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SHORT COMMUNICATION

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Chiral nematic phase in hydrogen-bonded blends of a side-chain smectic polymer with low molar mass dopants

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Abstract The possibility of chiral nematic mesophase induction in blends of a smectic A side-chain liquid-crystalline copolymer with low molar mass dopants was studied. The chirality of the initial copolymer was determined by the cholesterol optical active groups; however, in the individual state it was not able to form any chiral liquid-crystalline phases. We have shown that the induction of the chiral nematic phase becomes possible in blends of such a copolymer with low molar mass dopants that are stabilized by hydrogen bonding. Phase behavior and optical properties of the blends were studied with X-ray scattering, differential scanning calorimetry and polarizing microscopy. Owing to hydrogen bonding the blends are stable over a wide range of contents and temperatures. The nature of the end group in the dopant molecules is shown to have an important influence on the chiral mesophase induction concentration and the clearing temperatures of the blends. Temperature and concentration dependences of the selective reflection maximum wavelength in the chiral nematic phase were also studied.

Keywords Chiral nematic mesophase · Smectic liquid-crystalline copolymer · Hydrogen bonds · Polymer blends · Phase

Introduction

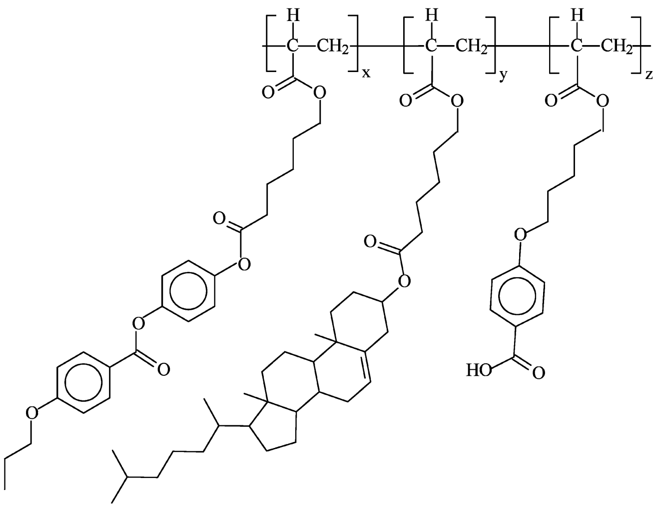
Since their discovery liquid-crystalline (LC) polymers that form chiral mesophases have drawn the attention of researchers owing to their unique optical properties combined with favorable physical and mechanical characteristics of polymeric materials [1, 2, 3, 4]. At the current time there are two basic approaches to obtain such macromolecular compounds. The first approach is based on copolymerization of nematogenic and optically active monomers [5]. The second one is the introduction of a low molar mass chiral dopant into the preliminary synthesized nematic polymeric matrix [6]. An interesting modification of the latter approach assumes the use of dopants that are capable of hydrogen-bond formation with functional fragments of nematic LC copolymers [7]. It allows one to expand the temperature and concentration intervals of the compatibility of the blends and is a good solution to the problem of phase separation [8, 9, 10].

The main limitation of the approaches discussed is due to the fact that nematic LC polymers are less widespread then smectic systems [11]. However there are some publications that consider the induction of less ordered phases (nematic or cholesteric) in low molar mass smectic mixtures [12, 13, 14] and some smectic LC polymers [15, 16, 17, 18]. For example, Bobrovsky et al. [18] investigated a number of side-chain LC copolymers of SmC and amorphous menthone chiral monomers. It was discovered that for certain copolymer compositions a high-temperature chiral nematic phase is formed. This phenomenon was explained by the "degeneration" of the layer structure because of bulky menthone groups of the second comonomer [18].

In our recent works the analogous effect of the specific influence of low molar mass dopants on the phase behavior and the structure of LC polymeric blends was found. It was shown that introduction of pyridine-containing compounds into smectic copolymers in some cases results in disordering of the system and leads to a nematic mesophase [19, 20, 21]. This phenomenon was associated with the formation of stable hydrogen-bonded complexes between dopants and functional carboxylic groups of the polymer matrix. The as-formed complexes play the role of extended mesogenic groups that do not fit well into the initial layer packing of side groups and in that way disrupt smectic ordering. On the basis of this observation we have assumed that if optically active units are initially incorporated into such a smectic copolymer, the formation of the chiral nematic phase may become possible under a similar forced destruction of the layer structure.

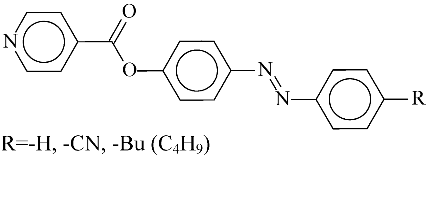
To check the suggested approach of the chiral nematic phase induction we studied hydrogen-bonded blends of ternary smectic copolymer P (Structure 1)with low molar mass pyridine containing dopants, Py*R* (Structure 2). Despite the fact that P contains 29 mol% of chiral side groups it is not able to form chiral LC phases (N*, SmA*, etc.) in the temperature interval of the mesophase owing to the strong lateral interactions of the mesogenic groups. It is necessary to note that such substances are widely spread between side-chain LC polymers [1, 2, 3, 4, 11]. However their applicability to the creation of chiral blends has not yet been reported in the literature.

The Ternary Polymer (Px=39,y=29,z=32mol%):



Structure 1

The Pyridine Containing Dopants (PyR):



R=-H, -CN, -Bu (C_4H_9)

Structure 2

So, the main goal of our work was to check the possibility to induce a chiral nematic phase in LC copolymer P by the disruption of smectic ordering in hydrogen-bonded blends with low molar mass dopants Py*R*. We also studied how the chemical structure of the tail fragment *R* influences the phase behavior and optical properties of the blends.

Experimental

The monomers and dopants PyH (Cr 145 I), PyCN (Cr 160 N 192 I), PyBu (Cr 124 N 130 I) were prepared by ordinary synthetic procedures. Copolymer P (Glass 34 SmA 120 I) was synthesized by free-radical copolymerization of the monomers in absolute tetrahydrofuran (THF); 2,2′-azobis(isobutyronitrile) was used as the initiating agent. The as-synthesized copolymer was purified by repeated reprecipitation from THF solution by hexane.

The Fourier transform IR spectra of the copolymers were recorded at 22 °C using a BIORAD FTS6000 spectrometer at a resolution of 4 cm^{-1}. Selective light refection of chiral polymers was studied using a Hitachi U-3400 UV–vis–IR spectrometer equipped with a Mettler FP-80 hot stage. The 20-μm-thick samples were sandwiched between the two flat glass plates. The thickness of the test samples was preset 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 the tests, the samples were annealed for at least 20–40 min.

The blends of copolymer P with dopants Py*R* were prepared by dissolution of the components in absolute THF and slow-drying in a vacuum. The formation of hydrogen bonds between functional carboxylic groups of the polymeric matrix and pyridine fragments of the dopant molecules was confirmed by IR spectroscopy data as described later.

Discussion of results

To confirm the possibility of chiral nematic phase induction on the basis of smectic LC copolymers we used ternary copolymer P. The choice of its chemical composition was caused by the following requirements. First, it should contain mesogenic fragments that are responsible for the realization of LC ordering. Second, the copolymer should include optically active centers (like a cholesterol derivative) and finally, the third component is responsible for the formation of stable hydrogen-bonded complexes with dopant molecules. To satisfy the last requirement we chose carboxylic functional groups of *n*-alkyloxybenzoic acid that are capable of forming hydrogen bonds with pyridine fragments of low molar mass dopants Py*R*.

Hydrogen bonding in functionalized LC copolymers P and blends was investigated by IR spectroscopy. The characteristic IR spectrum of LC copolymer P in the region 1,550–1,800 cm^{-1} is shown in Fig. 1. Several overlapping bands can be seen in the "carbonyl region". The monomer unit of alkyloxybenzoic acid exhibits two characteristic bands at 1,684 and 1,744 cm^{-1} assigned to stretching vibrations of the carbonyl, $\nu_{[C=O]}$, in the carboxylic group. The 1,744-cm^{-1} bend is assigned to the "free" (monomer) form and the one at 1,684 cm^{-1} to the dimer form of the acid [22]; the bands at 1,728 and 1,735 cm^{-1} are assigned to stretching vibrations, $\nu_{[C=O]}$, of the ester groups. The incorporation of Py*R* groups in the polymer matrix leads to the disappearance of the band at 1,744 cm^{-1} and to an increase in the intensity of the band at 1,684 cm^{-1}, which proves hydrogen-bond formation between the initial compounds. The structure of the hydrogen-bonded complexes is shown in Structure 3.

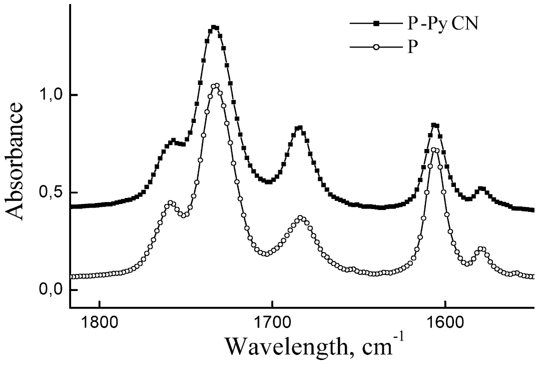
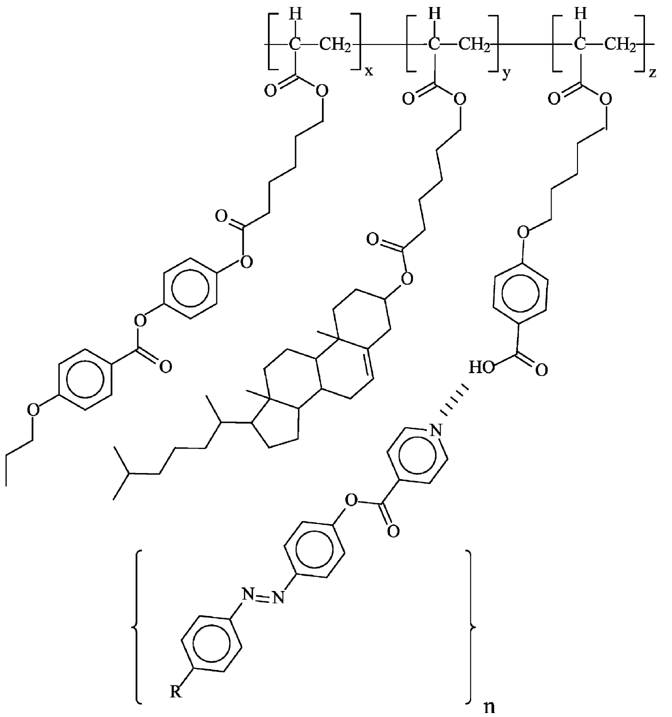


Fig. 1 The fragments of Fourier transform IR spectra for ternary liquid-crystalline copolymer P and its blend with low molar mass dopant PyCN



Structure 3

The phase diagrams of the P–Py*R* blends obtained are shown in Fig. 2. The initial copolymer P is characterized by a smectic type of LC ordering. It is proved by the presence of a peak (d = 30.4 Å) in its small-angle X-ray scattering patterns and typical fan-shape texture. The incorporation of dopant molecules in polymer P results in the disruption of the layer organization of the lateral mesogenic groups and the formation of a chiral nematic mesophase at high temperatures close to the clearing point. This was confirmed both by the observation of the characteristic texture with polarizing

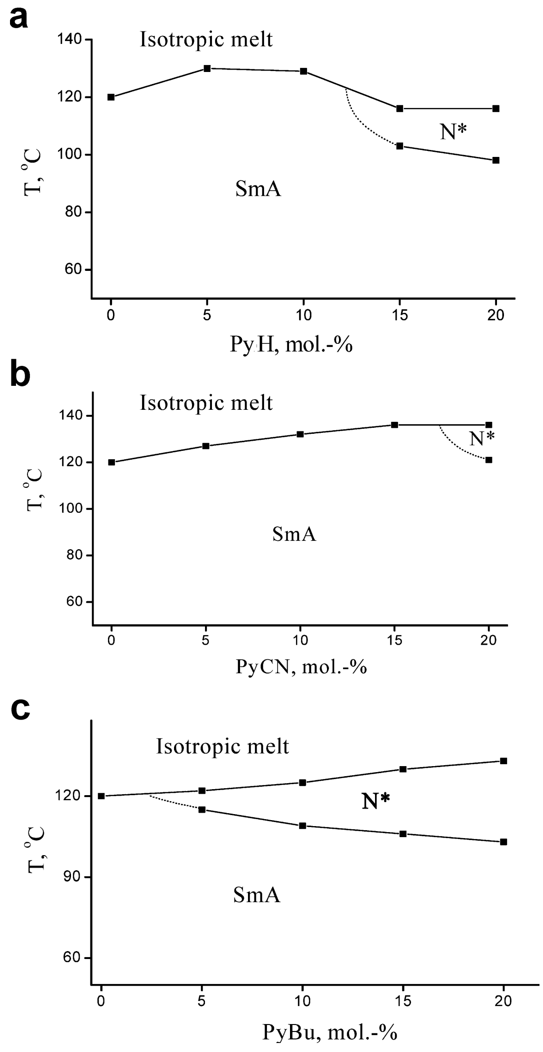


Fig. 2 Phase diagrams of the polymer blends: **a** P–PyH, **b** P–PyCN, **c** P–PyBu

optical microscopy and by the selective light reflection, discussed later.

From the comparison of the phase diagrams it is clearly seen that the lowest concentration of chiral nematic phase induction (about 5 mol%) is observed for PyBu (Fig. 2c). For the other two dopants the same effect is achieved only in the interval 10–20 mol% (Fig. 2a, b). It is also necessary to note that no phase separation was observed for the blends at all temperature–concentration intervals studied. This is additional proof of the usefulness of hydrogen-bond formation for the compatibilization of polymer blends.

The dopant molecules Py*R* differ from each other only in the structure of their tail fragment *R*. So, this factor, apparently, controls the phase behavior of the blends investigated. The bulky aliphatic tail in case of PyBu results in the lowest concentration being required for the disruption of the smectic layer structure. At the same time for PyH and PyCN the steric factor appears to be weakened and the chiral nematic phase is induced appreciably later.

Despite the disruption of the layer organization and the induction of the nematic mesophase it is necessary to mention that with the increase of the PyBu or PyCN concentration a smooth increase of the clearing temperatures of the blends is observed (Fig. 2a, b). This phenomenon can be explained by the formation of extended mesogenic groups (linear hydrogen-bonded complexes) and is in good agreement with literature data [8, 9, 10]. However P–PyH blends do not submit to this regularity. After an initial increase (up to a concentration of less than 10 mol%) a drop in the clearing temperature is observed. Further studies are required to understand the nature of such behavior.

Thus, the analysis of the phase diagrams shows that the incorporation of low molar mass dopants into a smectic polymer results in the disruption of the layer ordering and the induction of a chiral nematic mesophase. There is no doubt that the optical properties of the substances obtained and their comparison with systems on the basis of nematic copolymers represents essential scientific interest.

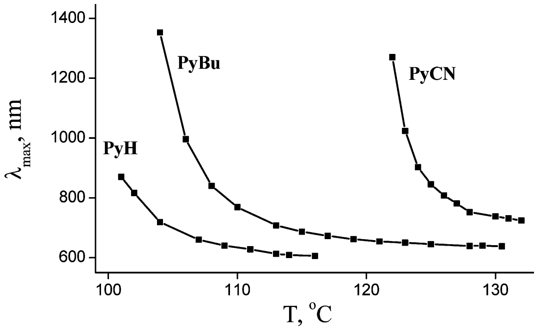


Fig. 3 Temperature dependence of the selective reflection wavelength maxima

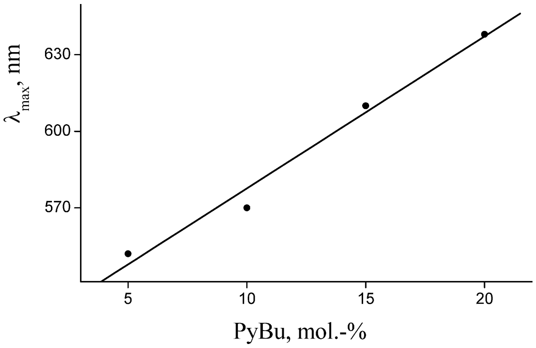


Fig. 4 Concentration dependence of the selective reflection wavelength maximum for P–PyBu at the derived temperature $\tau = 0.98T_{cl}$

The temperature dependences of the selective reflection maximum wavelength for P–Py*R* blends are presented in Fig. 3. Independently of the chemical structure of the dopant all the blends investigated submit to the well-known regularity consisting in the growth of λ_{max} at the downturn of the temperature [1]. It is the consequence of the existence of a low-temperature smectic mesophase (Fig. 2).

However in the example of the P–PyBu blend one can see that the dependence of λ_{max} on the concentration of the dopant molecules is characterized by the important difference from the polymer systems on the basis of hydrogen-bonded nematic polymeric matrixes and chiral low molar mass compounds [7]. With the growth of the dopant content in the polymer matrix the untwisting of the cholesteric helix is observed (Fig. 4).

To understand the nature of the given phenomenon it is necessary to consider the following circumstances. As already mentioned, in the case of the chiral nematic phase induced by traditional methods optically active fragments or dopants are incorporated into the nematic LC polymeric matrix. In contrast, in the case of P–Py*R* blends low molar mass additives Py*R* do not possess optical activity. Hence, the incorporation of dopant molecules in polymer P reduces the effective concentration of the chiral units.[1] This explains the observed untwisting of the cholesteric helix (Fig. 4).

Conclusions

In the present work a new original approach to obtain chiral nematic LC polymer blends was described. It differs essentially from traditional methods of helicoi-

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[1] The effective concentration is the concentration related to the total mass of the polymer matrix and incorporated dopant

dal supramolecular structure induction, because it assumes the use of smectic polymers that contain optically active units, but are not capable of forming chiral mesophases in the individual state. Nevertheless the induction of the chiral phase is shown to be possible in blends of such copolymers with optically inactive low molar mass dopants owing to the disruption of smectic layers. The temperature dependence of the selective reflection wavelength maximum of the blends investigated submits to the well-known regularities. The untwisting of the cholesteric helix with the increase in the concentration of the dopants can be explained by the reduction of the effective concentration of the chiral fragments.

Thus, we have developed a new approach to obtain a chiral nematic mesophase in polymer blends. It allows us to expand essentially the area of functional polymeric matrixes owing to the exploitation of widespread smectic LC polymers.

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