

Induction of the cholesteric mesophase in hydrogen-bonded blends of polymers with a low molecular mass chiral dopant

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A family of new hydrogen bonded complexes based on comb-shaped LC copolymers containing alkyloxy-4-oxybenzoic acid mesogenic fragments and chiral dopant molecules, derivatives of pyridine-4-carboxylic acid has been prepared. At concentrations of chiral groups in the range 1–25 mol%, induction of the cholesteric phase is observed. The temperature dependences of the selective light reflection wavelength were studied, and the helix twisting power was calculated. Depending on the type of polymer nematic matrix, this value varies in the range 12.1 to 18.3 μm^{-1} . With respect to optical properties, the chiral nematic phase in the hydrogen-bonded complexes is comparable to that in classical cholesteric copolymers in which the chiral group is covalently bound to the polymer chain.

1. Introduction

In 1989, Kato and Frechet advanced a new concept for the construction of liquid crystalline compounds [1–3], which involves the processes of molecular recognition and self-organization. The authors used the idea of the construction of a mesogenic molecule via the development of hydrogen bonds between a pyridine-containing group (proton acceptor) and a carboxyl group (proton donor).

Then an alternative approach for the construction of mesogenic systems was successfully applied by Ujii *et al.* [4–6], Zentel *et al.* [7] and later on by Bazuin *et al.* [8, 9], Paleos *et al.* [10], and Talroze *et al.* [11, 12] in the preparation of LC comb-shaped polymers, where side mesogenic groups are formed by ionic interactions between oppositely charged main chains and fragments of the side groups. In the latter case, the mesogenic group may be formed either at the polymerization stage [13] or via a polymer analogous reaction [4–12].

Later, these methods for the preparation of the LC comb-shaped polymers were complemented by the introduction of complex-bound metal-containing fragments between main chain and side group [14].

This approach offers substantial advantages for the controlled tailoring of the supramolecular structure of LC polymers as shown by Lehn [15] and opens new ways for the preparation of functional LC polymers.

In connection with the foregoing special attention should be focused on photochromic and ferroelectric LC polymers, which are used as electro-optical and photo-optical media for optical data recording and storage, for the preparation of optical disks, etc. Application of the idea of ‘guest–host’ complexes formed by hydrogen-bonding between molecules of LC copolymer, containing, for example, vinylpyridinium units, and dye molecules with acidic groups allows one to prepare stable photochromic compounds without phase separation by varying the content of photochromic compound [16, 17]. The advantages of this approach are the following: (i) a simple procedure for the preparation of complexes by mixing of two components and (ii) the high degree of freedom of the photochromic group, which is non-covalently bound to the polymer chain, may increase the rate of data recording.

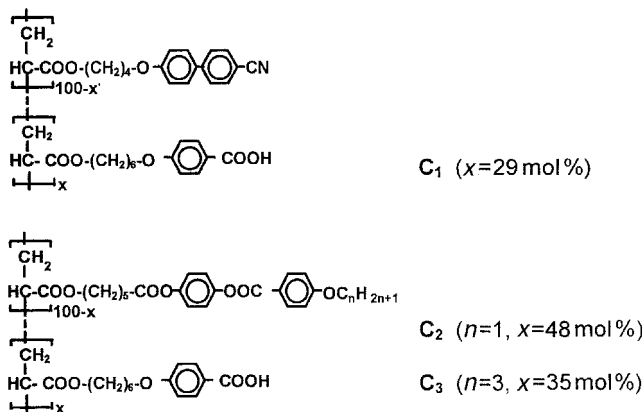
An interesting example of the synthesis of ferroelectric polymers is described in ref. [18], where the preparation of chiral SmC* phases with a spontaneous polarization involves stoichiometric hydrogen-bonded complexes of polysiloxanes with chiral derivatives of stilbazole. However, despite the obvious advantages of this approach for the preparation of functional polymer materials, recently published work continues on the development of polymer chiral nematic phases [19].

The objective of this work is to study the optical properties of the chiral nematic phases of new hydrogen-bonded complexes of LC polymers containing acidic groups with low molecular mass chiral additives,

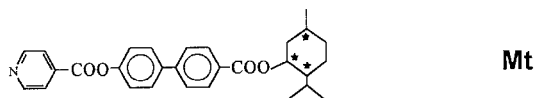
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derivatives of pyridine carboxylic acid. The formulae of the synthesized copolymers and low molecular mass dopant are presented below.

LC COPOLYMERS



CHIRAL DOPANT



The above compounds were used for a systematic examination of the effect of the polymer matrix on phase behaviour and optical properties of the hydrogen-bonded blends.

2. Experimental

All monomers 4-(4-cyanobiphenyl-4'-yloxy)butyl acrylate (M1), 4-(6-acryloyloxyhexanoyloxy)phenyl 4-methoxybenzoate (M2), 4-(6-acryloyloxyhexanoyloxy)phenyl 4-propoxybenzoate (M3), 4-(6-acryloyloxyhexyl-1-oxyl)-benzoic acid (A6) and 1-menthyl 4-(pyridine-4-carboxyloxy)biphenyl-4'-carboxylate (Mt) were synthesized according to the procedures described in refs [20–22, 24] (table 1).

Copolymers were obtained by radical copolymerization of monomers M1, M2, or M3 with A6 in absolute THF; AIBN was used an initiating agent. The as-synthesized copolymers were purified by repeated reprecipitation from THF solutions by hexane; copolymers are soluble in THF and in hot ethanol. The composition of the copolymers was determined by NMR spectroscopy.

The blends of copolymers with the pyridine-containing chiral additive were prepared by dissolution of their mechanically produced mixtures in various compositions in THF and drying of the solution in vacuum.

Phase transitions of the synthesized copolymers were studied by differential scanning calorimetry (DSC) using a scanning rate of 10 K min^{-1} . All experiments were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarization microscope. Selective light reflection of chiral polymers was studied using a Hitachi U-3400 UV-Vis-IR spectrometer equipped with a Mettler FP-80 hot stage. The $20 \mu\text{m}$ thick samples were sandwiched between the two flat glass plates. The thickness of the test samples was pre-set by Teflon spacers. Planar textures were obtained by shear deformation of the samples, which were heated to temperatures above the glass transition temperature. Prior to tests, samples were annealed for 20–40 min. X-ray diffraction analysis was carried out using a URS-55 instrument (Ni-filtered CuK_α radiation).

3. Results and discussion

As known, a traditional method for the preparation of chiral nematic polymer phases involves covalent binding of chiral molecules as side group fragments of comb-shaped polymers [23]. The binding may be accomplished by copolymerization of two monomers, one of which is a nematogenic monomer (the corresponding homopolymer forming a nematic phase), whereas the second monomer contains one or several asymmetric

Table 1. The transition temperatures of the monomers and chiral dopant.

Compound	Chemical structure	Phase behaviour/ $^{\circ}\text{C}$
M1		Cr 93 I
M2		Cr 82 I (N 53 I)
M3		Cr 66 I (N 55 I)
A6		Cr 85 SmA 96 N 103 I
Mt		Cr 115-116 I [α] _D ²² = -32.4° , [M] = -148°

carbon atoms which are responsible for the development of a twisted structure in the copolymer.

In this work, the chiral nematic phase was prepared by an alternative approach involving introduction of a non-covalently bonded low molecular mass chiral dopant to a nematic polymer matrix containing free carboxylic acid groups. Hence, the first stage of this work involved the preparation of LC copolymers (the matrix), which satisfy the following criteria. First, this copolymer should form a nematic phase; second, it should contain a high content of carboxylic acid groups (not less than 30 mol %), which are necessary for the formation of hydrogen bonds with the pyridinium fragment of the chiral additive. Hence, let us first consider the properties of the synthesized copolymers.

3.1. Phase behaviour of copolymers C_1 , C_2 , and C_3

Optical microscopic and X-ray studies showed that all the synthesized polymers give a nematic phase (table 2). On cooling from the isotropic melt, the copolymers form a marbled texture, which is a specific feature of the nematic phase and is preserved until room temperature. The corresponding X-ray patterns of the copolymers show only a diffuse halo at wide scattering angles ($D = 4.6\text{--}4.9\text{ \AA}$), and the DSC scans exhibit a single endothermic peak with a heat of fusion $\Delta H = 1.3\text{--}1.9\text{ J g}^{-1}$, which is associated with the transition from the nematic liquid crystal to the isotropic melt.

3.2. Phase behaviour of the blends

Let us consider now the phase state of the copolymers C_1 , C_2 , and C_3 with chiral additive Mt; figure 1 shows the phase diagrams of the corresponding blends. As can be seen, the development of the nematic phase is observed for the C_1 -Mt blend over the whole concentration range and for the C_2 -Mt and C_3 -Mt blends at a low content of chiral additive (up to 8.5 and 2.8 mol % of Mt, respectively). In the case of C_2 -Mt (11.0–21.0 mol % of Mt) and C_3 -Mt (5.6–16.1 mol % of Mt), the corresponding DSC curves show two poorly resolved peaks with a total heat of fusion of $\sim 3\text{ J g}^{-1}$. This fact suggests the development of not only a nematic, but also a low temperature smectic phase.

The corresponding X-ray patterns of the above copolymer blends show two reflections. In addition to the

Table 2. The transition temperatures and molecular mass characteristics of the LC copolymers.

Copolymer	M_n	M_w	M_w/M_n	Phase transitions/ $^{\circ}\text{C}$
C_1	3300	5000	1.5	g 30 N 88 I
C_2	3800	5700	1.5	g 15 N 90 I
C_3	3700	5000	1.3	g 12 N 94 I

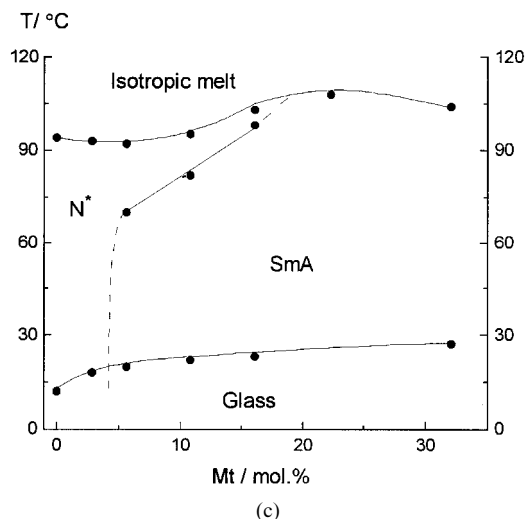
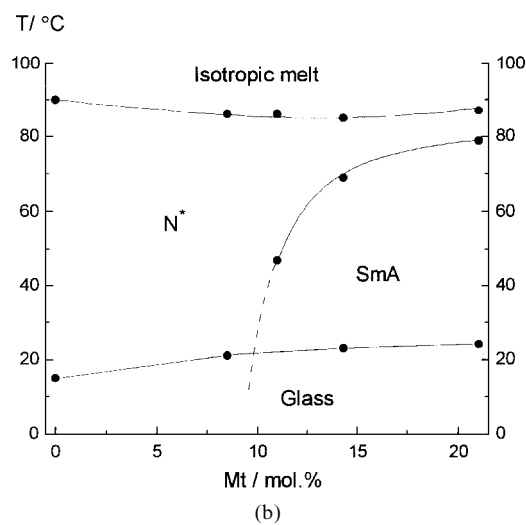
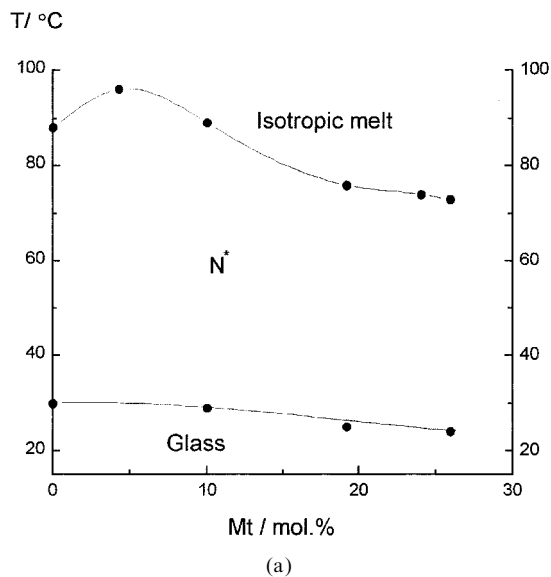


Figure 1. Phase diagrams for chiral mixtures (a) C_1 -Mt, (b) C_2 -Mt, (c) C_3 -Mt.

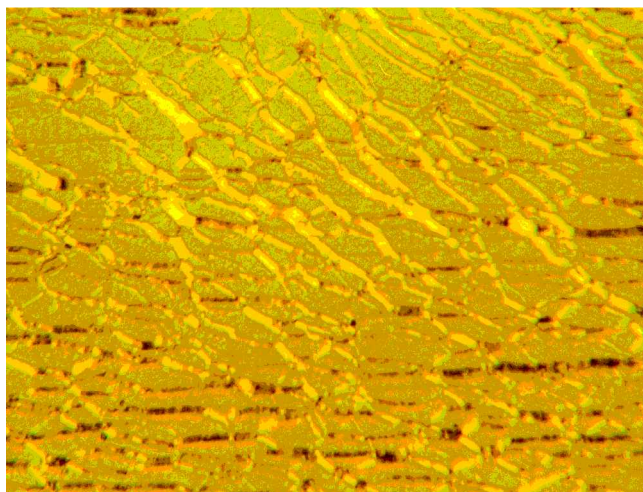


Figure 2. Optical polarizing photomicrograph of blend C₃-Mt-6 (N*, 75°C).

diffuse reflection corresponding to a distance $D = 4.8 \text{ \AA}$, two other reflections correspond to $d_1 = 29.8 \text{ \AA}$ and $d_2 = 16.3 \text{ \AA}$ (for the C₃-Mt-16.1[†] blend). The presence of small angle reflections in the X-ray patterns of the blends and the fan-shaped texture observed by optical microscopy suggest the occurrence of a SmA phase. As the concentration of chiral additive in the C₃-Mt blends (22.3–32.1 mol % of Mt) is increased, the nematic phase disappears, and development of the SmA phase is observed over the whole mesophase temperature interval. This conclusion is confirmed on cooling from the isotropic melt which leads to the development of bâtonnets, which are typical of the SmA phase.

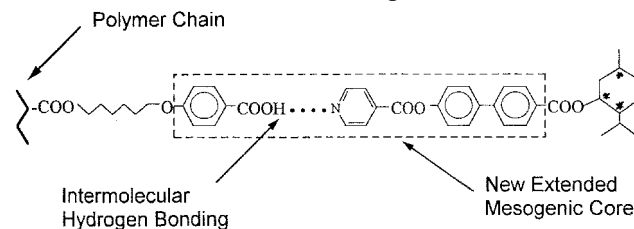
Note that, as evidenced by polarizing optical microscopy studies, the above nematic phases are helical. On cooling from the isotropic melt, one may observe in the blends the development of a planar texture with oily streaks, which is typical of chiral nematic phases (figure 2).

Hence, examination of the phase states of three sets of nematic copolymers shows that upon mixing with a non-liquid crystalline chiral additive Mt, thermodynamically stable blends without any phase separation are produced.

Usually, the introduction of non-mesogenic chiral additives dissolved in a nematic mesophase leads to depression of phase transition temperatures. However, as was mentioned in [1–3], the situation dramatically changes when additional intermolecular interactions between nematic matrix and chiral additive are possible. As schematic representation of hydrogen bond formation

[†]The number corresponds to the concentration of Mt additive, in mol %.

between a monomer fragment of alkyloxybenzoic acid A6 and the chiral additive Mt is presented below.

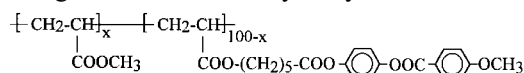


The energy of the hydrogen bond between carboxylic acids and pyridines is characterized by high values of $\Delta H \sim 45 \text{ kJ mol}^{-1}$ [25], which should associate a rigid fixation of the two components in the blend. Hence, the formation of a new mesogenic fragment with a rod-like shape should increase the clearing temperature of the blends. However, as the fractional content of chiral molecules is increased, the clearing temperatures of the different blends do not increase in a regular, steady manner, and in the case of the C₁-Mt blends, they decrease after an initial rise. At the same time, the T_g for the C₁-Mt blends stay about the same, while those of the C₂-Mt and C₃-Mt blends slightly increase. The anticipated improvement in thermal stability of the blends with increasing content of Mt is likely to be compensated however by the destabilizing steric effect of the chiral additive due to the bulky menthyl group that it contains.

3.3. Optical properties of the blends

Figure 3 shows the transmission spectra of samples with a planar orientation. As follows from figure 3, on average the selective light reflection band half width is changed in the range from 50 to 100 nm. The same values of half width are typical of menthyl-containing copolymers described in [20, 26]. The blended compositions formed are thermodynamically stable systems, and prolonged storage of the samples (several weeks) at 50°C does not lead to crystallization of the low molecular mass chiral additive Mt.

To prove the marked role of hydrogen bonds in the formation of blends without phase separation, we prepared blends of Mt with the following LC copolymer containing 39 mol % of methyl acrylate:



Similarly to C₂, this copolymer produces a nematic phase with a clearing temperature of 92°C. When the blend containing 12 mol % of Mt is annealed, phase separation and development of crystals of Mt is observed within 30–40 min. Hence, the absence of additional non-covalent interactions leads to phase separation of the

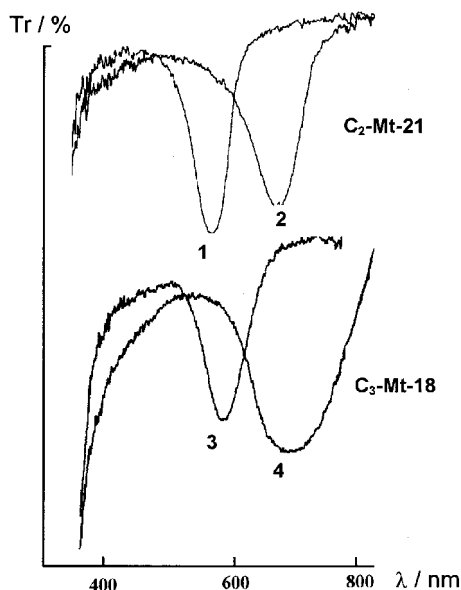


Figure 3. Transmittance spectra for blends: C₂-Mt containing 21 mol% of chiral groups at 83°C (1) and 80°C (2); C₃-Mt containing 18 mol% of chiral groups at 70°C (3) and 60°C (4).

composition and, as a result, this composition could not be used as a stable optically active material.

Figure 4 shows the temperature dependences of the maximum selective light reflection wavelengths. On cooling, the selective reflection peak shifts to a longer wavelength region, and this shift is associated with enhanced fluctuations of smectic order with decreasing temperature and with the approach to any nematic–smectic phase transition. Earlier, this behaviour was observed generally for cholesterol-containing copolymers [27] and for copolymers with three-ring menthyl fragments [20, 26].

The effect of temperature on helix pitch is affected by underlying smectic phases and is most pronounced for the C₃-Mt blends. For the blends containing 11 mol% of chiral component, as the temperature is decreased by 10°C, the maximum selective light reflection wavelength increases by a factor of 3, figure 4(c).

Helix twisting power is an important parameter which characterizes the ability of a chiral additive to induce helical supermolecular structure [28, 29]. To calculate the helix twisting power, A , the reciprocal selective light reflection wavelength (at reduced temperature $T = 0.98T_c$) was plotted against molar fraction of chiral component X . Figure 5 shows the typical dependences of λ_{\max}^{-1} on X . Helix twisting power was calculated by approximating experimental data through the following function [20, 26]:

$$\lambda_{\max}^{-1} = AX/(1 + BX)$$

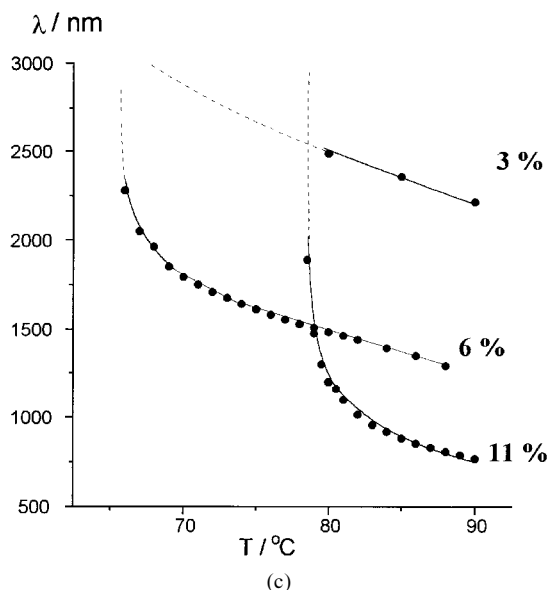
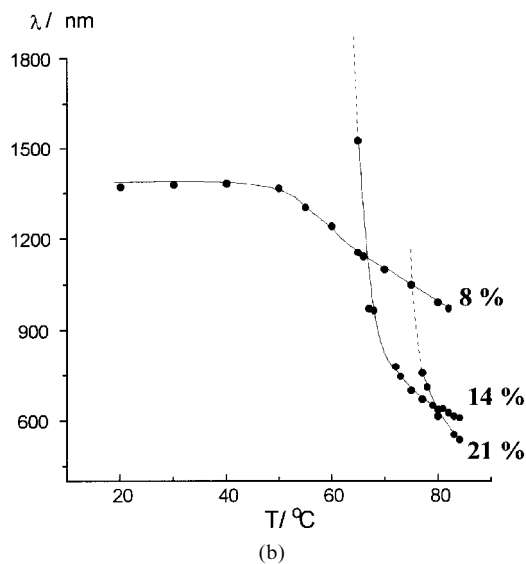
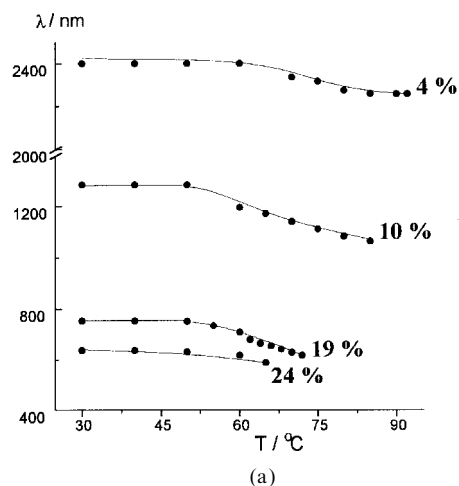


Figure 4. Temperature dependence of the maximum of selective light reflection for blends C₁-Mt (a), C₂-Mt (b), C₃-Mt (c).

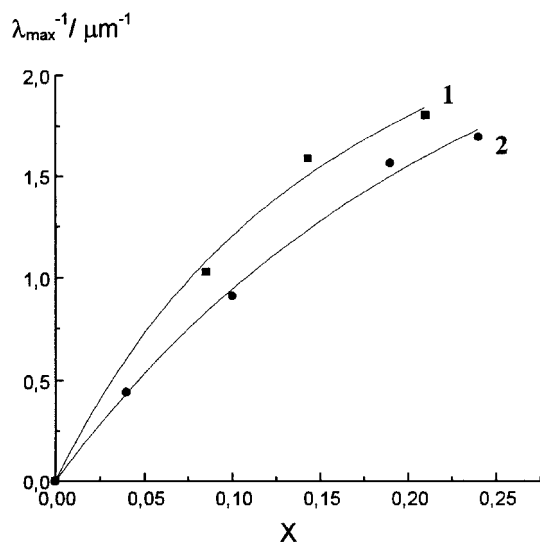


Figure 5. Dependence of λ_{\max}^{-1} on the molar fraction of chiral units X : C₂-Mt (1) and C₁-Mt (2).

Table 3. Helical twisting power A and parameter B for blends.

Blend	$A/\mu\text{m}^{-1}$	B
C ₁ -Mt	12.1 ± 1.1	2.8 ± 0.7
C ₂ -Mt	18.3 ± 1.1	5.5 ± 1.0
C ₃ -Mt	17.3 ± 0.8	4.1 ± 0.7

where B is a parameter which characterizes the deviation from linear character. Parameter B may be associated with a decrease in order parameter of the N* mesophase or with the presence of fragments with smectic order [20, 26].

Table 3 summarizes the values of A and B for all the blended compositions. Analysis of these data allows one to see the effect of the copolymer matrix on the helix twisting power of the chiral additive. For example, the maximum values of helix twisting power were obtained for the blends of Mt with copolymer C₂; somewhat lower values were obtained for the C₃-Mt blend and the cyanobiphenyl matrix is characterized by the minimum values of the twisting power of Mt. This fact is likely to be related to the presence of marked dipole-dipole interactions of the cyanobiphenyl mesogenic units, which increases the twist constant K_{22} . In turn, the high values of K_{22} prevent effective twisting of the cyanobiphenyl matrix.

4. Conclusions

The above experimental evidence allows one to draw the following conclusions:

- (1) A family of new hydrogen-bonded complexes based on comb-shaped LC copolymers containing alkyloxy-4-oxybenzoic acid mesogenic

fragments and chiral molecules, derivatives of pyridine-4-carboxylic acid, has been prepared.

- (2) At concentrations of the chiral groups from 1 to 25 mol %, development of a cholesteric phase is observed. The temperature dependences of the selective light reflection wavelengths were studied, and the helix twisting power was calculated. Depending on the type of polymer nematic matrix, this value is in the range $12.1\text{--}18.3\mu\text{m}^{-1}$.
- (3) With respect to optical properties, the chiral nematic phase in the hydrogen bonded complexes is comparable to that of classical cholesteric copolymers in which the chiral group is covalently bonded to the polymer chain.

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