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New Chiral Nematic Ionomers Containing Metal Ions

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ABSTRACT: The series of new chiral nematic ionomers containing 0.7–9.0 mol % ions of alkali metals Na and transition metals Co(II) were synthesized by the exchange reaction between chiral nematic N* functionalized liquid crystalline (LC) copolymers bearing the phenylbenzoate mesogenic fragment, optically active moiety (derivatives of cholesterol), and carboxylic groups with acetate of cobalt and sodium. For ionomers containing 0.7–9 mol % sodium ions the melting point is independent of temperature. At the same time, the incorporation of cobalt ions in the polymer matrix leads to decreasing of clearing temperature and destruction of the mesophase at the concentration of transition metal higher than 6 mol %. All ionomers produce the chiral nematic phase, which is characterized by selective light reflection the spectral range 500–2000 nm. The introduction of even small amounts of metal ions to functionalized LC copolymer prevents untwisting of pitch of the helix with decreasing the temperature. This tendency is related to a limited translational mobility of side groups in the LC copolymer, which produce helical structure, due to the physical network as formed by charged groups.

1. Introduction

Liquid-crystalline polymers containing metal ions^{1–3} and organic ions^{4–9} constitute a new subclass of functionalized LC polymers. A keen interest to such polymers is primarily related to their potential capability for combining specific structural organization of ionomers, which appears as the development of ionic aggregates with charged groups, with molecular ordering of side mesogenic fragments, which is responsible for the formation of thermotropic liquid-crystalline phases.

For the past several years we are investigating thermotropic LC ionomers^{3,4} to find out the role of electrostatic noncovalent interactions in the mesophase formation and structure. Earlier studies on ionomers containing ions of alkali metals, alkali-earth metals, transition metals, and rare-earth metals allowed one to ascertain the specific effect of metal ions on the development of LC phase in ionomers. Phase state of LC ionomers and their structure are shown to be controlled by the following parameters: charge of metal ions, mean radius of metal ions, distance between charged ionogenic group and polymer chain, and molecular mass of polymer. The key factor responsible for the phase state of ionomers concerns the development of specific supramolecular structures referred to as multiplets.¹⁰

Presently, information concerning LC ionomers, which are able to produce two types of LC phases (nematic and smectic phases), is available in the literature.^{1–4} At the same time, synthesis of optically active ionomers, which are able to produce, for example, the chiral nematic phase has attracted great scientific and practical interest. The attention to such systems is primarily related to unorthodox optical characteristics of their cholesteric phase such as selective reflection of circularly polarized light and gigantic optical activity.

This work aims at the synthesis of new chiral LC ionomers (Figure 1c) which are able to produce helical

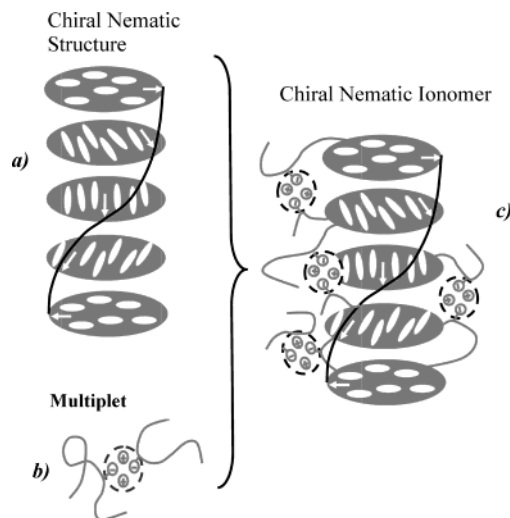


Figure 1. Schematic representation of helical structure of cholesteric phase (a), ionic multiplet of ionomers (b), and chiral nematic ionomers (c).

structure, which is characteristic of chiral nematic phase (Figure 1a), and multiplet structure, which is typical of ionomers (Figure 1c). Here, the main problem concerns the feasibility of the preparation of metal-containing LC ionomers, and the solution of this challenging task presents the principal objective of our studies.

To approach the above problem, we synthesized chiral nematic functionalized copolymer with carboxyl groups (derivatives of *n*-alkyloxybenzoic acid), which are able to participate in exchange reactions when hydrogen atoms are replaced by metal ions. Figure 2 shows the chemical structure of functionalized LC copolymer and related LC ionomers containing sodium ions.

In this work, synthesis of new LC ionomers containing ions of alkali (Na) and transition metals (Co) is described, and specific features of the formation of chiral nematic phase in ionomers are established. Optical

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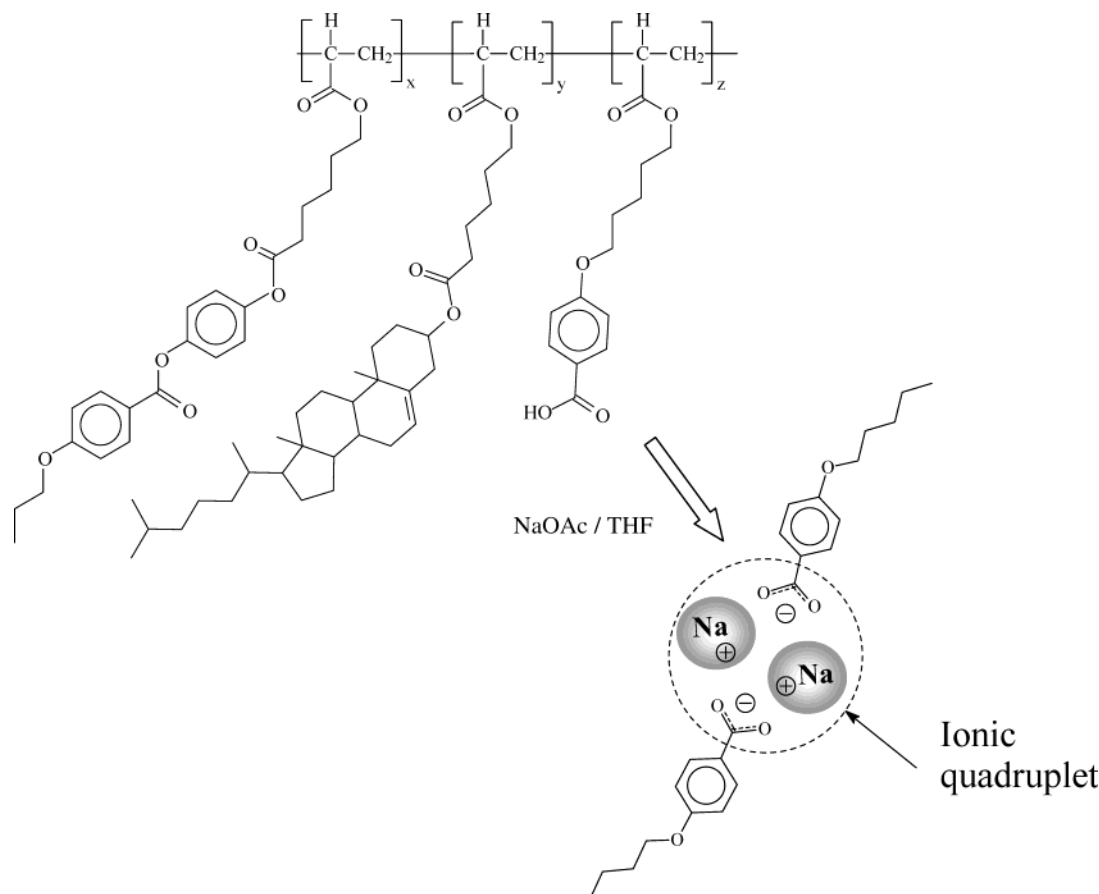


Figure 2. Chemical formulas of functionalized LC copolymers P1 and P2 and ionomers containing sodium ions (P1-Na).

Table 1. Composition, Phase Transitions, Maximum Value of Selective Light Reflection (λ_{\max}) of Planar Polymer Film at 100 °C, and Molecular Mass Characteristics for Functionalized LC Copolymers P1 and P2

sample	composition, mol %	phase transitions, °C	λ_{\max} , nm	M_w	M_w/M_n
P1	$x(55)-z(30)-y(15)$	glass 29 SmA 63 N* 106 I	786	10 300	1.4
P2	$x(50)-z(30)-y(20)$	glass 31 SmA 76 N* 116 I	657	11 800	1.5

properties of N* phase are considered, and the effect of temperature and content of metal ions on the value of selective light reflection of cholesteric films is studied.

2. Experimental Section

2.1. Synthesis of the Functionalized LC Copolymers. All monomers 4-(6-acryloyloxypropyloxyphenyl)-4'-propoxybenzoate, 4-(5-acryloyloxy-pentyl-1-oxy)benzoic acid, and cholesteryl-5-acryloylpentanoate were synthesized according to the earlier described procedures.³ Copolymers P1 and P2 were obtained by free-radical copolymerization of monomers in absolute THF; AIBN was used as initiating agent. The as-synthesized copolymers were purified by repeated reprecipitation from THF solutions by hexane. Compositions of the copolymers were determined by NMR spectroscopy (Supporting Information).

2.2. Synthesis of the LC Ionomers. Ionomers were obtained by the following method:³ 0.2% ethanol solution of the metal acetate was added to a 0.1% solution of functionalized LC copolymer in THF. The solution was evaporated and dried in a vacuum at 100–110 °C for 1 h. The substitution of carboxylic groups protons on metal ions was confirmed by elemental analysis and IR spectroscopy observing the appearance of a characteristic carboxylate ion band $\nu_{C=O}$ at 1544 cm^{-1} .

2.3. Characterization. Phase transitions in the synthesized copolymers and blends were studied by differential scanning calorimetry (DSC) at a scanning rate of 10 °C min^{-1} from –10 to 150 °C in nitrogen. The DSC cell was calibrated

with indium. Optical polarization microscopy was performed using a Mettler FP90 thermal analyzer and a Zeiss polarizing 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 μm thick samples were sandwiched between the two flat glass plates. 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 at least 20–40 min.

The IRFT spectra were recorded by a FTIR spectrometer (Biorad FTS 6000) in the region 400–4000 cm^{-1} at a spectral resolution of 4 cm^{-1} and an uncertainty <5% in absorbance. For the absorbance measurements, the sample was confined on KBr windows.

Relative molecular weights of 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 (Table 1). Measurements were made by using a UV detector, THF as solvent (1 mL/min, 25 °C), a set of PL columns of 100, 500, and 10³ Å, and a calibration plot constructed with polystyrene standards

3. Results and Discussion

3.1. Synthesis and Phase Behavior of Functionalized LC Copolymers and Ionomers. To prepare chiral LC ionomers, we used functionalized polymer, which satisfies the following criteria. First, this polymer

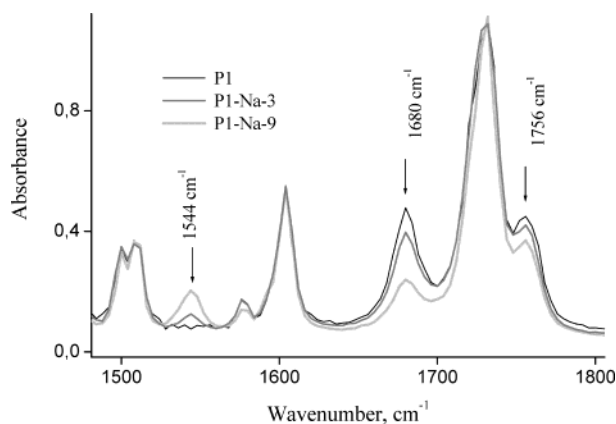


Figure 3. IR spectra for functionalized LC copolymer P1 and LC ionomers P1-Na.

contains free carboxyl groups (30 mol %) which may be used for the incorporation of metal ions to LC copolymer. Second, this copolymer is able to produce chiral nematic phase. Therefore, this copolymer contains nematogenic units (50–55 mol %), which are responsible for the formation of nematic structure, and optical active monomer units (cholesterol derivatives, 15–20 mol %).

Table 1 shows the phase transitions, molecular mass characteristics, and optical properties for functionalized LC copolymers P1 and P2. According to optical polarization microscopy, differential scanning calorimetry (DSC), and X-ray scattering, copolymers P1 and P2 are able to form the cholesteric LC phase in the wide temperature range. The chiral nematic phase of LC copolymers P1 and P2 exhibits characteristic oil strikes texture. A smectic A (SmA) phase was identified by the development of a fan-shaped texture and by the presence of an intense peak on diffractograms at small scattering angles ($2\theta = 2.9^\circ$ – 3.0°) that corresponds to the layered packing of mesogenic groups (Supporting Information).

LC ionomers were obtained by the partial substitution of protons of the functional carboxyl groups in the P1 and P2 copolymers by sodium and cobalt ions. Figure 3 shows the IR spectra of the LC copolymer P1 and LC ionomers P1-Na of various compositions. The formation of ionomers is proved by the presence of an absorption band of a carboxylate ion at 1544 cm^{-1} . The appearance of a COO^- ion is also supported by a reduction in the intensity of the bands at 1680 and 1756 cm^{-1} with increasing concentration of sodium ions. This fact indicates that the intensity of the bands at 1756 cm^{-1} due to free carboxyl groups and at 1780 cm^{-1} due to the carboxyl groups of the functionalized LC polymer P1 bound via hydrogen bonds (cycled dimer) reduces.

Let us consider in more detail the phase state of LC ionomers. Figure 4 shows the phase diagrams for LC ionomers P1-Na and P2-Co; the diagrams are constructed according to the data of optical polarization microscopy and DSC. First, one should mention that, upon introduction of single-charged and double-charged metal ions to functionalized LC copolymers, the temperature interval of chiral nematic phase is seen to increase. This behavior is likely to be related to a narrowing in the temperature interval of the SmA phase, which completely disappears when the content of metal ions becomes equal to 1.5 and 3.0% for sodium and cobalt ions, respectively.

As was found, LC ionomers containing sodium and cobalt ions are characterized by different dependences

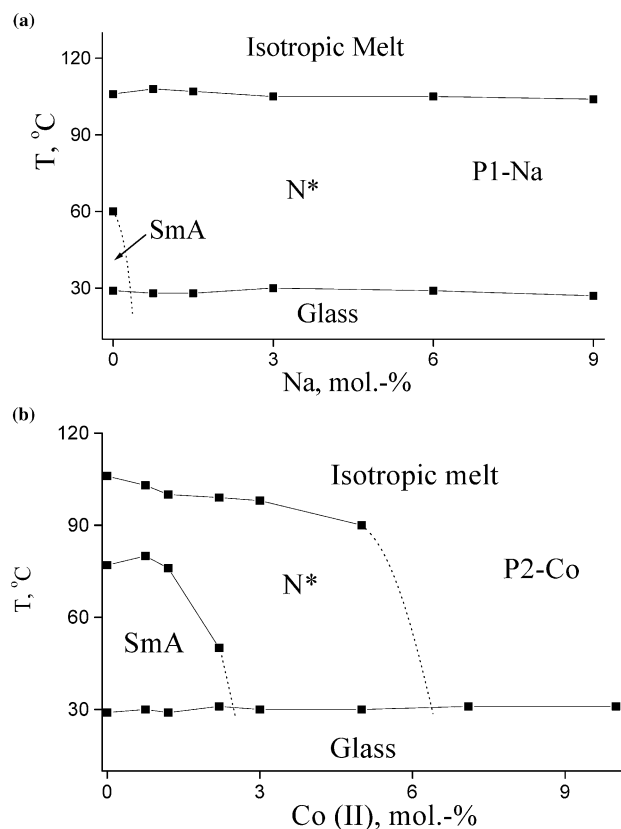


Figure 4. Phase behavior of LC ionomers P1-Na (a) and P2-Co (b).

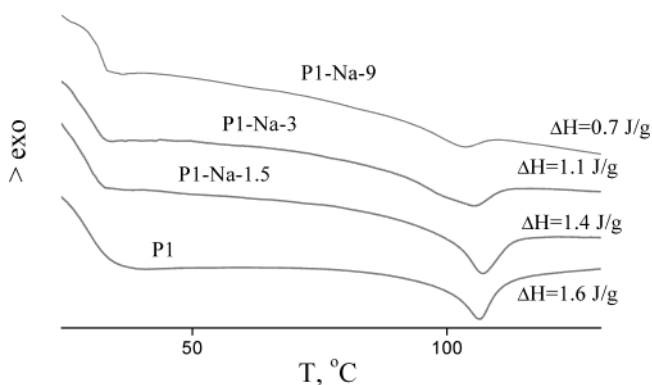


Figure 5. DSC curves for functionalized LC copolymer P1 and LC ionomers P1-Na.

of clearing temperature as plotted against the content of metal ions. As the concentration of sodium ions in P1-Na ionomers increases, the melting temperature of the chiral nematic N^* phase slightly decreases. One may observe a well-pronounced tendency that, with increasing the content of metal ions, enthalpy of the N^* –Iso transition decreases (Figure 5). At the same time, for P2-Co ionomers, as the content of cobalt ions is increased, the corresponding clearing temperature markedly decreases, and at a concentration of metal ions of 7 mol %, a complete disruption of LC order takes place.

Let us discuss the possible reasons of the above behavior. The first factor providing the destruction of the layered packing of copolymers and a decrease in the clearing temperature of ionomers is related to the development of ionic associates (multiplets). As was shown in our earlier works,⁴ for the copolymers, in which the charged carboxyl groups are located at a certain distance from polymer backbone, with increasing

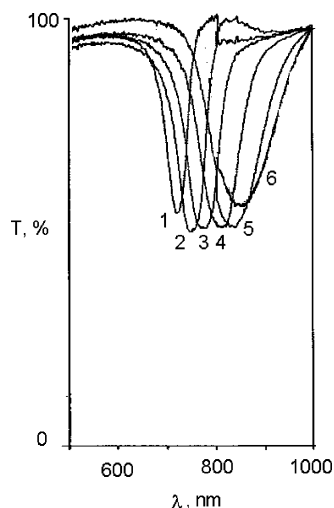


Figure 6. Transmittance spectra in the temperature range 105–65 °C: (1) 105, (2) 100, (3) 95, (4) 90, (5) 85, and (6) 65 °C. The interval between spectral recordings was 30 min.

the concentration of charged groups, the number of defects in mesophase increases. Ionic multiplets serve as defects of LC structure because they appear to be located in the layers that involve mesogenic groups. This factor is responsible for the deterioration of lateral interactions between side groups of copolymer and leads to a decrease in clearing temperatures and melting enthalpy of ionomers.

Furthermore, one should also take into account the tendency of transition metal atoms for the formation of various coordination compounds.¹¹ For example, cobalt atoms tend to occupy their coordination sphere by ligands until coordination number of 4–6 is achieved (Supporting Information). Oxygen atoms of ether and ester bonds of mesogenic fragment of LC copolymer as well as carboxyl group may serve as ligands. Therefore, in contrast to the alkali metal atoms, transition metals may interact with polymer matrix not only due to electrostatic forces but also via the formation of coordination bonds; as a result, the level of defectness markedly increases, and steric hindrances in polymer matrix are developed.³ Hence, even at a low concentration of metal ions, one may observe a complete breakdown of LC ordering in P2–Co ionomers.

3.2. Optical Properties of Functionalized LC Copolymers and LC Ionomers. The analysis of phase diagrams attests that all ionomers are able to produce the chiral nematic phase. The development of the N* phase is proved by studying the polarization optical structures. As was mentioned above, cholesteric phase forms a typical oil strikes texture. The transmission spectra of thin films (Figure 6) show well-pronounced peaks of selective light reflection, and this trend unequivocally suggests the formation of cholesteric phase. One should mention that well-developed planar textures with their selective light reflection were obtained for many LC copolymers and ionomers. At the same time, for P1–Na ionomers with a concentration of sodium ions of 3–9 mol %, no planar textures were obtained, and this is likely to be related to a high viscosity of the test samples.

Let us consider in more detail the optical characteristics of the N* phase of initial copolymers P1 and P2. In this case, as the temperature is decreased, selective light reflection maximum λ_{\max} is shifted to a longer wavelength region. Figure 7 presents the temperature

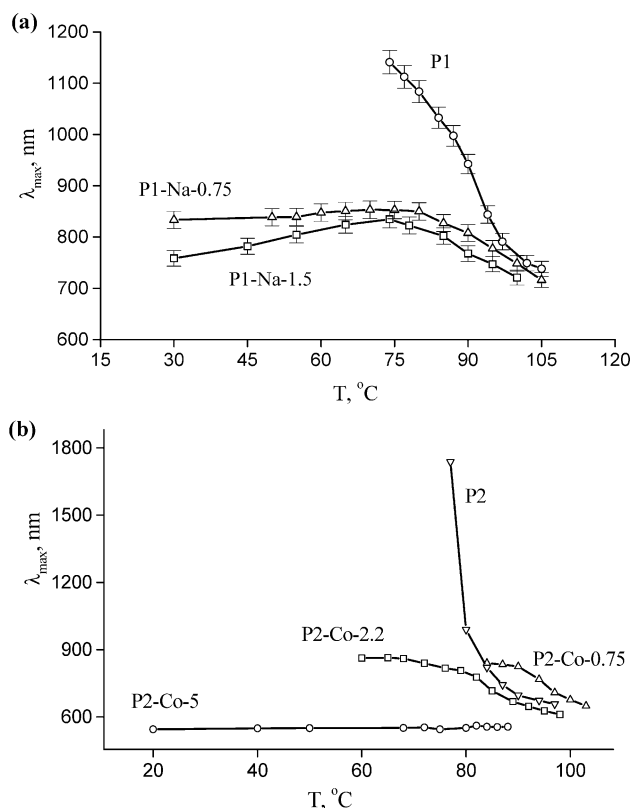


Figure 7. Temperature dependence of the maximum of selective light reflection wavelength for functionalized LC copolymers P1 and P2 and LC ionomers P1–Na (a) and P2–Co (b).

dependence of λ_{\max} for copolymers P1 and P2. For P1 and P2 polymer matrices, with decreasing the temperature, a dramatic untwisting of cholesteric helix takes place; as a result, selective light reflection maximum λ_{\max} markedly increases as the temperature is decreased. This tendency may be explained by the formation of smectic-order fluctuations in the vicinity of the N*–SmA transition. Upon any further decrease in temperature, selective light reflection peak is fully degenerated, and this fact unequivocally attests to the development of the SmA phase.

As is well seen, for ionomers, the temperature dependence of λ_{\max} appears to be quite different from those as observed for the above copolymers P1 and P2. The introduction of metal ions to polymer matrix prevents the untwisting of cholesteric helix with decreasing the temperature. For example, for P1–Na-0.75 and P2–Co-0.75 ionomers, untwisting of their cholesteric helix appears to be dramatically frozen as compared with that in copolymers P1 and P2. One should especially emphasize that, in this case, ionomers P2–Co and polymer matrix P2 are characterized by the same phase state. Copolymer P2 and ionomers with a content of cobalt ions below 2.5 mol % are able to form SmA and N* phases. However, for copolymer P2, as the temperature is decreased, λ_{\max} noticeably increases, whereas, for ionomers, λ_{\max} remains almost unchanged in the vicinity of the N*–SmA transition. Therefore, the above optical behavior may hardly be explained by any changes in the phase state of ionomers P2–Co but is likely to be related to a somewhat different but powerful factor. Note that, for ionomer P2–Co-5, helix pitch appears to be fully independent of temperature; that is, ionomers become monochromatic. Quite similar profiles of the

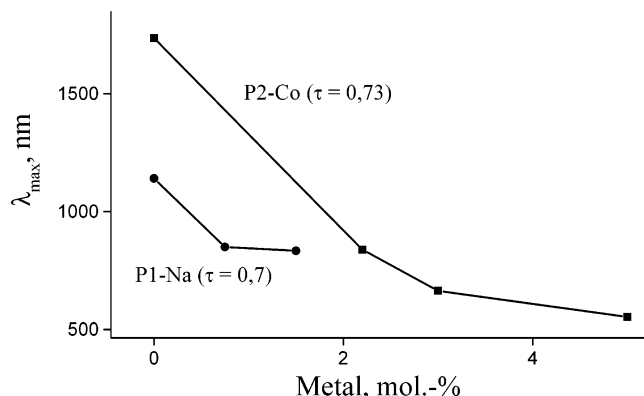


Figure 8. Maximum of selective light reflection wavelength vs of metal content at reduced temperature $\tau = T/T_c$.

dependences of λ_{\max} are observed for both families of the ionomers under study.

Figure 8 also illustrates the above phenomena. One may easily see that, upon the incorporation of metal ions to LC copolymer, a concomitant decrease in λ_{\max} takes place; that is, twisting of pitch of the helix is enhanced. Undoubtedly, the above phenomena are provided by the multiplet structure of ionomers. In ionomers, cholesteric helix is fixed to a physical network as formed via ionic associates. According to the above scheme, multiplets may be considered as junctions of physical network; fixation of polymer chains at the above network junctions may be compared to covalent (chemical) bonding. Therefore, no temperature variations may exert any marked effect on the mobility of side mesogenic groups and, hence, change its supramolecular organization.

4. Conclusions

A new series of functionalized chiral LC ternary copolymers and chiral ionomers containing the ions of alkali metals and transition metals were synthesized. For ionomers P1–Na containing 0.7–9 mol % sodium ions, the clearing temperature appears to be independent of temperature. At the same time, for ionomers P2–Co, as the content of d-metal is increased, the clearing temperature decreases; as a result, their LC phase vanishes at a content of Co ions of 7 mol %. For both ionomers under study, as the content of metal ions exceeds 1–2 mol %, one may observe the disruption of lamellar packing, which is typical of initial copolymers P1 and P2 and development of N* phase. As was found, the above ionomers produce chiral nematic phase, which is characterized by selective light reflection in the spectral range 500–2000 nm. As was shown, the introduction of even small amounts of metal ions to functionalized LC copolymer prevents untwisting of cholesteric helix with decreasing the temperature. This tendency is related to a limited translational mobility

of side groups in the copolymer, which produce helical structure, due to the physical network as formed by charged groups.

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Supporting Information Available: Text giving information on the NMR spectrum of copolymer, X-ray diffraction scattering of copolymers P2 and LC ionomer P2–Co(3), and UV spectra of ionomer P2–Co (7). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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