

Side-chain functionalized liquid crystalline polymers and blends, 10: phase behavior and structure of side-chain liquid crystalline ionomers containing ions of d-metals[☆]

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Abstract

Novel side-chain liquid crystalline (LC) ionomers containing d-metals Co(II) and Ni(II) were synthesized and characterized. Both families of the ionomers are characterized by the same influence of charged group content in polymer on their phase behavior. The incorporation of 2–3 mol% of metal ions in the nematic polymer matrix leads to the induction of SmA phase and rise in the clearing point. The peculiarity of their phase behavior in comparison with the earlier investigated LC ionomers with alkaline or alkali-earth metals is the full destruction of the mesophase at the concentration of d-metal higher than 12 mol%. This phenomenon was associated with the well-known ability of the transition metal ions to form various complexes that, in the case of LC ionomers, can negatively influence the ordering of the side mesogenic groups. The proposed structure of the LC ionomers is discussed in comparison with the metallomesogenic polymer systems. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

One of the most promising and perspective directions in the polymer chemistry is the synthesis and investigation of metal containing polymers, especially of those that possess additional functional properties such as electric conductivity, magnetic activity, special optic properties, catalytic activity, etc. [1–3]. Polymers with transition and rare-earth metals are the best candidates for developing materials with controlled magnetism due to the unique combination of fine physico-mechanical properties of polymers (the ability to form films and fibers, durability, rough-service, etc.) with the magnetic activity. The interest in such polymers nowadays is most vividly demonstrated in the fields of nanotechnology and magnetic data recording, where they may find applications as functional protective layers and interphases or be used for the preparation of metal nanoparticles, organic semiconductors, etc.

The most important tasks in the chemistry of metal

containing polymers possessing magnetic properties (or magnetic active polymers) are the development of new effective methods of metal incorporation into polymer matrix, study of the influence of metal atoms on polymer physico-chemical properties, targeted regulation of magnetic activity as well as the control of polymer supra-molecular structure and metal distribution. A new interesting direction covering the last two points is the investigation of the liquid crystalline (LC) metal containing polymers that can be roughly divided into two big families: polymer metallomesogens [4,5] and LC ionomers [6–21]. Polymer metallomesogens usually inherit the distinctive feature of their low molecular weight analogs, where metal complex is the main structure-forming element of the mesogenic group. On the contrary in LC ionomers, which have been investigated to a much lesser extent to date, metal ions are bounded by coulomb forces with functional groups of LC polymer and influence on mesophase by the formation of ion associates (multiplets) [22].

In our earlier publications [19,20] we have, for the first time, synthesized a family of copper (II) containing LC ionomers and investigated their magnetic properties. We have discovered that LC ionomers possess anti-ferromagnetic properties with the strong coupling interaction $J = 148\text{--}174\text{ cm}^{-1}$. Their temperature dependencies of

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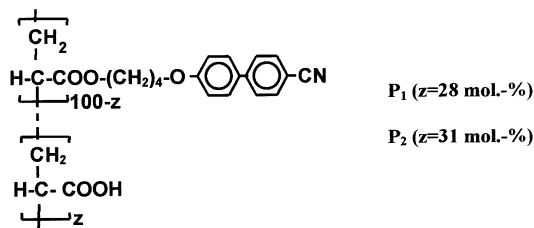
Table 1
Molecular mass characteristics (GPC, polystyrene standard) and phase transitions of LC copolymers P₁ and P₂

Sample	Acrylic acid units (mol%)	$M_w \times 10^4$	M_w/M_n	Phase transitions (°C)
P ₁	28	1.46	1.5	Glass 39 N 101 I
P ₂	31	1.30	1.4	Glass 38 N 92 I

magnetic moment are satisfactorily described by the one-dimensional Heisenberg linear-chain model. It is important to note that anti-ferromagnetic properties of the investigated LC ionomers become apparent at amazingly low content of copper ions (2 mol%) and not less than 90% of metal atoms take part in coupling interactions [20]. This is a direct confirmation of the metal ions activity towards the formation of ion associates (multiplets) in such polymer systems.

Further investigation on the magnetic properties of LC ionomers containing various d-metals and materials on their base may be perspective due to the following reasons. In LC ionomers, unlike the earlier investigated polymer metallo-mesogens, it is quite easy to control the metal content and that way influence the magnetic properties. Furthermore metal atoms in LC ionomers, as a rule, are not incorporated or bounded directly with mesogenic groups, which gives an opportunity to control separately the contributions of supra-molecular LC polymer structure and metal atoms magnetism in the target substance properties.

The present work is devoted to the investigation of phase behavior and structure peculiarities of the new LC ionomers, containing transition metals Ni(II) and Co(II) that, just as Cu(II), are able to take part in coupling interactions governing the magnetical activity of a substance. To synthesize the LC ionomers and compare their properties with the earlier investigated systems we have chosen two fractions, with close molecular mass, P₁ and P₂ of the functional LC copolymer. We were also interested in the comparison of metal influence on the phase behavior and the structure of LC ionomers and polymer metallo-mesogens to estimate further research of the materials on their basis.

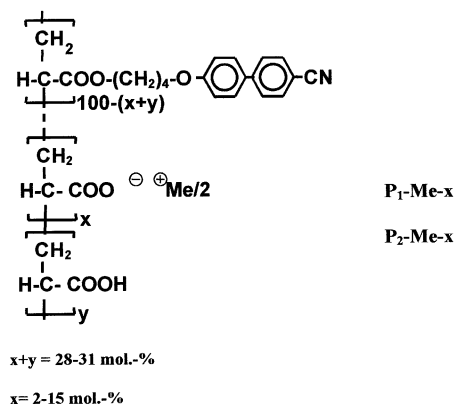


2. Experimental

The LC copolymers P₁ and P₂ that contain functional carboxylic groups and mesogenic 4-cyano-4'-biphenyloxy

groups were synthesized as described in Ref. [23]. Their molecular mass and phase transitions are listed in Table 1.

LC ionomers were obtained by the following synthetic approach [16–21]. The chemical formulae of the LC ionomers are given below.



An ethanol solution of metal acetate (0.1–0.2 wt%) was added to a solution of a LC copolymer in THF (0.1 wt%). The resulting solution was evaporated and dried under vacuum at 100–110 °C over a 1 h period. The content of metal ions in polymer matrix was estimated by atomic absorption spectroscopy. The degree of conversion of exchange reaction is 96–98%.

The substitution of protons of carboxyl groups by the metal atoms was proved by FTIR spectroscopy. The appearance of COO[−] ions is supported by the growth of an absorption band at 1578 cm^{−1} and the reduction in the intensity of the high-frequency wing (~1700 cm^{−1}) of a complex ν_{C=O} band (1770–1690 cm^{−1}) and is related to the vibrations of free (1740 cm^{−1}) and coupled (1703 cm^{−1}) carboxylic groups, with an increase in the concentration of metal (Fig. 1). In some LC ionomers the observation of the individual absorption band at 1578 cm^{−1} is impossible because of its overlapping with the bands of skeleton vibrations of benzene rings (1580 and 1603 cm^{−1}).

Microcalorimetric measurements were carried out with a Mettler differential scanning calorimeter at a heating rate of 10 K min^{−1}. Optical polarizing microscopic experiments were performed with a POLAM-R-211 optical polarizing microscope equipped with a Mettler FR-82 hot stage.

The X-ray diffraction patterns of polymers were recorded with a URS-55 instrument using Cu-Kα radiation with a wavelength of 1.54 Å. The FTIR spectra of the copolymers

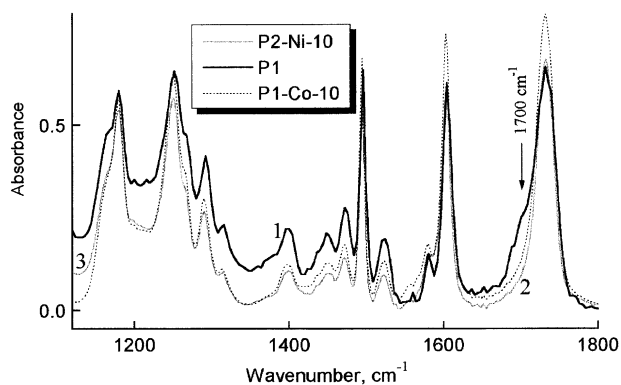


Fig. 1. The fragments of IR spectra of the LC copolymer P₁ and LC ionomers P₁-Co-10.0 and P₂-Ni-8.0.

were recorded at 60 °C using a BIORAD FTS6000 spectrometer at a resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Synthesis, structure and phase transitions of the LC ionomers

LC ionomers P₁-Co and P₂-Ni were synthesized by the ion exchange reaction described in detail in our earlier publications [16–21]. Their phase diagrams are shown in Fig. 2. The phase state of the parent LC copolymers P₁, P₂ and their related LC ionomers were studied by DSC, optical polarization microscopy, and X-ray scattering. For these ionomers a nematic LC phase that is typical of the parent LC copolymers is realized only for two compositions (2.0 and 3.0 mol% of metal). A further increase in the concentration of metal ions (5–12 mol%) in the polymer matrix first leads to the development of SmA phase and increase in the clearing point and ends with the full distortion of mesophase (>12 mol%).

The nematic phase of LC ionomers exhibits a characteristic marble texture. A smectic A phase was identified by the development of a fan-like texture and by the presence of an intense peak in diffractograms (Fig. 3) at small scattering angles that corresponds to the layered packing of mesogenic groups. In X-ray diffraction patterns of the LC ionomers oriented in magnetic field a diffuse halo at wide scattering angles and a small-angle reflection split in mutually perpendicular directions are observed (Fig. 4). This observation clearly indicates the presence of SmA phase.

For all investigated ionomers forming SmA phase the maximum intensity of a small-angle reflection corresponds to an average interlayer distance of 34–35 Å (Co: 34.6 ± 0.2 Å, Ni: 34.4 ± 0.2 Å), which is related to the two-layer packing of cyanobiphenyl mesogenic groups (with a partial overlapping of the end cyano groups). An increase in the metal ions content in polymer matrix

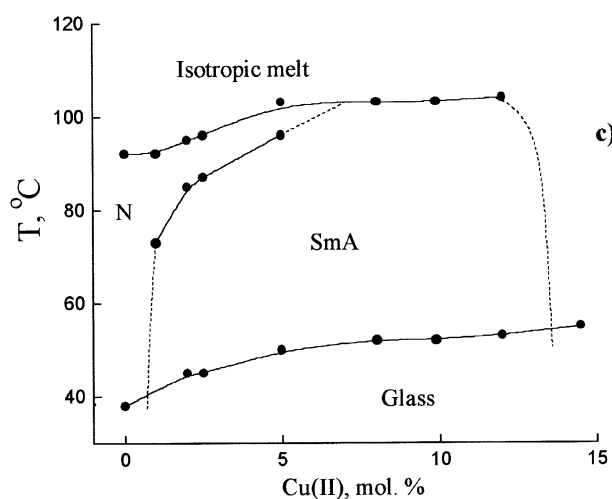
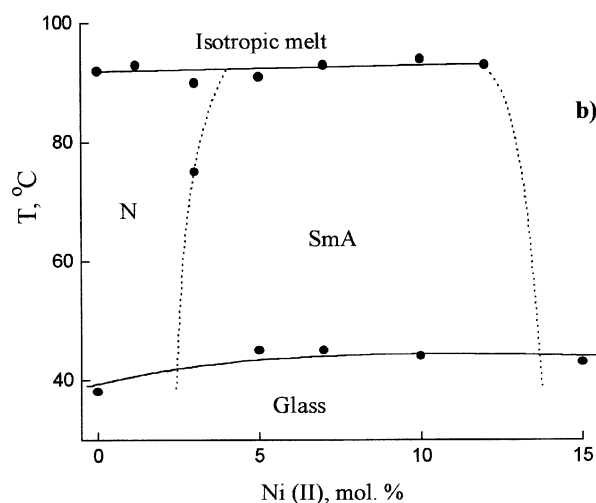
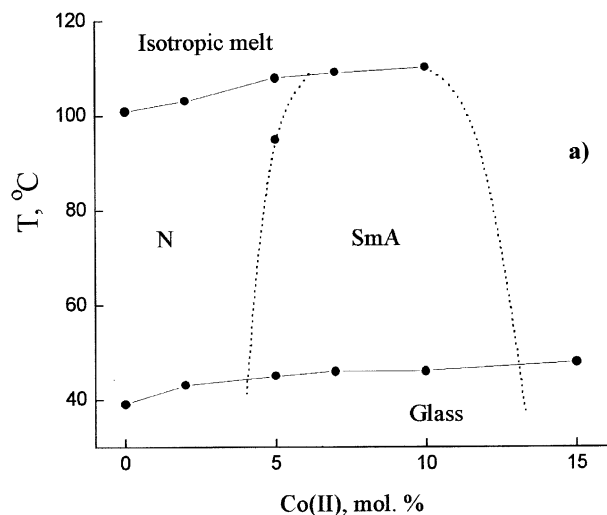


Fig. 2. Phase diagram of the LC ionomers: P₁-Co (a), P₂-Ni (b), P₂-Cu [19] (c).

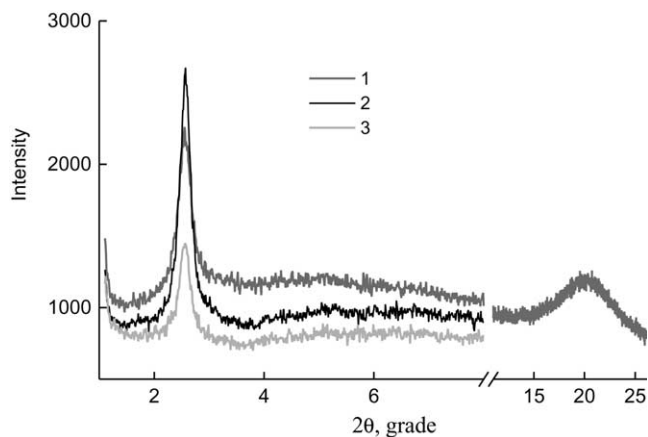


Fig. 3. Small angle X-ray diffractograms of the LC ionomers P_1 -Co-7.0 (1), P_2 -Ni-7.0 (2), P_2 -Cu-7.0 (3) [19].

(2–12 mol%) has no influence on the interlayer distance and packing of mesogenic groups.

Fig. 5 shows the DSC curves of the parent LC copolymers and their related LC ionomers. The DSC curves of the parent nematic copolymer P_2 and the LC ionomer P_1 -Co-2.0¹ exhibit endothermic peaks with the characteristic fusion enthalpies of 0.8–1.1 J g⁻¹, whereas for the LC ionomers that form smectic phase (for example P_2 -Ni-5.0) endothermic peaks are broader and the fusion enthalpies are larger 1.5–2.2 J g⁻¹. At high concentrations of metals (P_1 -Co-15.0, P_2 -Ni-14.5) peaks corresponding to melting of mesophase completely disappear.

The glass temperatures and clearing points of all LC ionomers under investigation (P_1 -Co, P_2 -Ni) increase with the growth of metal ion content in polymer matrix and, starting with 5 mol% of metal, maintain constant values that are on average 10° higher than the corresponding temperatures for parent LC copolymers P_1 and P_2 .

3.2. The influence of metal concentration on the phase behavior of LC ionomers

As it is clearly seen from Fig. 2 the phase behavior of the LC ionomers P_1 -Co, P_2 -Ni in general is subjected to regularities established earlier for LC ionomers P_1 -Cu [19,20], and also has many common features with systems P_1 -Ca [21]. This circumstance is not surprising, considering that the ions of all these metals have a charge of +2. In the correspondence with a model of LC ionomers, which was offered in our earlier publications [16–21], phase behavior of such substances can be explained by engaging the theory in detail developed for solutions and melts of statistical linear ionomers and basing on the consideration of the tendency of ion pairs to organize aggregates (multiples,

¹ The number corresponds to the content of metal (mol%) in the ionomers.

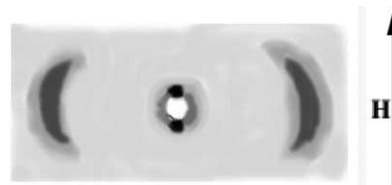


Fig. 4. X-ray diffraction pattern of the magnetically oriented LC ionomer P_2 -Ni-5.0.

clusters) [22]. We assume that for LC polymers, with functional groups located in the immediate vicinity of main polymeric chains, the formation of multiplet structures can render structuring effect on the LC phase. This effect is exhibited in the growth of clearing temperature and induction of smectic mesophase [16]. We have shown that for calcium containing LC ionomers P_1 -Ca the introduction of a small amount of metal atoms (3 mol%) into the polymeric matrix results in the growth of magnitude of orientation order parameter S [21]. It is also important to stress the complicated role of ion multiplets in the polymer matrix that may, on the contrary, lead to the distortion of mesophase especially in LC polymers where charged groups are removed from polymer chains by flexible spacers [16].

However, the phase behavior of LC ionomers P_1 -Co, P_2 -Ni, and P_1 -Cu is characterized by a very important feature, which distinguishes these systems from all those investigated previously. In an interval of concentration 12–15 mol% a full destruction of the LC phase is observed. In order to understand this phenomenon it is necessary to take into consideration the high activity of transitional metal atoms to form complexes (coordinate compounds). Different from atoms of calcium (described by the same charge of +2) ions of cobalt, nickel or copper tend to fill their coordinate spheres by ligands in order to reach coordinate numbers 4–6 [24]. Any atom or group of atoms of the

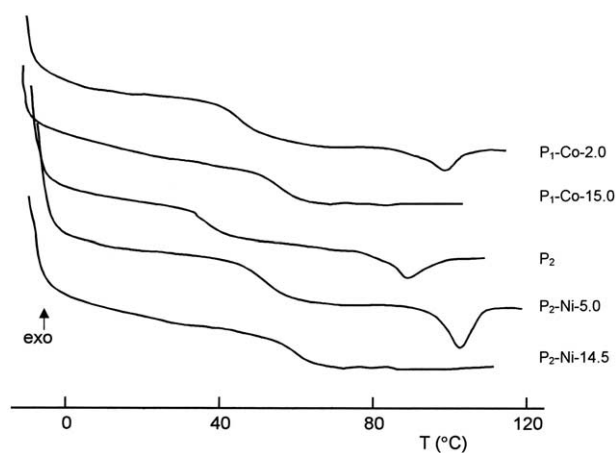


Fig. 5. DSC curves of the LC copolymer P_2 and LC ionomers P_1 -Co-2.0, P_1 -Co-15.0, P_2 -Ni-5.0, and P_2 -Ni-14.5.

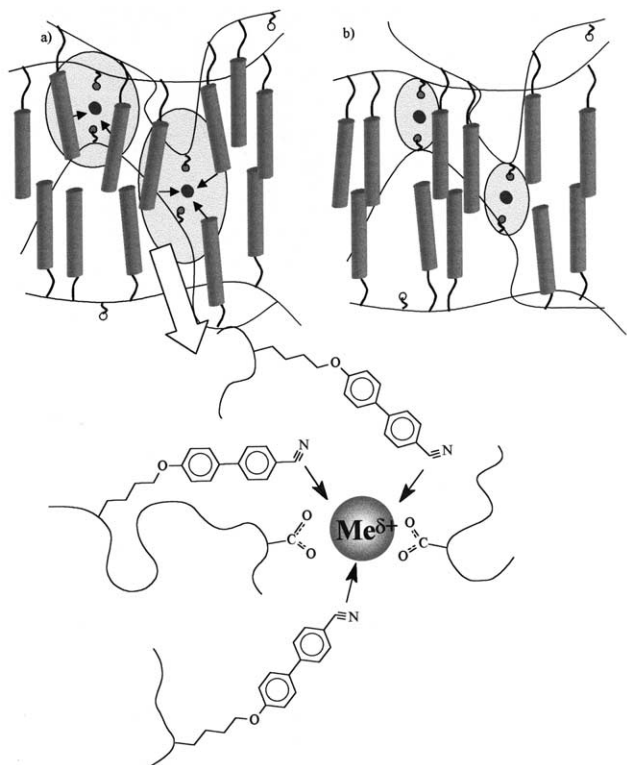


Fig. 6. Schematic presentation of the transition metal complexes with the side mesogenic groups (a) and simple ion link in the case of calcium atoms (b). Ovals filled with gray color show the area of metal influence on polymer matrix. Arrows show single atoms or groups of atoms that are capable of complex formation.

side-chain LC polymer possessing electron donor properties, for example, having an undivided pair of electrons, can take part in the formation of such complexes. In the LC copolymer matrix, chosen for the preparation of LC ionomers, the role of such atoms or groups could play oxygen in ester and ether groups, as well as the ending cyano groups of the mesogenic 4-cyano-4'-biphenyloxy side fragments (Fig. 6(a)). There are no doubts that the atoms of transitional metals will effectively organize different complexes with these elements of a polymeric matrix, which was proved by UV data (Fig. 7).

In the UV spectra of the LC ionomer's P₂-Cu-5.0, P₂-Cu-15.5 solutions and isotropic melts at 110 °C one wide band at 600–900 nm is observed (Fig. 7(a)). This absorption band corresponds to divalent octahedron or tetrahedron copper complexes and proves their formation in ionomers P₂-Cu. At the same time P₂-Ni-5.0 ionomer has two bands: an intensive one at 600–900 nm and a weak one at 1100–1250 nm. It is a confirmation of the tetrahedron structure of Ni complexes [24] in the LC polymer matrix, though further experiments are necessary to get additional evidence for that conclusion. In the case of melts of cobalt containing ionomers (Fig. 7(b)) a very weak band at 500–700 nm for P₁-Co-5.0 is observed. A better UV spectrum is recorded in the case of ionomer solution in THF. A shoulder is observed at

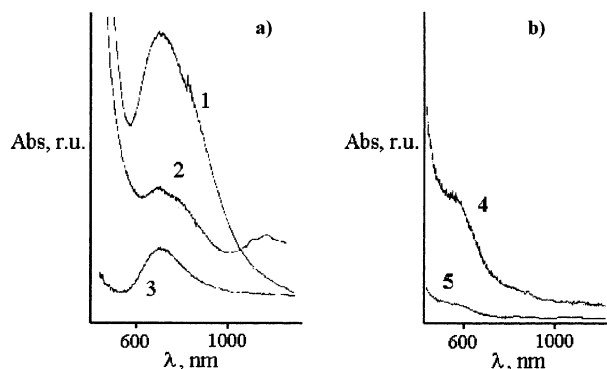


Fig. 7. Fragments of UV spectra for the LC ionomers P₂-Cu-15.5 (1), P₂-Ni-5.0 (2), P₂-Cu-5.0 (3) (a) and P₁-Co-5.0 (4,5) (b) in the isotropic melt at 110 °C (1–3, 5) and in THF solution (4).

550–600 nm and it probably corresponds to the presence of both octahedron and tetrahedron complexes. An attempt to analyze the structure of complexes in more detail meets serious experimental difficulties due to the possible formation of metal complexes with different structure and composition and hence overlapping of characteristic bands results in the broadening of absorption bands and gives some sort of average signal.

Thus, the transition elements will interact with a polymeric matrix not only by means of coulomb (electrostatic) forces, but also by the formation of coordinate complexes which is different from atoms of alkaline or alkaline-earth metals. It is logical to assume that the formation of additional contacts by transition metals with the side mesogenic groups results in essential growth of defects and steric hindrances in the packing of mesogenic fragments of LC ionomers. Earlier we have used a similar assumption for the explanation of difference in the phase behavior of LC ionomers with alkaline (P₁-Na, P₁-Rb) and alkali-earth metals (P₁-Ca). The ionomers with alkaline metals are characterized by the linear growth of clearing temperature with the increase in metal ion content in a polymer matrix [16], while for ionomers with calcium ions the clearing temperature quickly reaches constant values [21]. This phenomenon was explained by taking into account that, unlike one-charge cations of alkaline metals, each ion of calcium is connected with a minimum of two carboxylic groups with possible ionic linking of neighbor polymer chains together (Fig. 6(b)). As the ionic link is formed at an initial stage of synthesis, consequent evaporation of a solvent and annealing of a polymer can lead to unfavorable disposition of macromolecules, hindering the process of mesophase formation and increasing the defects of packing of side mesogenic groups.

While the formation of each ionic link that includes calcium atom results in the fixation of two carboxylic groups (and, therefore, polymer chains connected to them) (Fig. 6(b)), each atom of transitional metal can in addition interact with a minimum of two adjacent mesogenic groups

(Fig. 6(a)). As an outcome the size of defect area created by the atom of transitional metal in packing of side groups can essentially exceed its analog for alkaline and alkaline-earth metals. Finally at high concentrations of transitional metal ions (which for investigated LC ionomers is achieved at 12–15 mol%) the presence of defects can increase so significantly that it will lead to the disappearance of LC ordering totally.

This conclusion has basic significance, as certain restriction on the development of magnetic active LC polymer materials on the base of LC ionomers is imposed. It is possible to assume that in practically any LC polymer matrix (containing electron donor groups or atoms capable to play a role of ligands) the incorporation of large amount of transition metals will result in inevitable amorphisation of the macromolecular system. Let us note an exclusion from this rule for most of the polymer metallomesogens [4,5], in which metal atoms participate in the formation of mesogenic groups and are enclosed by a previously determined specific setup of ligands, which prevents their undesirable interaction with other fragments of a polymeric matrix.

It is possible to expect that in metals containing LC ionomers, with a charge of more than +2, positive influence of the ionic associates (growth of clearing temperature and the induction of smectic phase) on a LC phase can be completely suppressed. The practical study of such polymer systems is the subject of further work.

Acknowledgements

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