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Side group functionalized liquid crystalline polymers and blends VII. Phase behaviour and elastic constants K_1 and K_3 for hydrogen bonded blends of a functionalized LC copolymer with a low molecular mass non-mesogenic dopant

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New hydrogen bonded blends of LC copolymers containing functional carboxyl groups with a low molecular mass pyridine-containing dopant were obtained and the orientational, optical and elastic properties of the blends were measured using the Fréedericksz method of threshold transitions in a magnetic field. The averaged order parameter S of the hydrogen bonded blends is found to be lower than that of the initial functionalized LC polymers. Furthermore, a considerable increase in the K_3/K_1 ratio is observed caused by an increment in the average 'effective' length of the hydrogen bonded mesogenic group. For the first time it is proven that LC blends with hydrogen bonded mesogenic groups obey the same main relationship of orientational elastic deformations as common nematic LC polymers with covalent bonding of mesogenic side groups.

1. Introduction

Self-organization and molecular recognition have recently drawn much attention in the field of liquid crystalline (LC) polymers [1–16]. This is based on new possibilities for controlling the properties of LCs and designing novel types of supramolecular structures as a result of hydrogen bonded [1, 11, 12, 14–16], electrostatic (Coulomb) [4–9, 13] dipole–dipole [1, 4] or donor–acceptor [1, 10] interactions.

In this connection the important role of hydrogen bonds should be pointed out. Because of the relatively high stability of hydrogen bonds, they have been very extensively studied and applied in the chemistry of low molecular mass and polymeric liquid crystals. The use of non-covalent interactions provides great advantages for the preparation of functional LC polymer materials. The incorporation of functional (e.g. photochromic [1] or chiral [1, 14]) molecules of low molecular mass compounds (so called, dopants) into various parts of LC polymers by hydrogen bonding leads to the creation of new polymeric compounds. An essential advantage of hydrogen bonded blends is the convenience of preparation and the absence of microphase separation [14]. Moreover, the physical and technological performance of blends advantageously combine the properties and characteristics of both blended components (polymer and dopant).

Although there are many publications in this field, many specific properties of these hydrogen bonded polymer blends have not yet been established. There have been investigations of the orientational behaviour of blends in a magnetic field, and of the temperature dependences of the order parameter [12, 16], as well as of the orientational elastic deformations [15, 16]. These investigations are significant because the exploitation of most polymer materials in technology is based on the application of oriented, highly anisotropic films in optics, optoelectronics, holography and optical data storage. Before considering the study of the orientational behaviour of hydrogen bonded blends of functionalized LC polymers and dopants in a magnetic field, complete information should be available about the properties of the initial polymer matrix which is capable of forming hydrogen bonds.

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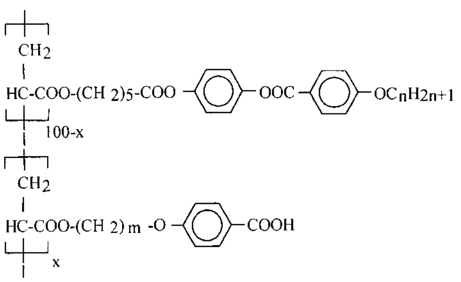
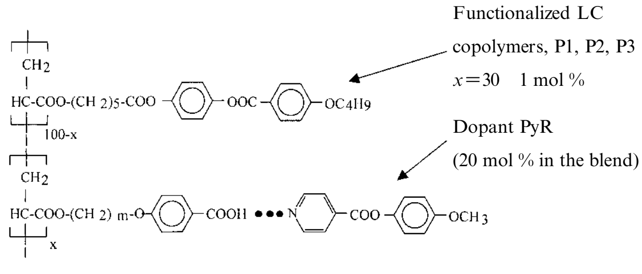
In our previous publications [14–16], the so-called functionalized LC polymers with the following chemical structure have been investigated (P1–P6):



P1 ($m=3$, $n=4$);
P2 ($m=6$, $n=4$);
P3 ($m=9$, $n=4$);
P4 ($m=3$, $n=3$);
P5 ($m=6$, $n=3$);
P6 ($m=9$, $n=3$);
$x=30$ 1 mol %

The functionalized LC polymers contain mesogenic groups (alkoxyphenylbenzoate) and acid groups which are derivatives of *n*-alkoxybenzoic acid with spacers of different length *m*. The presence of acid groups enables the polymer to form hydrogen bonds. The character of these bonds depends on the length of the spacer separating the acid group from the main chain. It was shown that in copolymers with a short flexible fragment ($m = 3$), mostly intramolecular hydrogen bonds were present (between the acid group and the ester fragment of the mesogenic group). In contrast, in the LC polymer with a longer spacer ($m = 6$ and 9), intermolecular hydrogen bonds were formed. The character of the hydrogen bonds affects the values of the order parameter *S*, the birefringence Δn and the orientational elastic constants K_1 and K_3. In the latter case, one may even speak about the hydrogen bonded LC 'quasi-network'.

The aim of the present work was to study the orientational behaviour in a magnetic field of hydrogen bonded blends of polymers P1–P3 with a low molecular mass dopant PyR.



Functionalized LC copolymers, P1, P2, P3
$x=30$ 1 mol %
Dopant PyR
(20 mol % in the blend)

Blends: P1-PyR; P2-PyR; P3-PyR

The presence of the pyridine ring in the molecule PyR allows the formation of hydrogen bonds of the donor–acceptor type (pyridine is the proton acceptor and the *n*-alkoxybenzoic acid is the proton donor). The pyridine dopant was chosen because the molecule is optically anisotropic and this is convenient for studying the blends by optical methods. Moreover, since the dopant is crystalline, it is a good model for studying miscibility by applying such standard methods as DSC and XRD.

The principal method used in this investigation was the Fréedericksz method of threshold transitions in a magnetic field. This enables information to be obtained about the value and temperature dependence of the birefringence Δn, the orientational order parameter *S*, and the splay K_1 and bend K_3 elastic constants. The study of orientational elastic deformations permits us to establish differences and similarities between the physical characteristics of the nematic phases of classical polymers (with covalent attachment of the mesogenic side groups) and of this same phase formed by hydrogen bonding between the LC polymer and dopant molecules.

2. Experimental

All the materials, 4-(6-acryloyloxycaproyloxy)phenyl 4-butyloxybenzoate (M1), 4-(6-acryloyloxypropyloxy)-benzoic acid (A3), 4-(6-acryloyloxyhexyloxy)benzoic acid (A6), 4-(6-acryloyloxynonyloxy)benzoic acid (A9) and the dopant, 4-methoxyphenyl pyridine-4-carboxylate (PyR) were synthesized according to procedures described earlier [16].

Copolymers (P1–P3) were obtained by free radical copolymerization of M1, M2, A3, A6 and A9 monomers in absolute THF; AIBN was used as initiating agent. The as-synthesized copolymers were purified by repeated precipitation from THF solutions by hexane. The composition of the copolymer was determined by ^{1}H NMR spectroscopy. The blends of copolymers with the PyR dopant (20 mol %) were prepared by dissolution of the components in THF and vacuum drying.

Phase transitions in the LC copolymers were studied by differential scanning calorimetry (DSC) at a scanning rate of 10 K min^{-1} and by polarizing optical microscopy. All experiments were performed using a Mettler FP90 thermal analyser and a Zeiss polarizing microscope. X-ray diffraction (XRD) analysis was carried out using a URS-55 instrument (Ni-filtered CuK$_\alpha$ radiation). Infrared spectra were recorded on a Biorad FTS 6000 Fourier transform infrared (FTIR) spectrometer at a spectral resolution of 4 cm^{-1} and an uncertainty $< 5\%$ in absorbance. For the absorbance measurements, the sample was contained between KBr windows. A standard GRAMS program was used for the separation of overlapping bands. Relative molecular masses (M_w and M_n) of the polymers were determined by gel permeation chromatography (GPC) using a GPC-2 Waters instrument equipped with an LC-100 column oven and a Data Modul-370 data station (see the table). Measurements were made by using a UV detector, THF as solvent (1 ml min^{-1}, 25°C), a set of PL columns of 100, 500 and 1000 Å, and a calibration plot constructed with polystyrene standards.

Orientational elastic deformations were studied by the Fréedericksz method of threshold transitions in a

Table. The transition temperatures and molecular mass characteristics of the functionalized LC polymers and the blends.

Sample	M_w	M_w/M_n	Phase transition temperature/°C
P1	7200	1.54	N 109 I
P2	8600	1.60	SmA 93 N 110 I
P3	8400	1.44	SmA 94 N 111 I
P1-PyR			SmA 65 N 103 I
P2-PyR			SmA 68 N 107 I
P3-PyR			SmA 92 N 106 I
P4[a]	5800	1.35	N 97 I
P5[a]	5100	1.31	N 94 I
P6[a]	6300	1.27	SmF 44 SmA 73 N 100 I

[a] Data from ref. [16].

magnetic field [17]. Application of this method to polymer nematics has been described in detail previously [18–20]. The liquid crystal under study is placed between a spherical and a plane surface of quartz glass. It was possible to obtain entirely homeotropic alignment for the LC blends (the director is perpendicular to the support plane). To achieve this, the surfaces of lenses and glasses were successively etched in sulphuric acid and washed with distilled water. The LC sample was observed using a polarizing microscope and a parallel light beam normal to the layer plane. The temperature T of the sample was controlled to within 0.5°C. Measurements were carried out in magnetic fields with strengths up to 26 000 Oe.

On exposure to the magnetic field applied normal to the director, orientational elastic deformations appear in the nematic phase. They are of the threshold type: a minimum critical thickness z_c of the LC film exists in which deformation in a magnetic field with a strength **H** is possible. According to the Fréedericksz law [17], the product $z_c\mathbf{H}$ is constant and determines the ratio of the elastic constant K_3 to the diamagnetic anisotropy $\Delta\chi$ for a unit volume of nematic:

$$z_c\mathbf{H} = \pi(K_3/\Delta\chi)^{1/2} \tag{1}$$

In the plane–concave nematic films deformed in the magnetic field (where the layer thickness $z > z_c$), one can observe a system of concentric interference rings. For a given thickness z, the birefringence $\Delta n(z) = n_e(z) - n_o$ may be easily determined using the following equation:

$$\Delta n(z) = m\lambda/z \tag{2}$$

where m is the interference ring number and $\lambda = 546$ nm is the light wavelength. The $\Delta n(z)$ value depends on the layer thickness. The decrease in birefringence in thin layers reflects the incomplete reorientation of the director in such films. According to the Saupe theory, this dependence may be used to determine the value of the ratio of the elastic constants K_3/K_1 [20]. On the other hand, the limiting value of the birefringence $\Delta n(z)$ attained in the region of large thicknesses $z \gg z_c$ gives the birefringence $\Delta n = n_e - n_o$ of the completely oriented nematic at a given temperature.

As mentioned, it was possible to obtain only homeotropic orientation for the LC blends studied, and in summary, investigation of the orientational deformations in this geometry has made it possible to obtain the values and temperature dependences of the birefringence, the ratio of the bend elastic constant K_3 to the specific diamagnetic anisotropy $K_3/\Delta\chi$ and the ratio K_3/K_1.

3. Results and discussion

3.1. *Phase behaviour of functionalized LC polymers and blends*

Functionalized LC copolymers P1–P3 with M_w = 7200–8600 and a polydispersity of 1.44–1.60 (GPC, polystyrene standards) were used to prepare the blends. The phase states of the LC copolymers and the blends were investigated by polarizing microscopy, DSC, and XRD. The nematic phase forms a characteristic marbled texture. The SmA phase forms a fan-shaped texture. The XRD patterns of the SmA phase after orientation in the magnetic field exhibit small and wide angle reflections split in mutually perpendicular directions. The DSC curves (figure 1) show a single endothermic peak with a heat of melting ΔH = 1.3–1.9 J g^{-1}.

As can be seen from the table, formation of the hydrogen bond (see § 3.2) between the acid group A3 of the functionalized nematic LC polymer P1 and the dopant molecule PyR leads to changes in the phase behaviour of nematic polymer P1. The P1-PyR blend forms a SmA phase. For blends P2-PyR and P3-PyR, only slight decreases (2–6°C) in clearing temperature and in the temperatures of the transition SmA↔N are observed. Prolonged annealing of the blends in the LC phase and in the isotropic melt (at 130°C) does not lead to phase separation or to changes in the transition temperatures of the blends. The DSC curves show only transitions corresponding to the clearing points. The individual melting peak of crystalline PyR dopant at 89–90°C was not detected on the DSC curves. None of

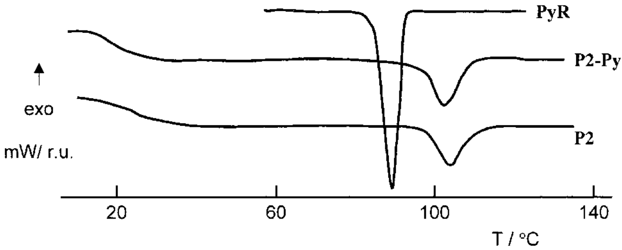


Figure 1. DSC curves of the functionalized LC polymer P2, the blend P2-PyR, and the dopant PyR.

the numerous reflections characteristic of the crystalline PyR structure was present in the XRD patterns of the blends. Consequently, blends formed as a result of hydrogen bonding represent individual compounds.

This conclusion is in good agreement with the results of investigations by Kato and Frechet [1]. They have shown that hydrogen bond formation between the acid group and the pyridine fragment by the donor–acceptor mechanism leads to new extended mesogenic fragments exhibiting mesomorphic properties. The formation of these mesogenic-like groups is accompanied by an increase in the clearing temperatures of the blend and the appearance of more ordered phases than the initial components used for its preparation.

Figure 2(*c*) shows the new extended mesogenic core constructed through hydrogen bonding between the A6 units of functionalized LC polymer P2 and the dopant PyR. It should be noted that the effect of the formation of the new hydrogen bonded group is most pronounced for the blend P1-PyR (functional monomer A3 has the shortest spacer $m = 3$). An induction of SmA phase is observed for this blend. For blends P2-PyR and P3-PyR, a slight decrease in the clearing temperature is observed. For the polymers with the spacer length $m = 6$ and 9 in the functional monomers, the effective length of the new hydrogen bonded group slightly exceeds that of the phenylbenzoate mesogenic fragment M1. This probably leads to a more defective mixed packing of the side groups. The expected improvement in thermal stability of the blends owing to formation of the new mesogenic group is probably compensated however by destabilizing steric effects [14–16].

3.2. *IR spectroscopic study of the hydrogen bonding in the functionalized LC copolymers and blends*

Figure 3 shows the IR spectra of the dopant PyR, LC polymer P1 and blend P1-PyR. It can be clearly seen that the range 1550–1850 cm^{-1} contains several overlapping

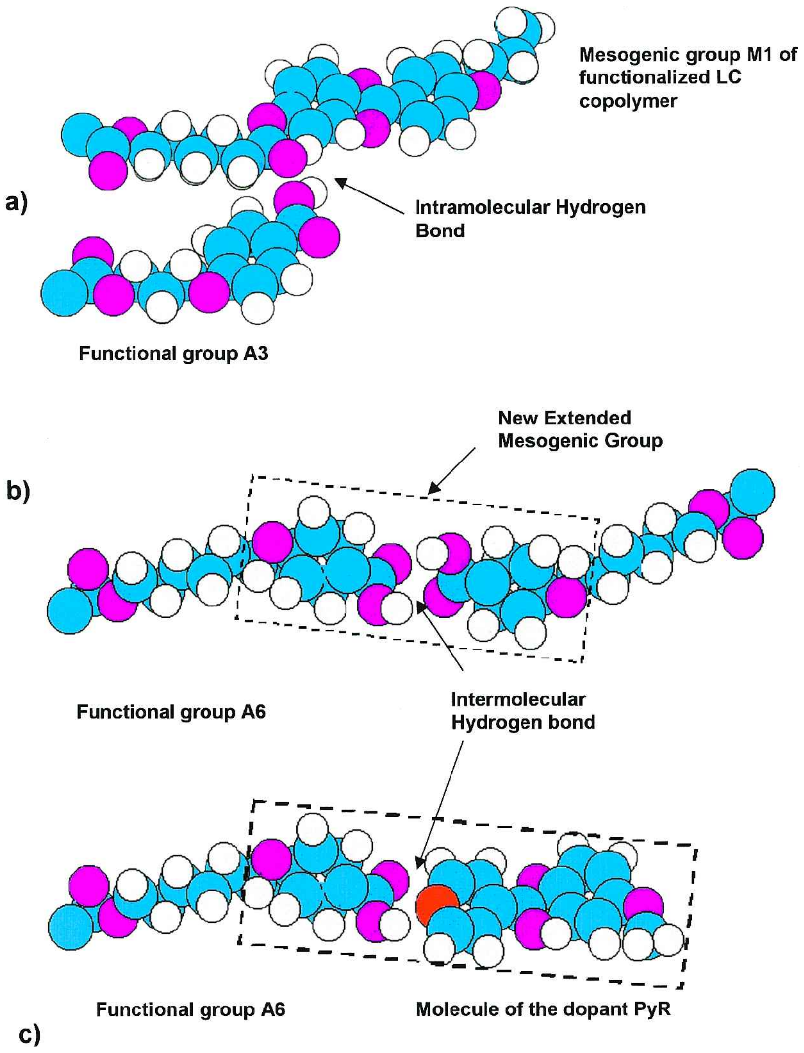


Figure 2. Different variants of hydrogen bonding in functionalized LC polymers and blends. For simplicity, the polymer main chain is not shown.

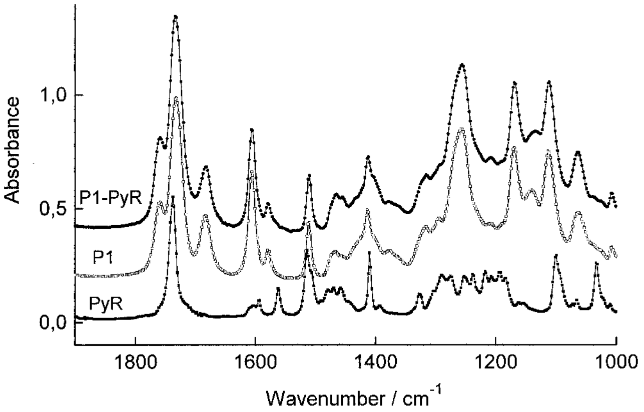


Figure 3. IR spectra for the dopant PyR, functionalized LC polymer P1 and blend P1-PyR.

bands assigned to the stretching mode [$\nu_{C=O}$] of the carboxyl groups. We assign the band at 1685 cm^{-1} to COOH groups bound by a hydrogen bond and the band at 1761 cm^{-1} to free COOH groups [1, 16].

Figure 4 shows the temperature dependences of the parameter $\beta = D([\nu_{C=O}]\text{free})/D([\nu_{C=O}]\text{bonded})$ corresponding to the ratio of the optical densities D of the stretching vibrations, [$\nu_{C=O}$], of free and bonded carboxyl groups for P1 and the blend P1-PyR. The temperature dependences β have a characteristic shape reflecting hydrogen bond breaking with increasing temperature. The dependences $\beta(T)$ for all functionalized LC polymers and blends that have been investigated have this same character. The $\beta(T)$ curve exhibits two characteristic portions with different slopes, corresponding to the liquid crystalline and the isotropic phases.

Before analysing the state of hydrogen bonding in the blends, the main relationship for the hydrogen bonding in the initial functionalized LC polymers P1–P3 should be considered [16]. The values of the parameter β reflecting the relative band intensity of the free acid groups at 40°C are given below.

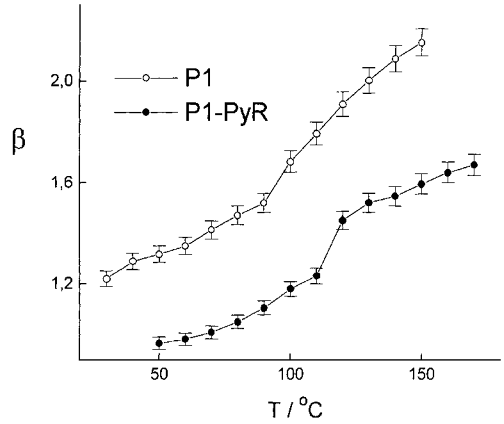


Figure 4. Temperature dependence of the parameter $\beta = D([\nu_{C=O}]\text{free})/D([\nu_{C=O}]\text{bonded})$ for the functionalized LC polymer P1 and the blend P1-PyR.

Sample:	P1	P2	P3	P1-PyR	P2-PyR	P3-PyR
β:	1.28	1.89	1.62	0.95	1.44	1.25

It is clear that in polymers P2 and P3 the increase in spacer length m in the A6 and A9 functional monomer units leads to an increasing probability of the formation of intermolecular hydrogen bonds: $\beta(\text{P2}) > \beta(\text{P3})$†, see figure 2 (*b*). At the same time, in polymer P1, favourable steric conditions are fulfilled for the formation of intramolecular hydrogen bonds (between the A3 acid group and the carbonyl group of the ester group binding the spacer to the aromatic ring of the mesogenic group M1), see figure 2 (*a*). This is reflected in a smaller fraction of free acid groups: $\beta(\text{P1}) < \beta(\text{P3}) < \beta(\text{P2})$, and in the specific character of the dependence of the elastic constant ratio K_3/K_1 on spacer length [16].

A similar relationship is observed for the polymer blends: $\beta(\text{P1-PyR}) < \beta(\text{P3-PyR}) < \beta(\text{P2-PyR})$. The same character of the change in β and the decrease in this parameter in the blends indicate that the formation of new hydrogen bonds between the acid fragment and the PyR dopant is due not only to the redistribution of existing hydrogen bonds, but also to the formation of new bonds. In fact, if new hydrogen bonds were formed only at the expense of the old bond distribution, the increase in intensity of bound carboxyl groups would not be observed. It might be supposed that new hydrogen bonds with the dopant molecule are possible even in those portions of the macromolecule in which hydrogen bond formation in the initial copolymer did not take place for steric reasons.

3.3. *Birefringence and modulus of the orientational elasticity of the LC blends*

During the investigation of the orientational elastic deformations in the hydrogen bonded blends under consideration and in processing the results, one had to take into account the fact that the blends contain a limited amount of PyR dopant (20 mol %). Correspondingly, the orientational elastic effect caused by the formation of a longer group is partially masked by the rest of the polymer matrix. This masking, without doubt, would make it difficult to establish the contribution of the new hydrogen bonded fragment to the orientational and elastic properties of the mesophase.

The birefringence value Δn can serve as a direct measure of the degree of intermolecular orientational order S of the mesophase. In fact, the birefringence is a unique function of the order parameter [20]. When

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†Here and in the ensuing text, the LC copolymer number is given in parentheses.

the values of Δn are not very high ($\Delta n < 0.2$), these dependences may be described by an approximate equation [21]

$$\Delta n = (2\pi/3n)(n^2 + 2)N_A(\Delta\alpha/M_o)\rho S \qquad (3)$$

where n is the mean refractive index and ρ is the density of the nematic, M_o is the molecular mass and $\Delta\alpha$ is the polarizability anisotropy of the nematic molecules. For the LC blends investigated, the use of even this approximate relation is difficult. Really, the number of hydrogen bonded mesogenic groups depends strongly on temperature (see, for example, figure 4). Hence, the average value of the polarizability anisotropy $\Delta\alpha$ may change with temperature. The character of this temperature dependence is unknown, and strictly speaking it is not clear what magnitudes must be chosen as the $\Delta\alpha$ and M_o values for the blends. Therefore, in this case it is not reasonable to attempt to estimate the order parameter using the birefringence data.

However, neglecting the weak temperature dependence of the density and the average refractive index of liquid crystals, it may be assumed that $\Delta n \sim S$. In other words, the temperature dependence of the birefringence in the first approximation reflects the change in the parameter S with T.

In figure 5, the values of the birefringence Δn of the LC blends are plotted against the relative temperature $\tau = T/T_{IN}$. Here T and T_{IN} are the absolute values of the temperatures of the sample and of the phase transition from the isotropic melt to the nematic phase. Just as for copolymers P1–P6, the value of Δn depends on spacer length in the functional component. The same tendency in the birefringence change is retained [16]. In the temperature range investigated, Δn is largest for the copolymer with the shortest spacer ($m = 3$) and smallest for $m = 6$.

The Δn value for the blends P1-PyR–P3-PyR is determined mainly by the polarizability anisotropy of the phenylene and pyridine rings. Hence, the change in the birefringence in the series of LC blends reflects the dependence of the average orientational order of these rings on variation in the spacer length. Since phenylene and pyridine groups are the principal structural elements of the anisotropic mesogenic cores of these LC blends, it may be assumed that on the average these cores are more ordered in the blend P1-PyR ($m = 3$) and less ordered in the blend P2-PyR ($m = 6$).

As shown in figure 2, several types of mesogenic groups are present in LC blends. Three of them are contained in the P1–P6 copolymers [16, 20]. They are (i) the mesogenic phenylbenzoate groups M1 proper of the LC copolymers, (ii) the mesogenic groups formed by predominantly intermolecular hydrogen bonds between functional groups A6 and A9, and (iii) the structures arising from intramolecular hydrogen bonds between the functional group A3 and an ester group in the mesogenic cores M1; new hydrogen bonded mesogenic cores (iv) are also formed in the blends as a result of interaction between the functional groups A3–A9 of the copolymers and the low molecular mass dopant PyR. Note (v) that in the P1–P6 copolymers and the blends, the formation of intramolecular hydrogen bonds between the monomers A3, A6, and A9 is also possible. However, the probability of this interaction is slight because of the low concentration of the functional groups in the LC copolymers.

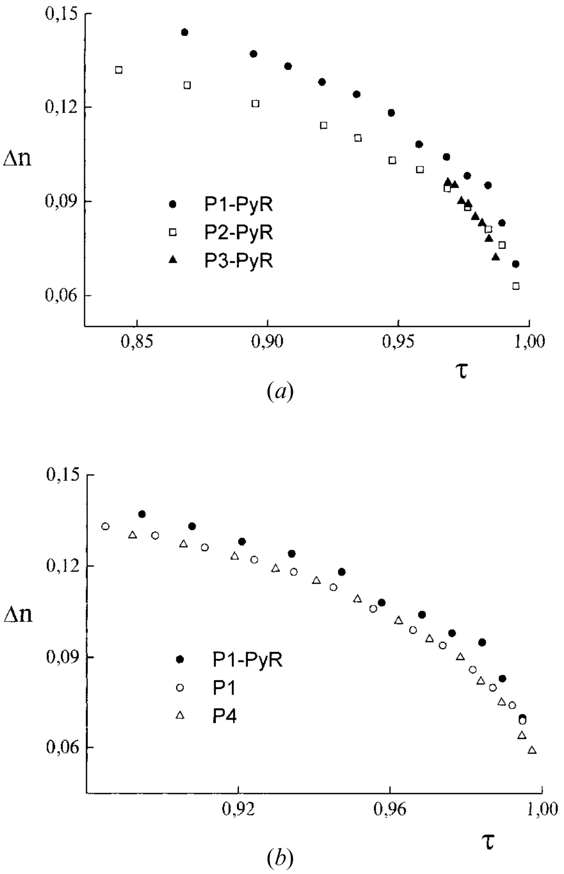
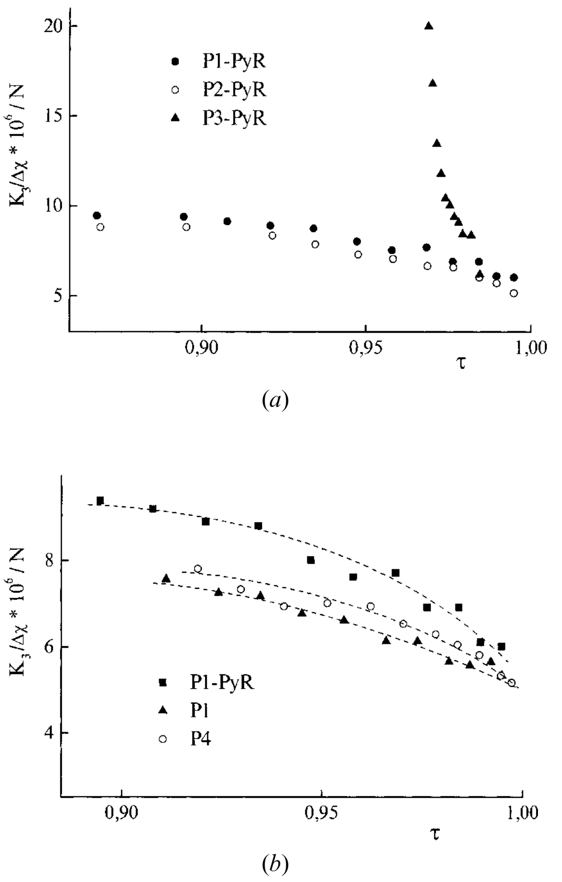


Figure 5. The birefringence Δn vs. the relative temperature τ for (a) the blends P1-PyR, P2-PyR, and P3-PyR, and (b) blend P1-PyR and copolymers P1 and P4.

The orientational order of the above-described types of mesogenic group may be different. Consequently, their relative contribution to the birefringence Δn will also differ. In particular, when PyR is added to the copolymer, one might expect a considerable (up to 25%) increase in the Δn values because of the very high anisotropic polarizability of the pyridine rings. However, this is not observed experimentally as shown by the example of the temperature dependences of the birefringence for P1-PyR and the corresponding polymers P1 and P4, see figure 5(*b*). At all relative temperatures τ the values of Δn for the blends are greater than those for LC polymers. However, this difference never exceeds 5%, i.e. it is within experimental error. A similar situation has been observed for other LC blends investigated.

These experimental facts agree with the results of the investigations of the order parameter S for the blend P2-PyR [22]. These data were obtained by ^{2}H NMR spectroscopy using selectively deuterium-marked mesogenic rings in the molecules of copolymer P2 and the dopant PyR. It was shown that the order parameter S of the new hydrogen bonded groups is considerably lower than that of the mesogenic groups in the functionalized LC copolymer. Consequently, the dopant contribution to the birefringence will be relatively small and the Δn value remains virtually unchanged on passing from the LC copolymers to their blends.

Figure 6 shows the temperature dependences of the $K_3/\Delta\chi$ ratio for selected functionalized LC copolymers and blends. For P1-PyR and P2-PyR, the curves have the usual shape for a nematic phase. For the blend P3-PyR, a drastic increase in $K_3/\Delta\chi$ is observed over almost the entire range of the nematic phase. This behaviour of the bend elastic constant K_3 is due to the formation of short range smectic order in the nematic phase. A critical increase in K_3 at the interface between nematic and SmA phases has been observed previously for low molecular mass [23] and polymeric [24, 25] nematics. In the following discussion, temperature ranges in which smectic order fluctuations exist will not be considered.



(*a*)

(*b*)

Figure 6. Dependences of the $K_3/\Delta\chi$ ratio on relative temperature τ for (*a*) the blends P1-PyR, P2-PyR and P3-PyR, and (*b*) blend P1-PyR, and copolymers P1 and P4. The dashed lines are guides for the eye.

The $K_3/\Delta\chi$ ratio for the blends differs only slightly from that for the corresponding LC copolymers. Figure 6(*b*) shows the dependences of $K_3/\Delta\chi$ on relative temperature τ for the blend P1-PyR and the copolymers P1 and P4. On passing from the LC polymers to the blend, the $K_3/\Delta\chi$ ratio increases by less than 20%. For the blend P2-PyR, this change is less than 10%.

However, these data do not enable us to determine the way in which the constant K_3 changes on passing from LC polymer to blend. For this purpose, the value and temperature dependence of the specific diamagnetic anisotropy $\Delta\chi$ of the nematic should be known. This can be evaluated precisely for the functionalized LC copolymers by using the conclusions in [26] where it was shown that the molar diamagnetic anisotropy $\Delta\chi_\mu$ of a nematic is determined by the number of phenylene rings in the mesogenic group. The temperature dependence of $\Delta\chi$ in the first approximation coincides with the dependence on the order parameter S. Data for the $\Delta\chi_\mu$ value for the molecules PyR or for pyridine rings are not available in the literature. Therefore, $\Delta\chi$ cannot be evaluated for the blends investigated and the bend elastic constant K_3 for these blends cannot be estimated.

An important feature of the nematic phase is the ratio of the elastic constants K_3/K_1. In particular, K_3/K_1 is very sensitive to the size and shape of the nematic molecule [26] and in the case of LC polymers to the mesogenic group size [19, 27, 28]. Systematic investigations of the elastic properties of polymer nematics carried out previously show that when the length of the spacer linking the rigid mesogenic groups increases, the K_3/K_1 ratio remains virtually unchanged [19, 25, 27]. However, increase in the mesogenic group length of the LC polymer is accompanied by an increase in the K_3/K_1 ratio [27, 28]. The K_3/K_1 ratios for high molecular mass nematics with mesogenic groups of similar size and shape virtually coincide [19, 27, 29].

The values of K_3/K_1 for the blends investigated are shown in figure 7, together with data for the corresponding LC copolymers. Results for the blend P3-PyR and the copolymers P3 and P6 are not reported since these nematic phases involve SmA order fluctuations over almost the entire temperature ranges of the nematic phases.

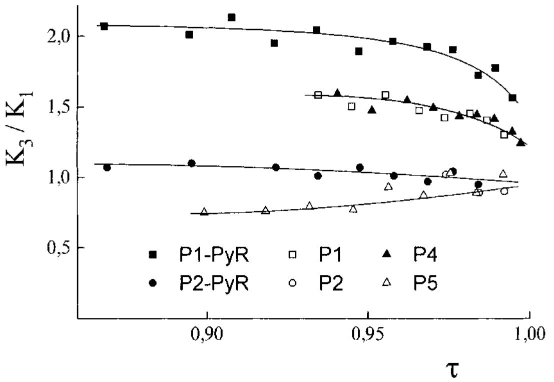


Figure 7. Dependences of the K_3/K_1 ratio on relative temperature τ for the blends P1-PyR, P2-PyR and copolymers P1, P2, P4, P5. The lines are guides for the eye.

For both LC blends, the K_3/K_1 ratio markedly (up to 50%) exceeds those for the functionalized LC copolymers. This experimental fact can be explained by the formation of new hydrogen bonded mesogenic cores as a result of interactions between the functional groups of the LC polymer and the molecules of low molecular mass dopant. As shown in figure 2 (*c*), the length of these cores exceeds by one third that of the mesogenic groups M1 of the LC polymers and those formed by intermolecular hydrogen bonding between the functional components of the copolymers. It is close to that of mesogenic groups formed by intramolecular hydrogen bonds, figure 2 (*a*). As a result, the average effective length of the mesogenic groups increases, and this leads to an increase in the K_3/K_1 ratio for these blends. At the same time, the new mesogenic group obeys the same relationships as those for classical nematic LC polymers with covalent bonding in the mesogenic side groups.

4. Conclusions

New hydrogen bonded blends of functionalized LC copolymers containing acid groups (proton donor) with 4-methoxyphenyl pyridine-4-carboxylate (proton acceptor) were obtained. It was shown by IR spectroscopy that the formation of new mesogenic groups takes place due to both the redistribution of existing hydrogen bonds and the formation of new bonds with the dopant molecules. The formation of a new longer mesogenic group leads to induction of the SmA phase.

The orientation of polymer blends in a magnetic field was studied. The slight difference in the birefringence for the initial functionalized LC polymers and blends indicates that the order parameter S of the blends decreases, which confirms previous conclusions [22].

Finally, it was shown that for the nematic phase of the blends the main relationships for orientational elastic deformations typical for LC polymers are retained. The formation of hydrogen bonds with dopant molecules leads to an increase in the K_3/K_1 ratio. The observed quantitative difference in the behaviour of the functionalized LC polymers and blends is due mainly to the formation of new extended mesogenic groups by hydrogen bonding between molecules of the low molecular mass dopant and the functional groups of the LC copolymers.

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