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Liquid Crystals

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Liquid crystalline phase transitions of the 2-(4′-alkoxybiphenyl-4-yl)-5-(4-methylphenyl)pyridines

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The mesomorphic phase transitions have been studied for a series of 2-(4′-alkoxybiphenyl-4-yl)-5-(4-methylphenyl)pyridines (4R-P*n*; the carbon number, *n*, of the alkoxy group is 1–10) by use of DSC and polarizing optical microscopy. The 4R-P*n* compounds showed only a nematic phase for $n=1$ and 2, but underwent characteristic polymesomorphic sequences when $n \geqslant 3$; $\mathrm{Cr} \rightleftarrows \mathrm{CrH} \rightleftarrows \mathrm{SmF} \rightleftarrows \mathrm{SmC} \rightleftarrows \mathrm{SmA} \rightleftarrows \mathrm{N} \rightleftarrows \mathrm{I}$ with $n=3$ and 4, and $\mathrm{Cr} \rightleftarrows \mathrm{CrH} \rightleftarrows \mathrm{SmF} \rightleftarrows \mathrm{SmA} \rightleftarrows \mathrm{N} \rightleftarrows \mathrm{I}$ with $n=5$–10. This mesomorphic phase transition behaviour was similar to that of the 2-(4-alkoxyphenyl)-5-(4-methylphenyl)pyridine (3R-P*n*) series reported previously and it is proposed that the 4R-P*n* and 3R-P*n* compounds have a minimum terminal alkoxy length (critical alkoxy length) for the generation of LC polymorphism.

1. Introduction

Recently, scientific and technical interest in polyphenylene derivatives containing the pyridine ring has increased, and also in *N*-heteroatomic compounds generally [1–13]. In a preceding work [13], a homologous series of 2-(4-alkoxyphenyl)-5-(4-methylphenyl)-pyridines (3R-P*n*, where *n* is the carbon number of the alkoxy group), whose chemical structure is shown in figure 1 (*b*), was investigated and the mesomorphic phase transition behaviour established as a function of the length of the terminal alkoxy group. The 3R-P*n* compounds showed only a nematic phase when $n \leqslant 3$, but gave the liquid crystalline (LC) polymorphism, $\mathrm{Cr} \leftarrow \mathrm{CrH} \rightleftarrows \mathrm{CrG} \rightleftarrows \mathrm{SmF} \rightleftarrows \mathrm{SmC} \rightleftarrows \mathrm{SmA} \rightleftarrows \mathrm{N} \rightleftarrows \mathrm{I}$, when $n \geqslant 4$. We noticed interestingly that the 3R-P*n* compounds generate the polymorphism suddenly when *n* is larger than 3; this result attracted us to study whether pyridine ring-containing polyphenylene compounds require a critical length of terminal group to give the polymorphism.

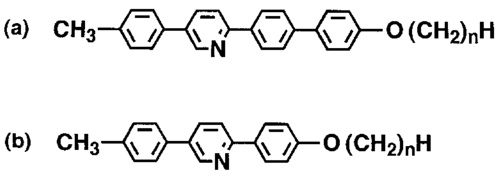

Figure 1. Chemical formulae of (*a*) the 2-(4′-akloxybiphenyl-4-yl)-5-(4-methylphenyl)pyridine (4R-P*n*, $n=1$–10) homologues, and (*b*) the 2-(4-alkoxyphenyl)-5-(4-methylphenyl)-pyridine (3R-P*n*, $n=1$–10) homologues.

The present work was aimed at studying the LC polymorphism of the 2-(4′-alkoxybiphenyl-4-yl)-5-(4-methylphenyl)pyridines (4R-P*n*), whose rigid core is more extended, by one benzene ring, than that of 3R-P*n*, shown in figure 1 (*a*), to ascertain the existence of the critical length of terminal alkoxy group for the generation of polymorphism.

2. Experimental

The 4R-P*n* ($n=1$–10) compounds were synthesized by almost the same procedure as that for the 3R-P*n* series described previously [13]: 4-(4-alkoxyphenyl)benzylamine (8·7 mol) and 2,2,-dichloro-1-(4-methylphenyl)-cyclopropanecarbaldehyde [13–15] (8·7 mmol) were dissolved in 1,3-dimethyl-2-imidazolinone (40 ml) with imidazole (20 mmol) and a small amount of hydroquinone. The solution was heated at 100°C for 30 min and further at 200°C for 24 h. The crude product obtained by evaporating the solvent was washed with 2M HCl, 2M NaOH and water, and column chromatographed ($\mathrm{SiO_2}$: $\mathrm{CHCl_3}$). The analytically pure 4R-P*n* crystals were obtained after several recrystallizations from

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ethanol: for example, for the $n=6$ compound, ^{1}H NMR (400 MHz, CDCl$_3$); δ 8·93 (m, 1H), 8·10 (d, 8·5 Hz, 2H), 7·95 (m, 1H), 7·82 (m, 1H), 7·69 (d, 8·5 Hz, 2H), 7·60 (d, 6·6 Hz, 2H), 7·56 (d, 6·3 Hz, 2H), 7·31 (d, 7·8 Hz, 2H), 7·04 (d, 8·8 Hz, 2H), 4·02 (t, 6·6 Hz, 2H), 2·43 (s, 3H), 1·82 (m, 2H), 1·25 ∼ 49 (m, 6H), 0·92 (t, 7·1 Hz, 3H). EI-MS (70 eV); m/z 337 (100), 421 (M$^+$, 65), 308 (7). FTIR (KBr) 1604, 1582, 1527, 1473, 1252, 811. Elemental analysis, observed (calculated): C 85·74 (85·47), H 7·45 (7·41), N 3·30 (3·32)%.

The ^{1}H NMR spectra were measured using CDCl$_3$ solutions with an internal standard of TMS by use of a JEOL JNM-A400 spectrometer. The thermal data were recorded on a differential scanning calorimeter (Seiko Instruments DSC 210) at a heating/cooling rate of 5 K min^{-1} over a temperature range from 300 K to above the clearing point. The textures of the liquid crystalline phases were observed with a polarizing microscope, Nikon Optiphot-pol XTP-11, equipped with a Mettler hot stage FP-82, at a heating/cooling rate of 5 K min^{-1} crossed polarizers were used. The IR spectra were measured using KBr disks and a Perkin Elmer FTIR 1600 spectrometer. Mass spectra were recorded by the EI method at 70 eV using a Shimazu QP 1000 mass spectrometer.

3. Results and discussion

The DSC thermograms are shown for the $n=1$ and 5 homologues of the 4R-Pn series in figure 2. The $n=1$ homologue shows an exothermic peak near 535 K in the cooling process and an endothermic peak near 537 K in the heating process. As is seen in the third heating to 650 K, the compound gradually decomposes above 600 K and does not show any further thermal peak upto 650 K. Polarizing microscope observations were made for the $n=1$ homologue; using crossed polarizers, a typical nematic schlieren texture, exhibiting disclination lines with $s=\pm 1$ and $s=\pm 1/2$ [16], was observed during cooling until 535 K, showing the existence of a nematic phase, but the clearing point was not seen up to 650 K in the DSC runs and by polarizing microscope observations. The $n=2$ homologue also showed only a nematic phase above 541 K, and it was, therefore, concluded that the $n=1$ and 2 compounds are purely nematogenic.

The longer alkoxy homologues with $n \geqslant 3$ showed polymesomorphic transitions. The typical DSC data are given for the $n=5$ homologue in figure 2. Now there are observed four exothermic peaks near 588, 548, 518 and 433 K on the cooling run and four endothermic peaks near 445, 519, 548 and 589 K on heating. By polarizing microscopy using crossed polarizers, we observed a schlieren texture with disclination lines with $s=\pm 1$ and $s=\pm 1/2$ above 588 K, and a fan texture between 588 and 548 K; these were assigned to nematic and smectic A phases, respectively. Moreover, we observed a schlieren mosaic texture between 548 and 518 K and a mosaic texture between 518 and 435 K, identified as SmF and CrH, respectively, by mixing tests with 2-(4-hexyloxyphenyl)-5-(4-methylphenyl)pyridine (3R-P6), as described later. An endothermic peak corresponding to the clearing point is observed at 654 K in the 3rd heating process, although gradual thermal decomposition occurs above 620 K. The longer alkoxy 4R-Pn homologues with $n \geqslant 3$ essentially showed a similar thermal behaviour to that for $n=5$. In the $n=3$ and 4 homologues, broken-fan and concomitant schlieren textures with disclination lines with $s=\pm 1$, reflecting the existence of a smectic C phase, were observed enantiotropically in a very narrow temperature range between the nematic and smectic A phases, but only in the polarizing microscopic observations.

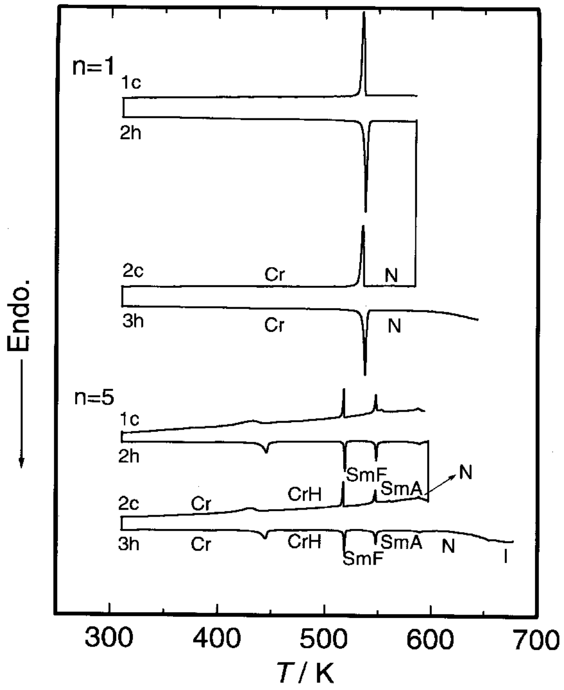

Figure 2. DSC thermograms for two 2-(4′-alkoxybiphenyl-4-yl)-5-(4-methylphenyl)pyridine (4R-Pn) homologues ($n=1$ and 5): mc = mth cooling, mh = mth heating.

We attempted a miscibility test of 4R-Pn with 2-(4-hexyloxyphenyl)-5-(4-methylphenyl)pyridines (3R-P6) to identify the types of mesophase. 3R-P6 has the polymorphic phase sequence Cr–(394 K–CrH)–398 K–CrG–403 K–SmF–427 K–SmC–441 K–SmA–447 K–N–491 K–I [13], where the CrG–CrH phase transition is monotropic. The results for the binary mixtures of 4R-P5 with 3R-P6 in figure 3 were obtained mainly by DSC measurements, but also by texture observations for the SmC–SmA and CrG–SmF phase transitions because of

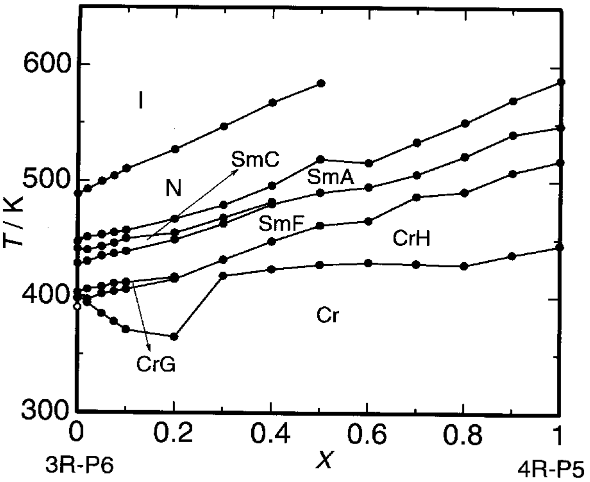

Figure 3. Miscibility diagram of 4R-P5 with 2-(4-hexyloxyphenyl)-5-(4-methylphenyl)pyridine (3R-P6); ○ = monotropic.

their very small enthalpy changes. The clearing points for the mixtures with 4R-P5 content ($x > 0{\cdot}5$) could not be determined due to gradual thermal decomposition above 600 K. The N, SmA and SmF phases were separately miscible over all the mixing ratios, but the SmC and CrG phases disappeared for the higher 4R-P5 concentrations. When x is smaller than 0·1, the phase transition behaviour is complicated; the CrH phase seems not to exist when $x < 0{\cdot}01$, and this result is considered to be reasonable, since the CrH phase in pure 3R-P6 is monotropic. The CrH phase of 4R-P5 in figure 3 was assigned based on the following two facts. First, the phase transition entropies of the enantiotropic CrH–CrG phase transitions for 4R-P5 with $x > 0{\cdot}01$ ($\Delta S = 11\ \mathrm{J\ K^{-1}\ mol^{-1}}$ for $x = 0{\cdot}075$) were fairly well consistent with that of the monotropic CrG–CrH phase transition in 3R-P6 ($\Delta S = 9{\cdot}4\ \mathrm{J\ K^{-1}\ mol^{-1}}$). Second, the textures observed using crossed polarizers were similar to each other (a mosaic texture). Consequently, we concluded that 4R-P5 has successive phase transitions of Cr$\rightleftarrows$CrH$\rightleftarrows$SmF$\rightleftarrows$SmA$\rightleftarrows$N$\rightleftarrows$I. The thermal parameters are listed in the table for the 4R-Pn homologues and the phase transition temperatures are plotted against the carbon number of the alkoxy group (n) in figure 4. The 4R-Pn series shows only the nematic phase when $n < 3$, but the polymorphism when $n \geqslant 3$. As n increases, the N–I phase transition temperature gradually decreases with an even–odd effect, and noticeably the polymorphism appears suddenly at $n = 3$.

In conclusion, we have synthesized a homologous series 4R-Pn ($n = 1$–10) and investigated the phase transition behaviour. The 4R-Pn compounds show only the nematic phase when $n < 3$, but the LC polymorphism when $n \geqslant 3$ is Cr$\rightleftarrows$CrH$\rightleftarrows$SmF$\rightleftarrows$SmC$\rightleftarrows$SmA$\rightleftarrows$N$\rightleftarrows$I for the $n = 3$ and 4 homologues, and Cr$\rightleftarrows$CrH$\rightleftarrows$SmF$\rightleftarrows$SmA$\rightleftarrows$N$\rightleftarrows$I for $n = 5$–10. As is reported in a preceding paper [13], the 3R-Pn series ($n = 1$–10)

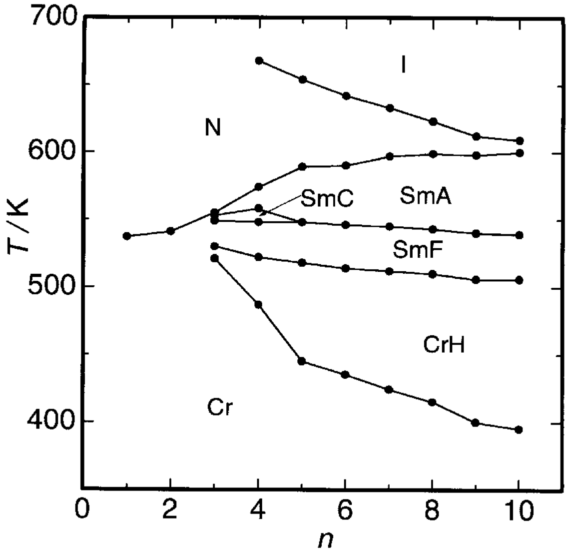

Figure 4. Phase transition temperatures versus carbon number of the alkoxy group (n) for the 4R-Pn homologues.

Table 1. Phase transition temperatures (T/K) and (in brackets) liquid crystalline phase transition enthalpies (ΔH/kJ mol^{-1}) of the 5-(4′-alkoxybiphenyl-4-yl)-2-(4-methylphenyl)pyridine (4R-Pn) ($\mathrm{CH_3C_6H_4C_5H_3NC_6H_4C_6H_4OC_{\mathit{n}}H_{2\mathit{n}+1}}$, $n = 1$–10).

n	Cr	•	CrH	•	SmF	•	SmC	•	SmA	•	N	•	I
1		—		—		—		—		537(23)		d^a	
2		—		—		—		—		541(20)		d^a	
3		522(2·8)		530(6·6)		549(6·4)		553(—)		555(0·4)		d^a	
4		487(7·1)		522(4·2)		548(4·5)		558(—)		574(0·8)		668(0·8)	
5		445(6·3)		518(4·0)		—		548(3·6)		589(1·4)		654(0·3)	
6		435(9·9)		514(4·1)		—		546(4·6)		590(1·5)		642(1·1)	
7		424(9·1)		512(4·0)		—		545(4·0)		597(1·2)		633(1·1)	
8		415(8·5)		510(4·0)		—		543(4·0)		599(1·6)		623(1·2)	
9		400(7·7)		506(3·9)		—		540(4·2)		598(2·0)		612(1·5)	
10		395(9·9)		506(3·7)		—		539(3·5)		600(2·0)		609(1·3)	

[a] Thermal decomposition.

show the LC polymorphism, Cr$\leftarrow$CrH$\rightleftarrows$CrG$\rightleftarrows$SmF$\rightleftarrows$SmA$\rightleftarrows$N$\rightleftarrows$I when $n \geqslant 4$ and only the nematic phase when $n < 4$. The polymorphic sequence in the 4R-P*n* series is similar to that in the 3R-P*n* series, but differs in the following points: (1) in series 4R-P*n*, the SmC phase exists only for $n = 3$ and 4, but appears for all the homologues in series 3R-P*n*; (2) the CrG phase exists in all the 3R-P*n* homologues, but does not in the 4R-P*n* series; (3) the CrH phase is monotropic for the 3R-P*n*, but enantiotropic for the 4R-P*n* series. Although these minor differences are seen in the LC polymorphism, both series fundamentally undergo almost the same polymorphism. However, we should emphasize that the LC polymorphism appears in the alkoxy homologues longer than $n = 3$ in series 3R-P*n* and $n = 4$ in 4R-P*n*; in other words, both homologous series have a critical, but different, alkoxy length for the generation of LC polymorphism.

The pyridine ring in the rigid polyphenylene core should give a dipole moment preferentially in a lateral direction to the molecular axis, so increasing intermolecular interactions, and this may be related to the generation of the polymorphism. By contrast for example, 4,4‴-dialkoxyquarterphenyls ($n = 1$–18) and dialkyl quarterphenyl-4, 4‴-dicarboxylates ($n = 2$–12) having the quarterphenyl moiety as the rigid core show only SmA or SmC phases and no polymorphism [17, 18].

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