (see figure 3(c)) in the infrared spectrum of 8BA:MBSB, but two new bands centred at 2450 and 1950 cm⁻¹ can be seen very clearly.

These two new bands are strong evidence of the intermolecular hydrogen bonding, which is of an unionized type between the pyridyl unit and the carboxylic acid [8, 12, 13]. Also, the carbonyl absorbance of the acidic group changes to 1689 cm⁻¹ from 1682 cm⁻¹ of the dimer of 8BA. This is attributed to the free carbonyl group formed as a result of the intermolecular hydrogen bonds [8].

The IR spectra of these complexes were also studied from their crystalline states to the isotropic phases. The IR changes resulting from formation of these complexes are very similar. In this paper, a typical example is given. Because the frequency shifts of carbonyl groups are very sensitive to changes of molecular conformation, inter- and intra-molecular interactions [6, 7] and intermolecular hydrogen bonding between acid and pyridyl units [8], our emphasis here is to study the changes or shifts for the ester and acid carbonyl groups at different temperatures. Figure 4 shows the IR spectra of 8BA:MBSB in the range 1800–1500 cm⁻¹ from 50 to 140°C.

In order to see the effects clearly, figure 5 illustrates the IR spectra of 8BA:MBSB at 50°C (crystalline state), 100°C (S_C^{*} phase), 115°C (S_A phase) and 140°C (isotropic phase).

From figure 5, we can see that the frequency shift of the ester carbonyl group (1759 cm⁻¹) is very significant on going from the crystalline state to the smectic C^{*} phase. Figure 6 shows the shifts for the ester carbonyl group with respect to different temperatures.

At the crystalline (Cr)–smectic C^{*} (S_C^{*}) phase transition, a sudden shift to higher frequency (7.8 cm⁻¹) was observed, and at the smectic A (S_A)–isotropic (I) phase transition, a small shift (2 cm⁻¹) was also found. But there

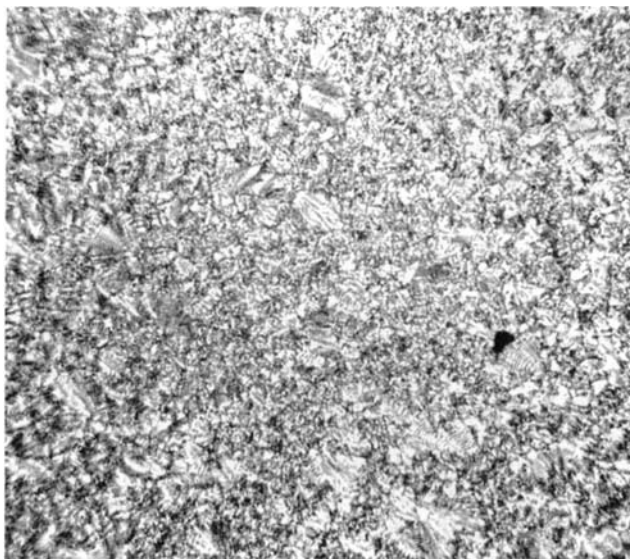


Figure 2. Mesomorphic texture of 4BA:MBSB at 118°C (S_C^{*} phase) (magnification: $\times 400$).

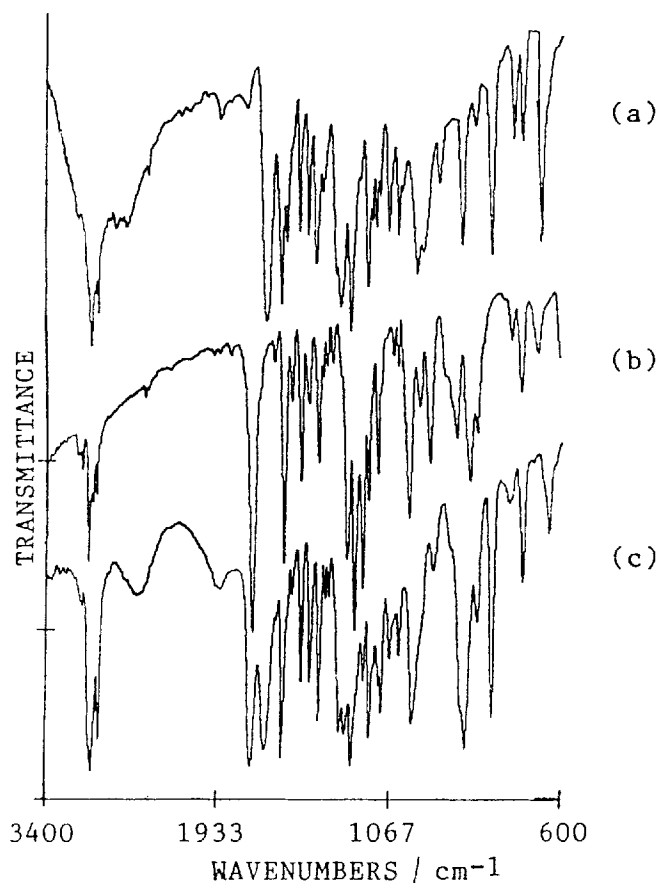


Figure 3. IR spectra of (a), 8BA, (b) MBSB and (c) 8BA:MBSB at room temperature.

were no obvious frequency shifts within the temperature ranges of the crystalline state, the smectic phases and the isotropic phase. These results could be attributed to the intramolecular hydrogen bonding formed between an aromatic hydrogen and the ester carbonyl group [6]. When the temperature rises to give the less ordered phases (smectic phases or the isotropic phase), the hydrogen bonds decrease, and the number of free carbonyl groups increases; as a result the ester carbonyl absorption changes to higher frequency [6, 14, 15]. The carbonyl band at 1689 cm^{-1} (see figure 5) also shows significant changes at the Cr-S_A^* and $\text{S}_A\text{-I}$ transitions. In the Cr state (see figure 5(d)), the frequency of the carbonyl bond is 1689 cm^{-1} which is attributed to the formation of intermolecular hydrogen bonding [8]. In the smectic phases (see figure 5(b) and (c)), the carbonyl band only becomes broader, but in the isotropic phase (see figure 5(a)), the carbonyl absorption is separated into four bands. The bands at 1705.9 cm^{-1} 1688.3 cm^{-1} are due to the hydrogen-bonded complex 8BA:MBSB [8]. The new band at 1718.2 cm^{-1} is associated with the existence of monomeric 8BA [8], and the new band at 1730 cm^{-1} is, we think, attributable to be a new carbonyl group

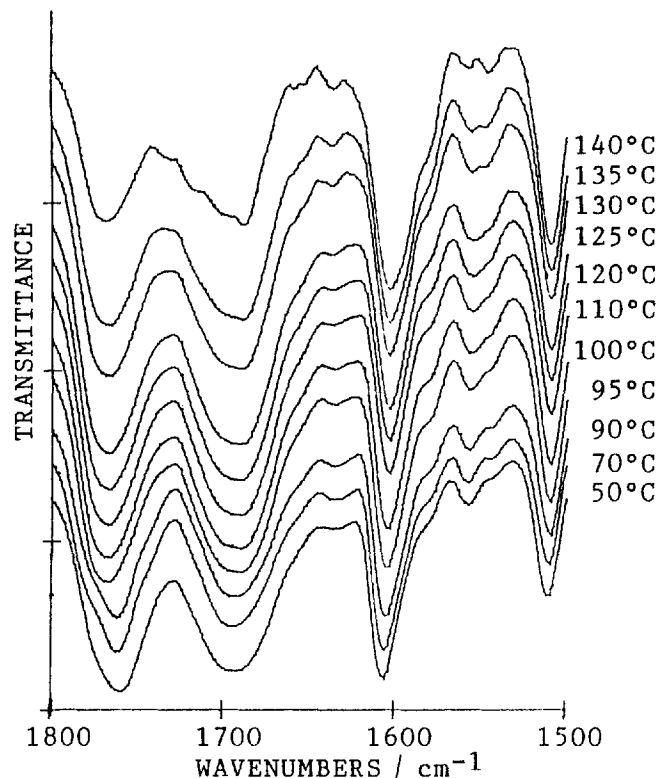


Figure 4. IR spectra of 8BA:MBSB in the range $1800\text{--}1500\text{ cm}^{-1}$ from 50°C to 140°C .

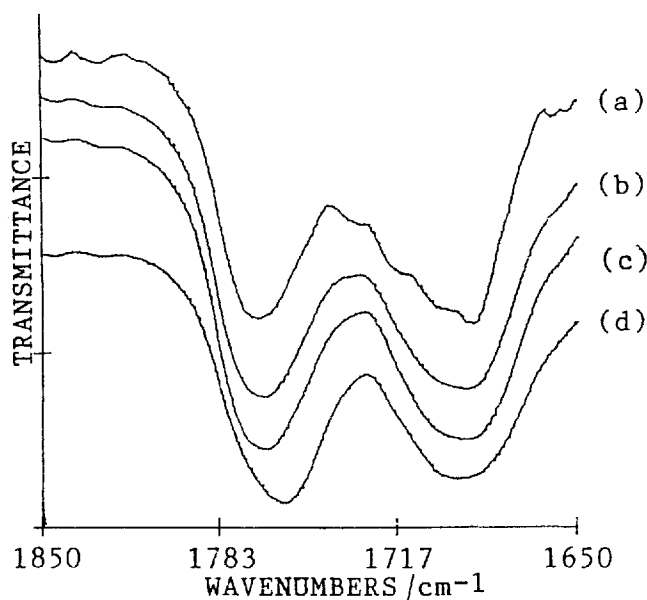


Figure 5. IR spectra of 8BA:MBSB at (a) 140°C , (b) 115°C , (c) 100°C and (d) 50°C .

($-\text{CH}=\text{CH}-\text{COO}-$). When the hydrogen bonds break down in the isotropic phase, the free form of the pyridyl group appears. Under these high temperature conditions, a hydrogen chloride molecule is lost and a conjugate

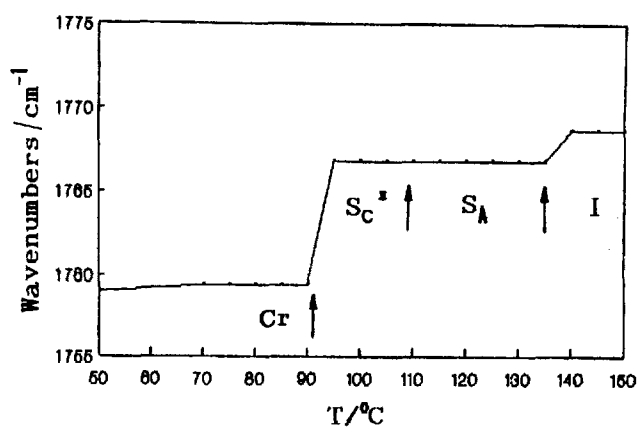


Figure 6. Frequency shifts of the ester carbonyl band at 1759.4 cm^{-1} with increasing temperature. The arrows indicate the phase transition temperatures obtained by DSC.

structure is formed, so generating a new ester carbonyl group. These results show that the stability of the hydrogen bond decreases greatly only when the temperature reaches that of the isotropic phase, and that at the same time the amount of free 8BA increases. This conclusion is also supported by the IR spectra from 3400 to 1500 cm^{-1} (see figure 7). From figure 7, we can see that as the temperature increases the carboxylic acid bands centred at 3000 cm^{-1} become broader and broader, and the amount of free carboxylic acid becomes more and more. On the other hand, the two bands centred at 1950 cm^{-1} and 2450 cm^{-1} still exist in the isotropic phase (see figure 7(a)), and we

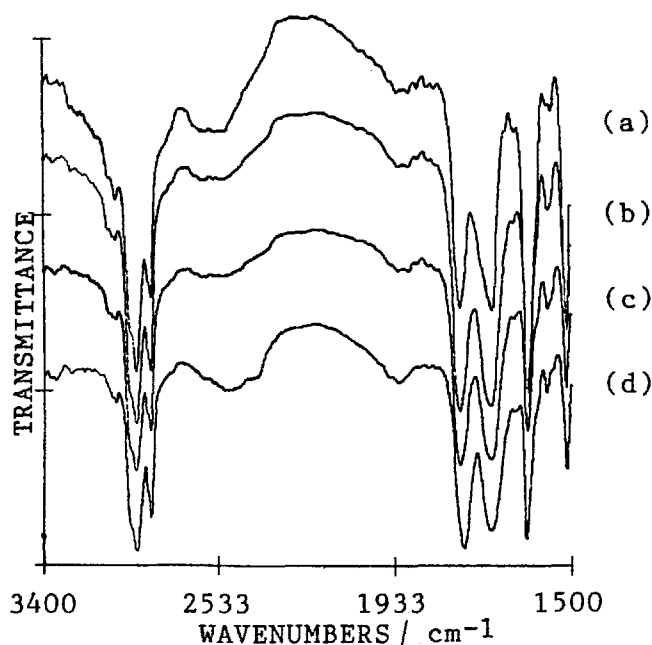


Figure 7. IR spectra of 8BA:MBSB from 3400 to 1500 cm^{-1} at (a) 140°C , (b) 115°C , (c) 100°C and (d) 50°C .

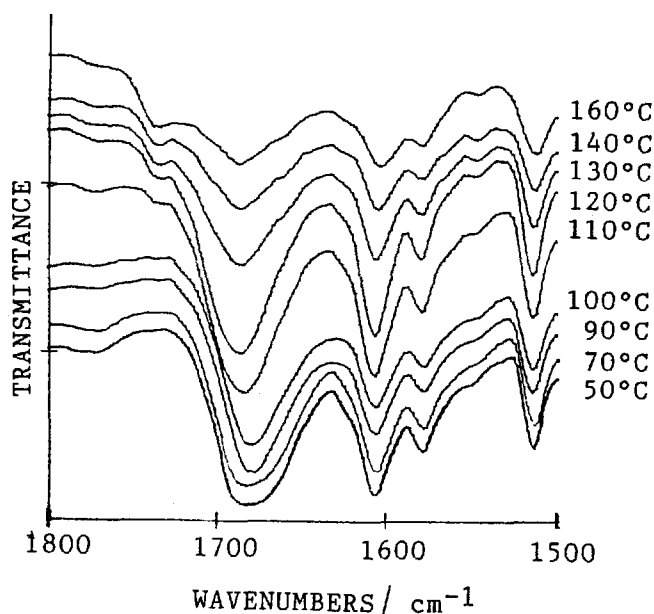


Figure 8. IR spectra of 8BA from 50°C to 160°C in the range 1800 – 1500 cm^{-1} .

think that although the intermolecular hydrogen bonding decreases greatly when the temperature is higher than the clearing point of the complex, the intermolecular hydrogen bond is stable enough to persist to some extent. This conclusion can be supported by data for a complex 6BA:3OSZ [8]. The amount of decomposition of 6BA:3OSZ is just 18 per cent when the temperature is 7°C higher than the clearing point [8].

As a comparison, the infrared spectrum of 8BA was also investigated on the heating sequence, and the result is shown in figure 8. The carbonyl band at 1682 cm^{-1} was observed at room temperature due to the formation of $(8\text{BA})_2$. When the temperature reaches 110°C , a new carbonyl band (1734 cm^{-1}) due to monomeric 8BA appears after the Cr–N transition, as the temperature increases, the carbonyl band becomes stronger and stronger. But for the complex 8BA:MBSB, no monomeric 8BA is observed at the Cr–S transition. The difference must be attributed to the hydrogen bond between the carboxylic acid and the pyridine fragment being stronger than the hydrogen bond between two substituted benzoic acid moieties. Actually, it is for this very reason that the intermolecular hydrogen bond between acid and pyridine groups can form in a stable way when mixing appropriate carboxylic acid and pyridine fragment in solution or by heating.

In summary, the five new hydrogen bonded chiral liquid crystal systems were prepared, and chiral nematic and chiral smectic C phases were observed as a result of the formation of intermolecular hydrogen bonds. The thermal stability of the hydrogen bond was studied by using

variable temperature FTIR spectroscopy, and the results show that the hydrogen bond between an acid and a pyridine group is relatively stable. These results imply that intermolecular hydrogen bonds represent a useful molecular design factor for the formation of new mesogens [2–4]

References

- [1] BRIENNE, M. J., GABRAD, J., LEHN, J. M., and STIBOR, I., 1989, *J. chem. Soc. chem. Commun.*, 1868.
- [2] YU, L. J., 1993, *Liq. Crystals*, **14**, 1303.
- [3] KUMAR, U., KATO, T., and FRÉCHET, J. M. J., 1992, *J. Am. chem. Soc.*, **114**, 6630.
- [4] GRANT, A., GRIFFIN, A. C., TAYLOR, P. L., YEATES, S. G., and SMYTH, M. G., 1994, *Proceedings of the International Conference on Liquid Crystal Polymers, Beijing, China*, 146.
- [5] KUMAR, U., FRÉCHET, J. M. J., KATO, T., UJILE, S., and ITMURA, K., 1992, *Angew. Chem. Int. Ed. Engl.*, **31**, 1531.
- [6] GHANEM, A., and NOEL, C., 1987, *Molec. Crystals liq. Crystals (b)*, **150**, 447.
- [7] NISHIYAMA, I., YOKOYAMA, A., and YOSHIZAWA, A., 1994, *J. mater. Chem.*, **4**, 983.
- [8] KATO, T., URYU, T., KANEUCHI, F., JIN, C., and FRÉCHET, J. M. J., 1993, *Liq. Crystals*, **14**, 1311.
- [9] JONES, B., 1935, *J. chem. Soc.*, 1874.
- [10] FU, S. C. J., BIRNBAUM, S. M., and GREENSTEIN, I. P., 1954, *J. Am. chem. Soc.*, **76**, 6054.
- [11] LEE, J. Y., PAINTER, P. C., and COLEMAN, M. M., 1988, *Macromolecules*, **21**, 346.
- [12] JOHNSON, S. L., and RUMON, K. A., 1965, *J. phys. Chem.*, **69**, 74.
- [13] ODINOKOV, S. E., and IOGENSEN, A. V., 1972, *Spectrochim. Acta A.*, **28**, 2343.
- [14] BENEDETTI, E., GALLESCHI, F., CHIELLINI, E., and GALLI, G., 1989, *J. Polym. Sci. B, Polym. Phys.*, **27**, 25.
- [15] WU, P. P., HSU, S. L., THOMAS, O., and BLUMSTEIN, A., 1986, *J. Polym. Sci. Polym. Ed.*, **24**, 827.