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Liquid-crystalline ionomers as a new class of mesomorphous polymeric systems

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Abstract. Data on the synthesis, structure and physicochemical properties of liquid-crystalline ionomers, a new class of mesomorphous polymeric compounds, are summarised. The main classes of the liquid-crystalline ionomers studied to date (including comb-like and linear) and liquid-crystalline chelato-telechelic polymers are considered. It is demonstrated that the ionomer phase state and structure are determined by the ability of ion pairs to form stable ionic aggregates. A new model of the structural organisation of liquid-crystalline ionomers is proposed. The bibliography includes 110 references.

I. Introduction

Mesomorphous polymeric systems including compounds with liquid-crystalline (LC) type of ordering belong to the most interesting aspects of modern chemistry and physics of high-molecular-mass compounds.[1–5] Based on such systems, new generations of polymeric materials and composites for application in holography, data storage systems, optoelectronics, optical filters and polarisers have been designed (and the work is in progress!). The most promising fields of application of LC polymers include reinforced organic fibre technologies,[6] fabrication of nonlinear optical media, ferroelectrics,[7,8] photonic crystals,[9] materials for recording and storage of optical information,[7,10–12] biologically active compounds,[13] *etc*.

Introduction of small amounts of metal ions (a few molar per cent) into copolymers of unsaturated hydrocarbons with aliphatic unsaturated acids (first of all, based on ethylene and acrylic acid) leads to fundamental changes in the physicochemical properties of the polymers, namely, a decrease in solubility, an increase in the glass transition temperature and improvement of mechanical characteristics.[14–16] Detailed investigations of such compounds, which were named ionomers, showed that in the solid phase or in nonpolar solvents they form complex ionic aggregates involving charged groups, which to a first approximation can be considered as noncovalent cross-link points of the polymer chains. It is ionic aggregates that are responsible for specific physicochemical and mechanical properties of ionomers and peculiar features of the supramolecular organisation and structure of such systems.[15–17]

In spite of considerable advances in research on mesomorphous polymers, the structure and properties of ion-containing LC polymers and LC ionomers have not been systematically analysed until recently. Taking into account the incessant interest of researchers in metal-containing polymeric systems,[18] this is more than strange. This review can help to some extent bridge the gap.

The increasing interest in studies of comb-shaped LC ionomers is due to their ability to combine the supramolecular organisation, which manifests itself in the formation of ionic aggregates, with the ordering of side mesogenic fragments, which governs the formation of thermotropic mesophases. Owing to the dual nature of the molecular organisation, the LC ionomers can 'inherit' valuable properties and characteristics of both these classes of high-molecular-mass compounds. Because of this, they are of interest for both basic research and applied science as model systems for the design of novel materials and composites based on them.

The variety of molecular architectures of LC ionomers and ion-containing LC polymers is due to the complex chemical structure of this class of high-molecular-mass compounds (Fig. 1). The most important characteristic of these compounds is the content of charged groups in the macromolecules. Note that an old classification, which is nevertheless used in most studies, treats LC ionomers as mesomorphous polymers containing at most 5 mol.% – 10 mol.% of charged groups. Polymers containing more than 10 mol.% – 20 mol.% of charged groups are called LC ion-containing polymers or LC polyelectrolytes.[19–21] In spite

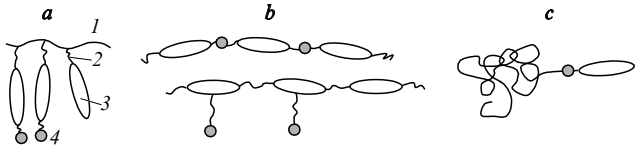


Figure 1. Structures of comb-shaped (*a*) and linear (*b*) LC ionomers and LC chelato-telechelic polymers (*c*).
The main polymer chain (*1*), side chain (spacer) (*2*), mesogenic group (*3*) and charged (ionogenic) group (*4*).

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of the limited use of this classification (see below), we will also use it in this review because it is commonly accepted.

Specific features of mesophase formation in comb-shaped and linear LC polymers have been reported.[4,22] With allowance for this fact it is logical to classify LC ionomers based on such a macromolecular topology parameter as the position of mesogenic groups (in the backbone, in side chains, *etc*.). Below we will show an important role of the chemical nature of the monomer units bearing charged groups, in particular, the charge of counterions, and of the distance between the monomer unit and the polymer backbone (the length of the spacer).

The authors of this review have first analysed the state-of-the-art in the field of research on thermotropic LC ionomers using the published data and the results of their own studies. First, we outline the fundamentals of physical chemistry of random amorphous ionomers and then consider thermotropic LC ionomers with various molecular architectures. The emphasis is placed on the publications reported in the last 10–15 years, because the pioneering studies on the physical chemistry of thermotropic LC ion-containing polymers and LC ionomers date back to the late 1980s and early 1990s. Thus, the authors have tried to make the review accessible to a broader spectrum of readers and, at the same time, to present a comprehensive treatment of the subject and report recent advances in this interesting field of polymer science.

II. Fundamentals of chemistry and physics of ionomers

1. Ionomers and polyelectrolytes

Traditionally, macromolecules containing charged groups are divided into two large classes, polyelectrolytes and ionomers.[14,16] Initially, ionomers included random copolymers comprised of monomers of the ethylene series and unsaturated acids (acrylic acid, methacrylic acid) in which a fraction of the protons of carboxyl groups (up to 10 mol.%) is replaced by alkali or alkali-earth metal ions. Such ion-containing copolymers are practically insoluble in conventional organic solvents.

Polyelectrolytes comprised[14] high-molecular-mass compounds containing a large amount of ionogenic groups, which can dissociate in polar solvents, *e.g*., salts of polyvinylsulfonic acid, polyacrylic acid and salts of polybases, *e.g*., quaternised (alkylated) polyvinylpyridine, *etc*. However, later this definition was recognised to be unsatisfactory, because essential differences in characteristics of the compounds belonging (from the standpoint of this definition) to the same class, were established.[16]

Basic to the modern classification of ion-containing macromolecules is the state of the charged groups they bear. To illustrate the fruitfulness of this approach, we will consider the simplest model of an ion pair as a constituent of a macromolecule (Fig. 2). According to the Coulomb law, the interaction energy of the point charges q_1 and q_2 of the ionogenic group and the counterion, respectively, separated by the distance r in the medium with the dielectric constant ε is given by[23]

$$U_q = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{\varepsilon r}. \qquad (1)$$

The ratio of the attraction energy between the counterion and the oppositely charged ionogenic group of the polymer (electrostatic attraction factor) to the average thermal energy of the counterion (thermal factor) has the form

$$\frac{2}{3}\frac{U_q}{kT} = \frac{1}{6\pi\varepsilon_0 k}\frac{q_1 q_2}{\varepsilon r T}. \qquad (2)$$

Two most important particular cases where this ratio is (i) much more and (ii) much less than unity are illustrated in Fig. 3. The former case (the electrostatic factor much exceeds the thermal factor) is characteristic of contact ion pairs. The latter case is typical of a dissociated pair in which the Coulomb attraction between ions cannot hold them together and the external ion not involved in covalent bonding with the polymer chain can experience Brownian motion.

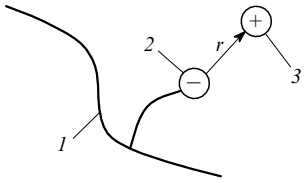


Figure 2. Model of an ion pair in a macromolecule. Backbone (*1*), charged ionogenic fragment (*2*) and counterion (*3*).

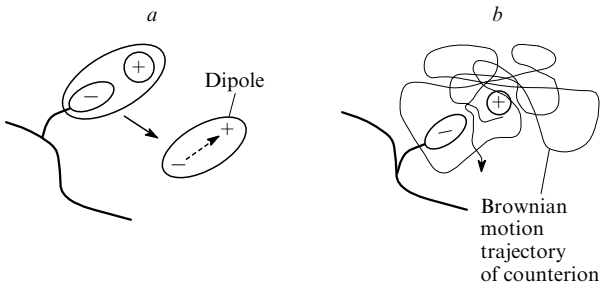


Figure 3. Ion pairs in the ionomer (*a*) and polyelectrolyte (*b*) regimes. Ratio (2): $\gg 1$ (*a*) and $\ll 1$ (*b*).

From expression (2) it follows that contact ion pairs will mainly exist in condensed media with low dielectric constant ($\varepsilon \approx 1$) at moderate temperatures, which is characteristic of the vast majority of organic compounds with the hydrocarbon skeleton in the solid phase or in nonpolar solvents. In modern literature, this state (or mode) is called the ionomer state (mode) and the corresponding high-molecular-mass compounds are called ionomers.[16]

Individual ion pairs are electric dipoles because the positive and negative charges are separated by the distance r (see Fig. 2). The electrostatic interaction energy of coplanar electric dipoles (Fig. 4) is given by[24]

$$U_d = \frac{1}{4\pi\varepsilon_0}\frac{\mu_A\mu_B}{\varepsilon d^3}\left(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\right), \qquad (3)$$

where μ_A, μ_B are the dipole moments of the ion pairs A and B, d is the distance between the centres of the dipoles, and θ_A and θ_B are the angles between the axes of the dipoles and the line connecting their centres.

From Eqn (3) it follows that at the dipole–dipole separations $d \approx 5$–10 Å at $r \approx 1$–2 Å, $\varepsilon = 1$ the attractive energy of the ion pairs is comparable with the energy of hydrogen bonding,[25,26] which plays the key role in biochemistry, in the supramolecular structural organisation and in physical chemistry of liquid crystals.[27–30] It will be shown below that it is the dipole–dipole interaction of ion pairs that governs the specific features of the physicochemical properties and the supramolecular structure of ionomers.

High dielectric constants of media ($\varepsilon \gg 1$, polar solvents) and an increase in temperature cause dissociation of ion pairs. This

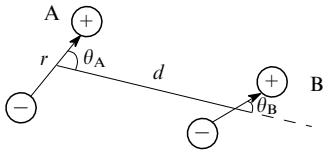


Figure 4. Electrostatic interaction between dipoles A and B.

mode is called polyelectrolyte mode and the corresponding compounds are called polyelectrolytes.[16,24] A macromolecule can contain thousands of ionogenic groups; therefore, it is clear that charges distributed over the polymer chain strongly affect the conformation and physicochemical properties of the polymer. For instance, it is repulsion between the similarly charged groups that is responsible for the well-known swelling of polyelectrolytes.[31,32]

Thus, depending on the particular conditions (primarily, on the dielectric constant of the medium and temperature), counterions near the charged groups of the same macromolecule can exist as free ions and as constituents of stable ion pairs. Correspondingly, such systems can possess the properties of both ionomers and polyelectrolytes. It seems likely that different conditions (modes) for the existence of ionogenic polymers rather than different classes of these compounds should be discriminated.[16] Since the ordering of macromolecules of thermotropic LC polymers occurs in the solid phase due to the interaction of anisometric mesogenic groups rather than in a particular range of concentrations, as for lyotropic liquid crystals, in the text below we will consider only the ionomer state of polymers and relevant features of their morphology and physicochemical properties.

2. Main models for the structure of ionomers

Pioneering experimental studies on the synthesis and properties of ionomers showed that introduction of charged groups into random alkene–unsaturated carboxylic acid copolymers leads to a decrease in their solubility and to an increase in the glass transition temperature.[15] One of the most significant factors indicating a complex supramolecular structure of ionomers is the detection of a characteristic maximum at small scattering angles in their X-ray diffraction patterns. The presence of this maximum, which is called the 'ionic peak', is indicative of the formation of ordered ionic aggregates within the nonpolar polymer matrix. Besides, analysis of the temperature dependences of the mechanical loss factor tan δ for these thin samples revealed two clearly seen maxima, which allowed the microphase separation in the samples to be suggested.[15] The model of formation of ionic aggregates in the polymer matrix has played an important role in the development of the concepts of structural organisation of ionomers.

One of the first and most significant theoretical studies in the field of physical chemistry of ionomers is the study by Eisenberg.[24] The model is based on the concepts of aggregation of ion pairs driven by the electrostatic dipole–dipole interaction (see above). Small aggregates comprising a few charged functional groups and corresponding counterions connected by strong Coulomb interactions were named 'multiplets'. In the original model, Eisenberg assumed that an increase in the content of ion pairs in the polymer matrix will favour further electrostatic aggregation of multiplets, resulting in clustering. Clusters containing tens of multiplets can be treated as domains of a new phase dispersed in the initial polymer.

To explain the influence of multiplets on the polymer matrix, in the study cited it was assumed that the conformational mobility of the polymer chain in the vicinity of a multiplet is significantly restricted compared to the conformational mobilities of distant fragments of the macromolecule. Therefore, steric interaction between the polymer chains coordinated to the multiplet through their own ion pairs and noncoordinated chains in the environment affects the polymer matrix oppositely to the effect of plasticiser because any multiplet becomes surrounded by a 'shell' comprised of chain fragments with restricted mobility (Fig. 5).

The thickness of the region of restricted mobility in the vicinity of the multiplet is primarily determined by the flexibility of the polymer chains, namely, the higher the flexibility the thinner the multiplet shell. The range of action of a multiplet (distance at which the polymer chains 'feel' the effect of the multiplet) can hardly be determined quantitatively, but it must correspond to the persistence length of the polymer in the solid phase or the length of the Kuhn segment.† The formation of the core of a multiplet is accompanied by attraction of all neighbouring charged groups; therefore, the shell of the multiplet must be considerably depleted of ions.

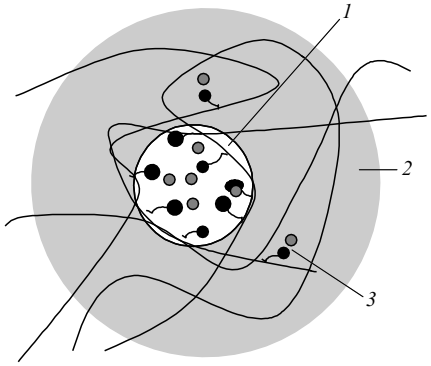


Figure 5. Structure of multiplets according to Eisenberg.[17,24] Multiplet core (*1*), multiplet shell (region of restricted mobility of the polymer chains) (*2*) and isolated ion pair (*3*).

From the aforesaid it follows that the effect of a multiplet comprised of a few ion pairs on the polymer matrix is weaker than the effect of a larger ionic aggregate. The smallest aggregate comprising two ion pairs, a quadruplet, plays the role of a conventional intermolecular cross-link, thus causing relevant changes in the physicochemical characteristics of the polymer sample. Generally, the region of restricted mobility of the polymer chains surrounding the multiplet is small and cannot be characterised by its own glass transition temperature; however, the presence of such regions favours an increase in the glass transition temperature of the whole polymer sample in accord with the mechanism considered above.[24]

The Eisenberg model provides no unambiguous interpretation of X-ray scattering data, but permits a qualitative explanation for the 'microscopic' two-phase morphology of ionomers. The model gave an impetus to further development of the theory of ionomers in the studies by Forsman,[33] Dreyfus,[34] Datye and Taylor,[35] Earnest *et al.*,[36] Squires *et al.*,[37] Marx *et al.*,[38] Yarusso and Cooper,[39] Ding *et al.*,[40] MacKnight *et al.*,[41] Roche *et al.*,[42] *etc.*

In 1989, Eisenberg's group proposed an improved model of ionomers,[17] which is used at present. The model considers a number of factors responsible for the formation of multiplets, *e.g.*, the force of electrostatic interaction between charged groups, the concentration of ions (ion pairs) in the polymer, the chemical nature of the polymer matrix and steric factors.

The most important factor is the force of electrostatic interaction between ion pairs, which is determined by the size of ions and by the contribution of the covalent component to the ion–ion interaction. It is assumed that ions of small radii interact more efficiently and form stronger aggregates than do large charged groups. If the Coulomb forces between the ion dipoles are too weak to overcome the 'elastic' resistance of the polymer chains to which they are connected, no aggregation occurs.

Low dielectric constant and low glass transition temperature of the initial (non-ionised) polymer favour the formation of multiplets. An important role of the parameter ε was mentioned above and the glass transition temperature correlates with the ease of deformation of the polymer chains, *viz.*, the higher the T_g the more difficult is to force the polymer chains to change their

† The persistence length is a measure of chain curvature of rigid-chain macromolecules. It is defined as half the length of the Kuhn segment, *i.e.*, the polymer chain segment in which the memory of the chain direction is retained.

positions at normal temperatures. Clearly, plasticisers present in a polymer composite can strongly influence the formation of ionic aggregates.

For the polymer chains of ionomers with bulky substituents one should expect the formation of very small multiplets. At the same time for the ionomers in which the charged groups are connected to the backbone through long and flexible side bridges (spacers), steric hindrances are weaker and large multiplets can form.[43,44] This is quite important for considering the molecular architecture of LC ionomers and for the interpretation of experimental data.

The average distance between multiplets must decrease on an increase in the concentration of ion pairs in the polymer matrix, which causes the shells of the neighbouring multiplets to overlap (Fig. 6). An increase in the number of overlapped fragments leads to the formation of extended regions in which the mobility of the polymer chains is restricted. Rather large regions with own glass transition temperatures are treated as clusters, *i.e.*, microdomains of a certain phase.[17]

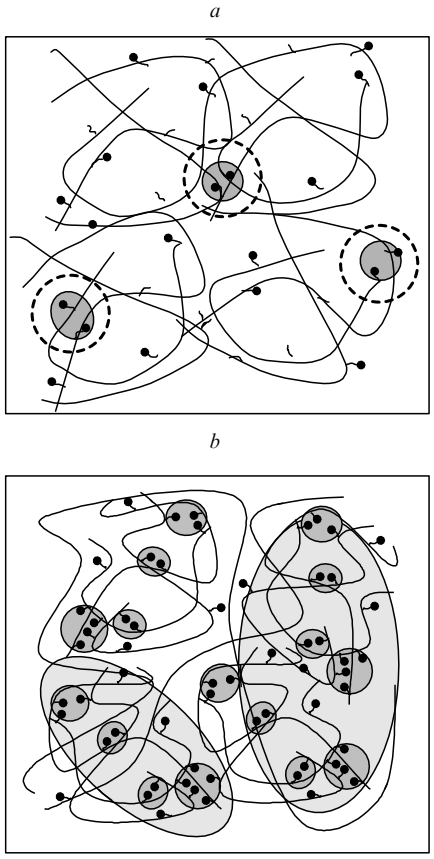


Figure 6. Transition from isolated multiplets (*a*) to clusters (*b*) caused by an increase in the content of ion pairs in polymer.
Dashed lines denote individual multiplet shells; clusters are shaded light grey.

A salient feature of the Eisenberg model is the absence of constraints imposed on the geometry (shape) of multiplets and clusters (ionic aggregates of various shape can be formed).[17] In the modern version of this model, in contrast to the first formulation[24] and a number of more recent studies,[33–37] electrostatic interactions between multiplets are not treated as *causa proxima* for clustering. It is assumed that multiplets in the cluster do not form a single aggregate and only contact one another owing to the overlap of their shells (*i.e.*, regions of restricted mobility of the polymer chains, see Fig. 6).[17]

Thus, the main elements of supramolecular organisation of ionomers are ionic aggregates comprising charged groups (multiplets and clusters). They strongly influence the surrounding polymer matrix, being responsible for the changes in its physicochemical properties (increase in the glass transition temperature, two-phase micromorphology, *etc.*).

Traditionally, LC polymers containing a low proportion of charged groups are treated as LC ionomers (see above). With allowance for the aforesaid, one can use this definition in a broader sense and consider LC ionomers as a specific class of high-molecular-mass compounds characterised by coexistence of the regions of LC ordering and ionic aggregates (multiplets or clusters of various shape). Below we will consider three main groups of LC ionomers, namely, comb-shaped ionomers (see Fig. 1 *a*), ionomers with mesogenic groups in the backbone (see Fig. 1 *b*) and telechelic polymers (see Fig. 1 *c*).

III. Thermotropic comb-shaped liquid-crystalline ionomers

The macromolecules of comb-shaped LC ionomers (see Fig. 1 *a*) contain two main types of side substituents, *viz.*, anisometric hard fragments (mesogenic groups) connected to the backbone through flexible spacers and charged ionogenic functional groups. They are responsible for the formation of LC order and the supramolecular structure characteristic of ionomers, respectively. Such a molecular architecture opens the possibility of using these compounds as promising models for studying the role of electrostatic interactions during the formation of mesophases in polymeric systems. Indeed, the concentration of charged groups can be varied with ease in the synthesis of LC ionomers; the upper limit of this concentration is governed by the proportion of functional fragments in the polymer matrix. This feature of the systems under study permits not only investigations of their phase states and structures upon a gradual change in the polymer composition but also, *e.g.*, efficiently influences the magnetic properties of ionomers containing transition-metal ions (see below). Besides, metal atoms can be introduced into virtually any part of a macromolecule (into the backbone, spacers, *etc.*); a vast variety of types of their bonding with the polymer substrate should also be pointed out. In other words, in comb-shaped LC ionomers it is possible to independently vary the nature and concentration of metal ions without changing the structure of the mesogenic fragment. This permits separate studies of the contributions of (i) mesogenic groups of the polymer matrix and (ii) metal atoms into the final characteristics of a compound.

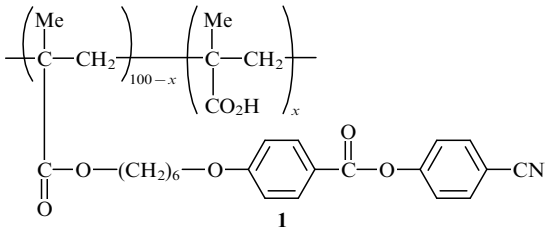
1. Metal-containing comb-shaped liquid-crystalline ionomers

There are only a few publications on the synthesis and investigations of comb-shaped LC ionomers available at the moment. Systematic studies in this field have been carried out by some research groups headed by Zhao (Canada),[45–49] by Zentel (Germany)[50–55] and by the authors of this review.[56–64] These studies concerned the synthesis and investigations of the general physicochemical characteristics[61,62,65,66] of LC ionomers containing alkali,[45–49,56,58] alkaline-earth,[60] transition-metal[50–55,61–63] and rare-earth metal ions.[64] The most important results of these investigations and the corresponding model for structural organisation of comb-shaped LC ionomers will be discussed below. This model, which is based on the concepts of formation of ionic aggregates and microphase separation of charged groups, relates the physical characteristics of a polymer to the concentration, chemical nature and charge of the metal ions and to the distance between the charged groups and the polymer backbone.

a. Liquid-crystalline ionomers containing alkali metals

Pioneering studies concerned with analysis of the phase characteristics and structure of comb-shaped LC ionomers containing metal ions were reported in the early 1990s. Zhao and Lei[45,46]

synthesised such compounds using radical copolymerisation of a mesogenic monomer with methacrylic acid.



1

x = 12.

Subsequent partial neutralisation of carboxyl groups of polymer **1** thus obtained with potassium carbonate in a benzene–methanol (95 vol.% : 5 vol.%)[45] mixture gave comb-shaped thermotropic LC ionomers **1**-K(x) containing at most 10 mol.% of potassium ions.‡ An increase in the degree of neutralisation of carboxyl groups led to an increase in the glass transition temperature, T_g, and in a decrease in the clearing point, T_c (*i.e.*, narrowing of the temperature range in which the mesophase exists (Fig. 7).

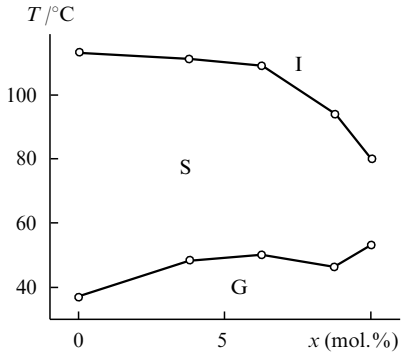
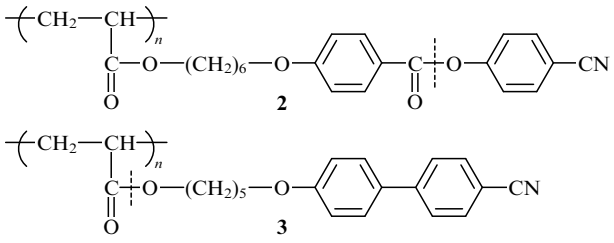


Figure 7. Phase diagram of LC ionomers **1**-K (x) containing potassium ions.[45]

Hereafter the following notations are used: I is isotropic melt, S is smectic phase and G is glassy state.

Another approach to the synthesis of ionomers involved partial alkaline hydrolysis of the side fragments of comb-shaped LC polymers **2** and **3**, which also leads to generation of charged groups.[46] The degree of hydrolysis was monitored using ^{1}H NMR spectroscopy, which revealed selective cleavage of the side groups of the LC polymers **2** and **3** (position of preferred hydrolytic cleavage of mesogenic groups under the action of alkali is shown by a dashed line). In the case of polymer **3**, charged groups appeared in close proximity to the backbone, whereas for polymer **2**, charged groups were distant from the backbone.



2

3

In contrast to LC ionomers **1**-K considered above, an increase in the content of sodium ions in the hydrolysis products of polymers **2** and **3** was accompanied by not only a decrease in the thermal stability of the liquid-crystalline phase but also a marked decrease in the glass transition temperature. Probably, hydrolysis of bulky side substituents favoured an increase in the kinetic flexibility of the backbone,[46] which leads to a decrease in T_g. Besides, the glass transition temperature could be strongly influenced by water molecules retained in the course of hydrolysis (they play the role of a plasticiser for ionic aggregates and, correspondingly, enhance the mobility of polymer chains).[17]

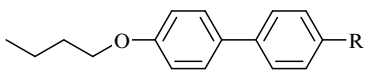
Based on the results obtained, Zhao and Lei concluded that the character of the influence of ionic aggregates on the formation of mesophase in comb-shaped LC ionomers is as follows. In accordance with the Eisenberg model (see above) they assumed that the mobility of mesogenic groups in comb-shaped macromolecules strongly depends on the conformational capabilities of the backbone in spite of the presence of flexible spacers. Mobility restrictions of the chains involved in the formation of multiplets cause defects in the packing of side mesogenic groups. As a consequence, the LC phase of ionomers becomes less stable with an increase in the content of the metal ion and its transition to isotropic melt is observed at lower temperatures as compared with the neutral polymer.[46] And although this explanation for the effect of ionic aggregates on the phase state of LC ionomers is questionable, it is based on commonly accepted concepts from physical chemistry of random ionomers[17] and is undoubtedly characterised by predictive power. This permits the use of the Zhao model for the interpretation of new experimental data.

A drawback of these methods for the synthesis of LC ionomers is the possibility of the hydrolytic cleavage of bonds in different positions of side groups with formation of products in which the charged groups are at different distances from the backbone. Investigations of such compounds revealed no influence of the position of the ionogenic groups on the physicochemical properties of the polymer phase. Besides, the polymer matrix must be purified of low-molecular-mass by-products and hydrolysis cannot be used for introduction of the transition metal and rare-earth metal ions, which significantly reduces the number of compounds to be studied. An exchange reaction involving an alkali[46] also seems to be somewhat inappropriate, because a strong base favours the occurrence of side reactions and the water molecules released play the role of a polar plasticiser and can therefore change the physicochemical properties of synthesised LC ionomers.

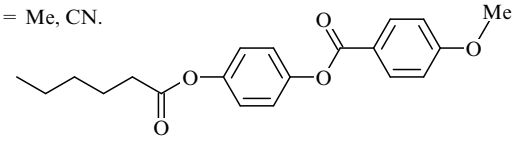
Recently, structurally similar polymeric systems have been investigated by researchers working at the Polymer Science Division (Department of Chemistry, M V Lomonosov Moscow State University), Institute of Macromolecular Compounds of the Russian Academy of Sciences and the Institute of Physics (Saint-Petersburg State University). Russian researchers first carried out a complex study of the dependence of the phase characteristics and structure of LC ionomers on the structure of initially functionalised LC copolymers (*i.e.*, on the chemical nature of mesogenic groups, length of aliphatic spacers, concentration of functional carboxyl groups), and on the concentration and charge (valency) of the metal ions.

It should be noted that the ionomers studied always contained not only loose and/or contact ion pairs but also a proportion of non-ionised carboxyl groups.

Mesogenic groups

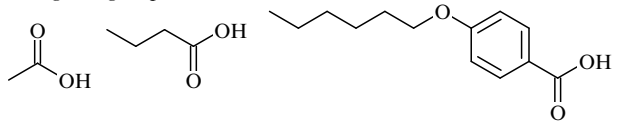


R = Me, CN.

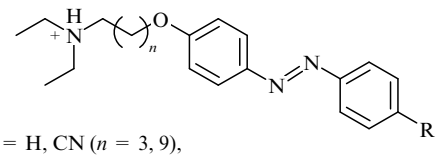


‡ Hereafter, hyphens in the notations of ionomers are followed by the type of counterion and its content (in mol.%) given in parentheses.

Ionogenic groups



Organic ions



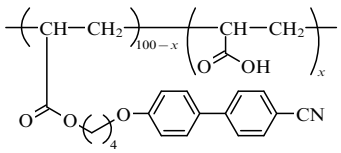
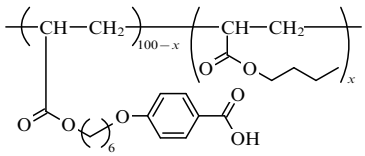
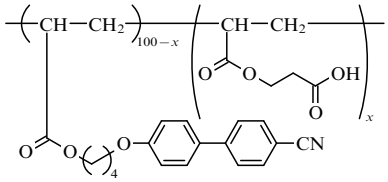
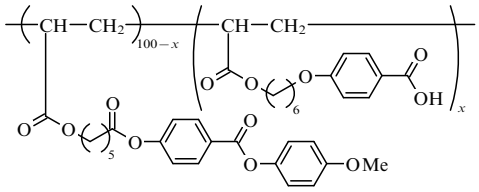
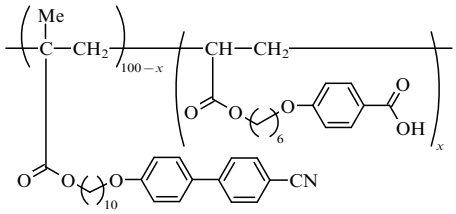
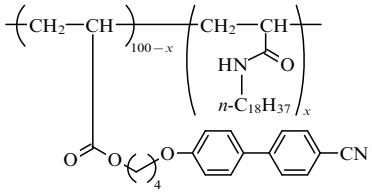
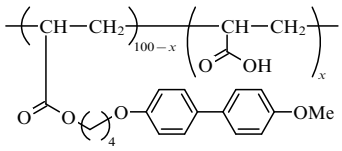
R = H, CN (n = 3, 9),

$H_3\overset{+}{N}-(CH_2)_n-Me$ (n = 9, 17);

counterions are Li^+, Na^+, Rb^+, Ca^+, Cu^{2+}, Co^{2+}, Ni^{2+}.

Comb-shaped LC ionomers were synthesised using an original two-step procedure.[56, 58, 67] The first stage involved a radical

Table 1. Random LC copolymers studied in Refs 56 – 65.

Chemical formula of copolymer	Compound	x (mol.%)	Degree of polymerisation	Phase transitions [a]
	**4a**	27	100	G 41 N 112 I
	4b	28	59	G 39 N 101 I
	4c	30	45	G 38 N 92 I
	4d	31	25	G 32 N 76 I
	4e	9	31	G 42 N 103 I
	4f	18	41	G 43 N 105 I
	**5**	30	45	G 40 SmA 109 I
	**6**	21	24	G 34 N 64 I
	**7**	28	14	G 18 N 95 I
	**8**	40	51	G 39 SmA 135 I
	**9**	10 – 39 45 – 60		N [b] SmB [b]
	**10**	44	55	S 144 I

[a] N is nematic; SmA, SmB are smectic types; figures denote transition temperature in °C. [b] Transition temperatures were not determined.

copolymerisation of two monomers (of, *e.g.*, acrylic or methacrylic series), one containing a mesogenic substituent (anisometric hard fragment) and the other bearing a functional substituent containing one or several ionogenic groups. In the second step the functionalised LC copolymers **4**–**10** thus obtained (see Table 1) were introduced into exchange reactions of functional carboxyl groups with metal acetates or metal acetylacetonates or with organic amine derivatives. For instance, metal-containing LC ionomers were obtained [56, 58] by adding a dilute solution of an acetate, $M(OAc)_n$, or acetylacetonate, $M(acac)_n$, in EtOH or THF to a dilute solution of the functionalised LC copolymer in dehydrated THF and subsequent stirring of the mixture for some hours and removal of low-molecular-mass reaction products *in vacuo*. This procedure offers a number of advantages over the alkaline hydrolysis of ester bonds considered above, because only functional carboxyl groups, whose proportion is specified in the stage of synthesis of LC copolymers, can react with salts of weak acids, and this method permits introduction of various metal ions M^{n+}. Acetic acid or acetylacetone released in the course of the reaction do not lead to hydrolytic cleavage of the side mesogenic groups, which is confirmed by the absence of hydrolysis products in the reaction mixture. The exchange reaction is characterised by high conversion. This is indicated by the absence of the unreacted salt in the polymer matrix after annealing of the polymer, confirmed by the data of polarisation optical microscopy and X-ray scattering.

Thus, the synthetic technique proposed allows a controlled amount of metal ions to be introduced into the macromolecules of comb-shaped LC copolymers with retention of the side mesogenic groups. By monitoring the formation of charged groups in macromolecules (as a rule, by IR spectroscopy [56, 67]) it is possible to establish the type of coordination between carboxylate ions and metal ions from the stretching vibration frequencies ν_{COO^-}. As applied to carboxylate complexes of the metal salts of low-molecular-mass monocarbonic fatty acids,[68] the monodentate coordination corresponds to the stretching vibration frequencies lying in the ranges $\nu_a = 1600-1630$ and $\nu_s = 1350-1380$ cm^{-1}; the frequency difference $\Delta = \nu_a - \nu_s$ in this case is 230–300 cm^{-1}. In the case of bidentate chelate coordination of the M^{n+} ion the band frequencies ν_a and ν_s approach each other (to 1500–1530 and 1440–1470 cm^{-1}, respectively).

In particular, the exchange reaction between ionogenic LC copolymer **4a** and sodium acetate is accompanied by the appearance of an absorption band of the carboxylate ion at 1578 cm^{-1}, the band intensity increasing with an increase in the metal content (Fig. 8 *a*). The formation of carboxylate ions was also indicated by a decrease in the intensity of the low-frequency and high-frequency wings of the complex band $\nu_{C=O}$ (1770–1690 cm^{-1}) corresponding to free (1740 cm^{-1}) and hydrogen bonded (1703 cm^{-1}) carboxyl groups of the initial LC polymer **4a**.[56, 67] Low frequency difference between the LC ionomers **5**-Rb and **5**-Na containing fragments of alkoxybenzoic acid ($\Delta = \nu_a - \nu_s = 46-53$ cm^{-1}) is an indication of bidentate chelate coordination. For **5**-Rb, the antisymmetrical and symmetrical stretching bands of carboxylate ions are shifted by 34 cm^{-1} to the high-frequency region compared to the frequencies of ionomers containing lithium ions (Fig. 8 *b*).

The authors of this review have synthesised metal-containing comb-shaped LC ionomers following the procedure mentioned above and studied their phase behaviour, structural and physicochemical characteristics. Differential scanning calorimetry (DSC) curves of a liquid-crystalline copolymer **4c** and ionomers **4c**-Na with various content of sodium ions are shown in Fig. 9. The DSC curves exhibit clearly seen characteristic transitions corresponding to the glass transition temperatures and endothermic peaks corresponding to the clearing point, *i.e.*, transition of the LC phase into isotropic melt. The introduction of alkali metal ions into the polymer matrix leads to marked broadening of the temperature interval of existence of the mesophase. For instance, the heat of transition to the isotropic phase ($\Delta H = 1-1.5$ J g^{-1})

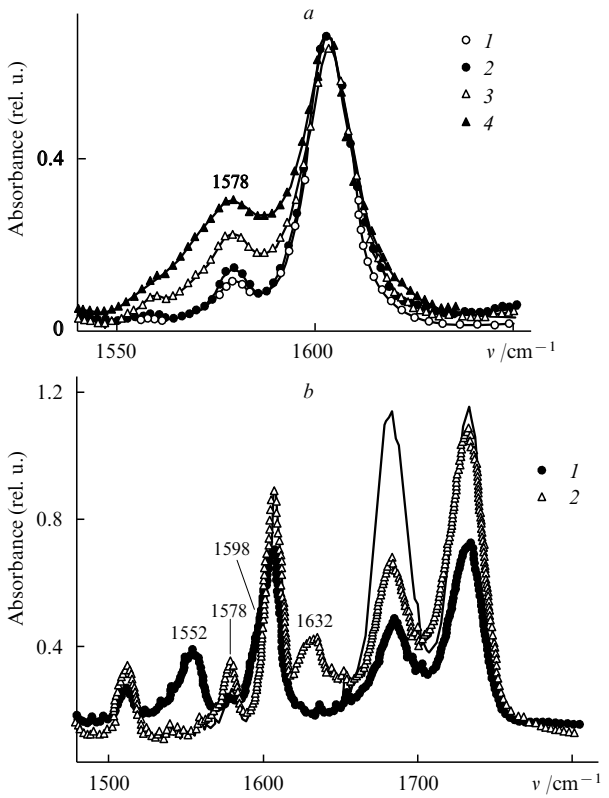


Figure 8. IR spectra of LC copolymers **4a** and LC ionomers **4a**-Na (*a*) and copolymer **5** (*b*) and ionomers **5**-Li and **5**-Rb (*b*).[67]
(*a*): **4a** (*1*), **4a**-Na(4%) (*2*), **4a**-Na(10%) (*3*) and **4a**-Na(20%) (*4*);
(*b*): **5** (solid line), **5**-Li (*1*) and **5**-Rb (*2*).

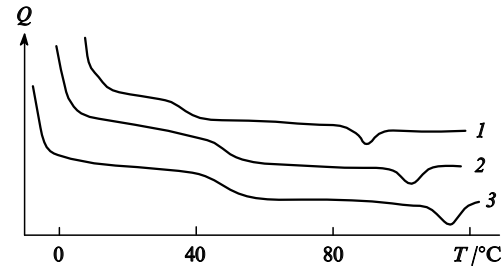


Figure 9. DSC curves of liquid-crystalline copolymer **4c** (*1*) and ionomers **4c**-Na(5%) (*2*) and **4c**-Na(10%) (*3*).[57]

obtained for the initial LC copolymer is characteristic of the nematic mesophase, being consistent with the polarisation microscopy data (Fig. 10 *a*). At the same time, ionomers are characterised by higher ΔH values ($\Delta H = 1.5-2.5$ J g^{-1}), which points to changes in their structure with an increase in the content of metal ions.

The liquid-crystalline phase of ionomers **4**-Na has a fan texture (Fig. 10 *b*); its SAXS diffraction patterns exhibit an intense maximum corresponding to the period $d_1 = 34.6 \pm 0.1$ Å (Fig. 11). Comparison of these data with the calculated length of mesogenic groups (~18 Å) suggests a layered packing of the polymer chains with partial overlap of side groups for **4**-Na.[56, 58] The 2D X-ray diffraction pattern of an oriented sample clearly demonstrates that diffuse large-angle and small-angle reflections are split in mutually perpendicular directions. Such a character of the X-ray diffraction pattern indicates that mesogenic groups of the polymer are oriented along the magnetic field direction and permits unambiguous identification of the LC phase as smectic A (SmA).

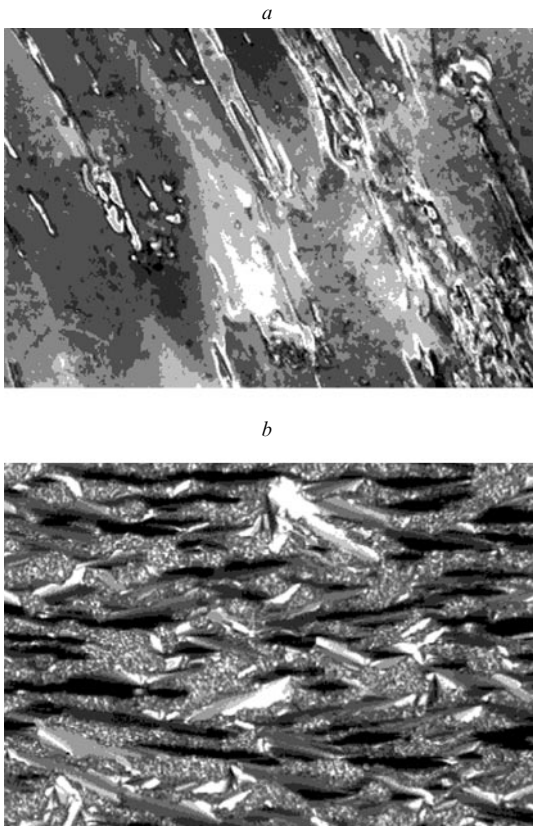


Figure 10. Characteristic optical textures of LC ionomers based on copolymer **4**.[57]
Texture: marble (*a*) and fan (*b*); magnification 200.

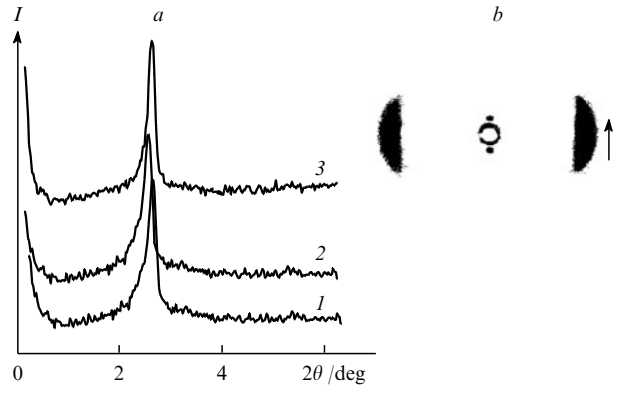


Figure 11. SAXS diffraction patterns (Cu K_α-radiation) of LC ionomers **4**-Na containing 1.2 (*1*), 5.0 (*2*) and 10.1 (*3*) mol.% of sodium ions (*a*) and 2D X-ray diffraction pattern of LC ionomer **4**-Na (2.3%) oriented in a magnetic field (*b*).[57]
The arrow denotes the magnetic field direction.

The phase diagrams of ionomers **4**-Na differing in degree of polymerisation P_w and content of carboxyl groups in the initial copolymer are shown in Fig. 12. Construction of typical phase diagrams of the ionomers based on the fractions of LC copolymers **4a**–**d** with a similar content of carboxyl groups and different molecular masses (MM) (Fig. 12 *a*) revealed the following.[56] First, replacement of protons in the functional carboxyl groups by Na^+ ions led to an increase in the temperature interval of existence of the mesophase §

§ The clearing point T_c and the glass transition temperature T_g respectively determine the upper and lower bounds of the existence region of mesophase in LC polymers.

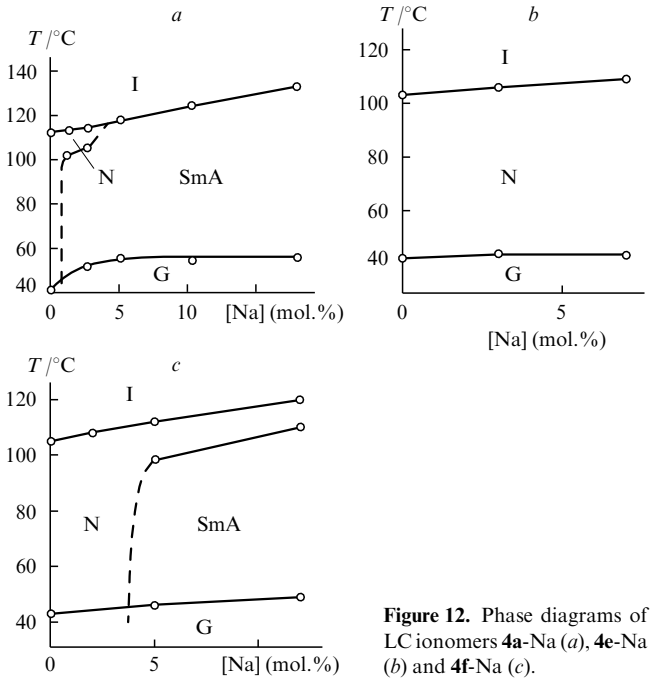


Figure 12. Phase diagrams of LC ionomers **4a**-Na (*a*), **4e**-Na (*b*) and **4f**-Na (*c*).

$$\Delta T = T_c - T_g .$$

Second, an increase in the content of sodium ions led to a nearly linear increase in the clearing point, whereas the glass transition temperature increased to some extent at Na^+ content of 2 mol.% – 5 mol.% and then remained unchanged. Third, introduction of metal ions into the polymer matrix led to a change in the phase state of the polymer, namely, not only the nematic phase but also the SmA phase was formed starting from a Na^+ content of 1.2 mol.%. The general pattern of the phase behaviour of LC ionomers **4**-Na was almost independent of the MM, whereas the clearing points of different fractions varied over a wide range upon variation of P_w (Fig. 13).

An extremely low concentration of charged groups inducing the appearance of a smectic phase should be pointed out. LC ionomers **4a**–**d**-Na are characterised by a similar content of sodium ions at which transition from the nematic to smectic mesophase occurs (< 1.2 mol.%). Nevertheless, even copolymers of identical composition contain different amounts of charged groups per macromolecule owing to a low degree of polymerisation and low concentration of metal ions. For instance, ionomers **4a**-Na(2%) with $P_w = 100$ contain on average two sodium ions per polymer chain, whereas the ionomers **4c**-Na(2%) ($P_w = 45$) and **4d**-Na(2%) ($P_w = 25$) contain the same number of sodium ions per two and four polymer chains,

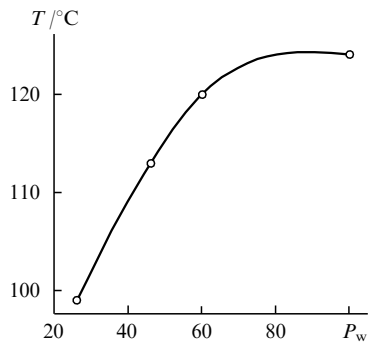


Figure 13. 'Liquid crystal – isotropic melt' transition temperature plotted *vs.* degree of polymerisation of LC ionomers **4**-Na(10%).[56, 57]

respectively. Thus, in the last-mentioned ionomer there are two polymer chains per Na^+ ion, *i.e.*, 50% of the total amount of polymer chains contain no charged groups at all. Meanwhile, even such a small amount of charged groups is sufficient to the change the phase behaviour of ionomers and to form a layered packing of the side mesogenic fragments. This observation has played a significant role in the development of model concepts of the structural organisation of LC ionomers (see below).

As shown above (see Section II), the modern theory of melts of random linear ionomers postulates the formation of ionic aggregates (multiplets, clusters) from charged groups in a nonpolar polymer matrix.[16,17] To a first approximation these aggregates can be treated as non-covalent cross-link points of the backbones. The authors assumed that it is the charged multiplets that have the structure-forming effect on the macromolecular system, resulting in broadening of the temperature interval of existence of the LC phases and in the appearance of the smectic phase.[56]

Often, the formation of smectic mesophases in comb-shaped LC polymers is attributed to microphase separation of the polymer chains and side mesogenic fragments.[3,5] The formation mechanism[57] of a smectic (lamellar) packing of side mesogenic groups involves the formation of a small amount of the simplest multiplets (quadruplets) comprising two ion pairs. Fixation of two polymer chains due to the formation of a quadruplet leads to a decrease in the entropy of macromolecules and facilitates the interaction of next ion pairs, resulting in the formation of a new ionic cross-link. Owing to a low degree of polymerisation (at most 100) the macromolecules of LC ionomers include only a few Kuhn segments.[69] Therefore, the presence of even a small amount of ionic cross-links must cause a substantial reduction of the number of possible conformations and rectification of the backbones of LC ionomers (because the number of segments between ionic cross-link points is insufficient for the formation of a bent chain fragment or a loop). It was theoretically substantiated[70] and experimentally proved[71] that the polymer chains of linear ionomers in the vicinity of multiplets are strongly rectified and their root-mean-square radii of gyration in the melt are larger than that of non-ionised copolymer. Rectification of polymer chains also reduces the translational mobility of side mesogenic groups, which apparently favours a transition from the nematic to smectic mesophase.

The molecular organisation of LC ionomers in the smectic mesophase is schematically shown in Fig. 14. Here, we deal with a 'shortcake'-type packing of macromolecules, which comprises layers formed by nonpolar (hydrophobic) mesogenic groups and layers formed by the main chains bearing ion pairs and functional carboxyl groups. It is logical to assume that an increase in polarity of the main polymer chains as a result of the presence of carboxyl groups and the appearance of charged groups will stabilise the layered structure, *i.e.*, favour broadening of the temperature interval in which the smectic mesophase exists.

The formation of multiplets was indirectly confirmed by a decrease in the solubility of ionomers in organic solvents and by an increase in the glass transition temperatures (see Fig. 12), which indicates that the polymer chains become more rigid. From the phase diagrams it is seen that changes in the glass transition temperature are most pronounced in a rather narrow range of compositions, being a maximum at 5 mol.% of Na^+ and then reaching a plateau. Probably, this means that at high content of charged groups in the polymer matrix the average distance between ionic cross-links of the polymer chains becomes shorter than the length of the Kuhn segment.

The size and structure of the multiplets responsible for the phase state of LC ionomers must depend on the chemical nature of metal atoms. Fig. 15 *a* presents the phase diagram of LC ionomers **4c**-Rb containing Rb^+ ions whose ionic radius exceeds that of Na^+ ion and Figure 15 *b* demonstrates the dependences of the clearing point on the concentration of alkali metal cation for related ionomers **4c**-Rb and **4c**-Na.

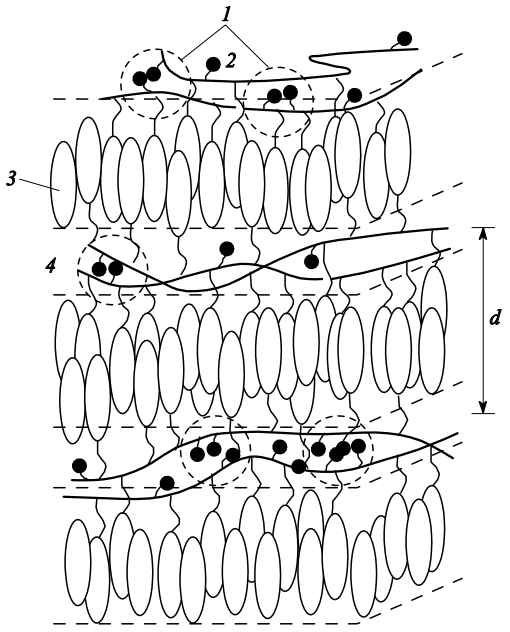


Figure 14. Model of the structure of smectic ionomer.
Multiplets (*1*), individual ion-containing groups (*2*), aggregation region of mesogenic groups in smectic layer (*3*) and aggregation region of the polymer chains and ion-containing groups in the interlayer space (*4*); *d* is the thickness of the smectic layer.

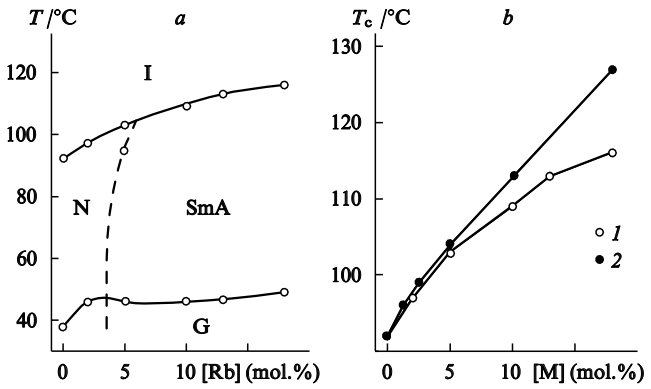


Figure 15. Phase diagram of LC ionomers **4c**-Rb (*a*) and clearing points (T_c) of ionomers **4c**-Na and **4c**-Rb plotted *vs.* metal content (*b*).[58]
Metal (M): Rb (*1*) and Na (*2*).

Comparison of the phase diagrams in Figs 12 *a* and 15 *a* shows that the phase behaviour of both types of LC ionomers obeys the same pattern. At the same time is it clearly seen that the clearing points of the ionomers containing Na^+ ions are somewhat higher than those of their Rb^+-containing analogues (Fig. 15 *b*). A higher rubidium concentration required for induction of the smectic phase should also be pointed out. We believe that this experimental result can serve as an additional substantiation of the formation of ionic aggregates in LC ionomers.[58]

Role of polymer composition. The results and model concepts considered above provide an incomplete explanation for the extremely low content of metal ions, which favours induction of the smectic mesophase in the LC ionomers **4**-Na. In this connection it is interesting to compare the character of the phase behaviour of ionomers with different side groups or differing in ratio of functional (ionogenic) and mesogenic fragments taking into account the published data for related comb-shaped LC ionomers.[45,46]

The effect of the composition and molecular architecture of the initial LC copolymers on the phase behaviour of corresponding ionomers was considered taking copolymers **4e**–**f** with smaller, compared to **4a**–**d**, initial content of carboxyl groups (see Fig. 12 *b*,*c*) as examples.[56] As can be seen in these phase diagrams, the increase in the clearing point with an increase in the content of metal ions becomes less pronounced (especially, for **4e**-Na), whereas induction of the smectic mesophase for **4f**-Na requires a higher concentration of Na^+; ionomers **4e**-Na retain the initial nematic phase over the whole range of investigated concentrations. Thus, a decrease in the total number of functional carboxyl groups in the initial LC copolymers **4a**–**f** makes the effect of metal ions much weaker, which is consistent with the concepts of microsegregation in comb-shaped polymeric systems (see Fig. 14).

The dependence of the phase state of LC copolymers **4** on the content of acrylic acid units (Fig. 16) shows that copolymers containing 30 mol.% carboxyl groups are near the induction region of the smectic mesophase. This means that a slight increase in polarity of polymer chains owing to introduction of additional carboxyl or ion-containing groups is sufficient for the formation of layered order. It is this effect that is achieved by replacing a small proportion of carboxyl protons by alkali metal ions. At the same time, polymer chains of the LC copolymers with a low content of acid groups are less prone to microphase separation and the induction of the smectic phase requires introduction of a much higher amount of charged groups into their macromolecules.

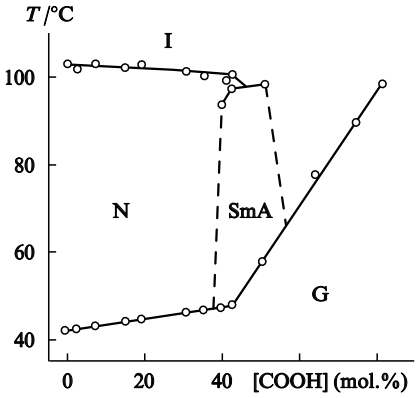


Figure 16. Phase diagram of copolymers **4** with different content of acrylic acid monomer units.[59]

It should be noted that consideration of the phase behaviour of LC ionomers in the framework of the modern theory of ionomers is consistent with its interpretation based on the concepts of microphase separation. Undoubtedly, the concept of microphase separation is more general in character because it can be applied to a broad range of polymeric systems containing structural units of different chemical nature. At the same time, model concepts in the field of physical chemistry of ionomers show how general regularities of the microphase separation work as applied to ion-containing macromolecules.

The model considered permits a clear interpretation of the increase in the clearing point of LC ionomers with an increase in the content of metal ions. Indeed, thermally induced disordering of the LC phase due to localisation of the mesogenic groups and main polymer chains in individual layers requires that not only the lateral interactions between mesogenic groups be overcome but also the layer comprising the main polymer chains and multiplets be broken down. The observed dependence can be explained by increasing the role of this additional structure-forming factor with an increase in the concentration of metal ions.

Role of the side chain length. From the modern theory of ionomers [17] and results of experimental studies [43, 44] it follows that an increase in the distance between charged groups and the polymer backbone can lead to more efficient formation of ionic aggregates due to lower steric hindrance. The influence of this effect on the phase behaviour of LC ionomers was studied taking copolymers [67] with functional groups linked to the backbone through flexible methylene spacers $(CH_2)_n$ as examples.

The phase diagram of LC ionomers **6**-Na containing charged carboxyl groups separated from the backbone by two methylene links is shown in Fig. 17 *a*. An increase in the proportion of charged groups in the polymer matrix causes a slight increase in the clearing point. At the same time these ionomers form only the nematic phase in the whole investigated range of Na^+ concentrations, which is confirmed by the polarisation microscopy and SAXS data.

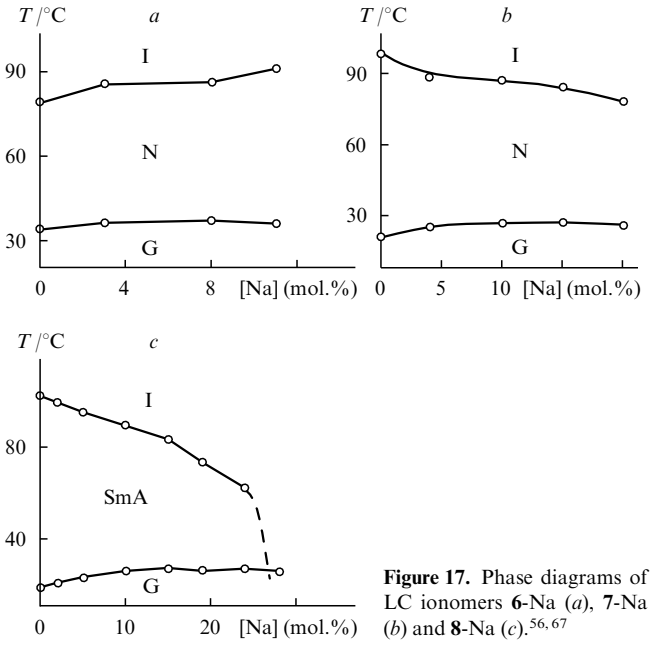


Figure 17. Phase diagrams of LC ionomers **6**-Na (*a*), **7**-Na (*b*) and **8**-Na (*c*).[56, 67]

Thus, in contrast to the ionomers **4**-Na and **4**-Rb containing functional carboxyl groups directly connected to the backbone, ionomers **6**-Na with distant ionogenic groups exhibit no induction of the smectic mesophase with an increase in the concentration of charged groups in the polymer matrix. The different character of the influence of metal ions on the phase behaviour of LC ionomers is schematically shown in Fig. 18 as the 'range of action' of multiplets on the polymer matrix. As can be seen, in the case of ionomers **4**-Na and **4**-Rb multiplets are formed in the vicinity of the backbone and can therefore decrease its entropy to the greatest extent by reducing the number of accessible conformations. At the same time in the ionomers with distant charged fragments (**6**-Na) this effect is weakened due to the presence of flexible spacers between multiplets and the backbone.

These effects must be even more pronounced with an increase in the distance between charged carboxyl fragments and the backbone. For instance, an increase in the concentration of sodium ions in LC ionomers **7**-Na with a long spacer $(CH_2)_6$ leads to reduction of the clearing point and only the initial nematic phase is retained over the whole range of compositions studied (Fig. 17 *b*). Thus, ionic aggregates formed in the ionomers under consideration play a destabilising role and cause disordering of the mesophase. A conclusion about the destabilising effect of the charged groups distant from the backbone on the ordering of side mesogenic groups in comb-shaped LC ionomers was also drawn earlier.[46]

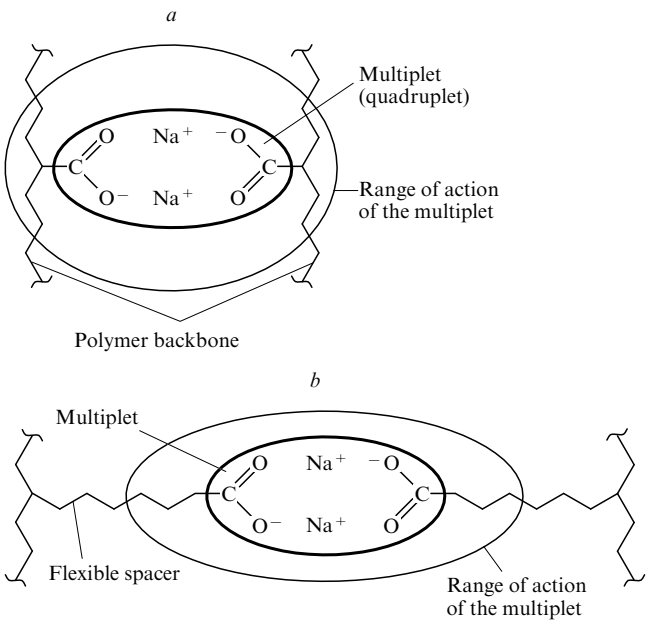


Figure 18. Schematic representation of the effect of ionic multiplets on the polymer matrix.[67]
Functional groups are bonded to the backbone (*a*), charged groups are distant from the backbone (*b*).

It was interesting to check for this effect in copolymers with a smectic rather than nematic ordering type of the side mesogenic groups. Figure 17 *c* shows retention of the smectic mesophase in LC ionomers **8**-Na in the Na^+ concentration range 0 mol.% – 25 mol.%; however, an increase in the content of metal ions in the polymer matrix leads to a decrease in the clearing point and breakdown of the liquid-crystalline state.[56]

Thus, by placing charged groups at longer distances from the backbone it is possible to efficiently influence the temperature range of existence of the mesophase in LC ionomers. As the length of a flexible spacer between charged carboxylate ions and the backbone increases, the trend towards formation of smectic phases becomes less pronounced; the clearing point decreases as the content of charged groups in the polymer matrix increases. Hence, the key parameters responsible for the formation of ionic aggregates and their influence on the phase state of ionomers include not only the composition of the polymer matrix, the chemical nature of the metal and the concentration of metal ions but also the distance between functional ionogenic groups and the backbone. In the text below we will show that most of these regularities governing the structure and properties of LC ionomers containing alkali metal ions also hold for more complex systems containing multiply charged ions.

b. Liquid-crystalline ionomers containing calcium ions

An increase in the content of Ca^{2+} ions in LC ionomers **4b**-Ca to 3 mol.% causes an increase in the melting point of the LC phase [60] (Fig. 19 *a*). According to solid-state ^1H NMR spectroscopy data, the incorporation of Ca^{2+} into the macromolecules **4b** not only presents no obstacles to the orientation of their side mesogenic groups in the magnetic field but is also accompanied by an increase in the orientation order parameter of the LC ionomers **4b**-Ca(3%). These results confirm the structure-forming effect of Ca^{2+} ions on the polymer matrix by the mechanism of ion association and microphase separation, which was considered above taking LC ionomers containing alkali metal ions as examples. But in contrast to Na^+-containing ionomers a further increase in the concentration of Ca^{2+} ions (> 3 mol.%) does not lead to an increase in the clearing point; this parameter reaches a constant value and then remains unchanged.

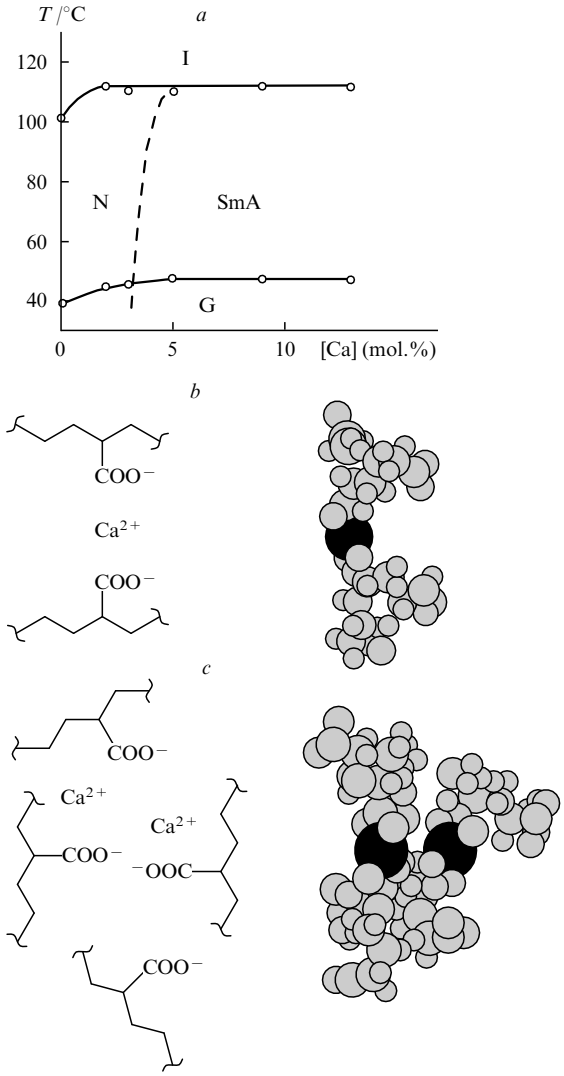


Figure 19. Phase diagram of LC ionomers **4b**-Ca (*a*), model of ionic cross-link (*b*) and the simplest multiplet (*c*) in LC ionomers containing calcium ions.[60]

This feature of the phase behaviour of Ca^{2+}-containing ionomers can be explained by a higher coordination ability of the doubly charged ions compared to alkali metal cations.[60] According to dynamic light scattering data, exchange of the polymer protons by singly charged ions (Na^+, Rb^+) in a dilute solution causes no aggregation of macromolecules that exist as isolated coils and the multiplets are formed only after removal of the solvent as a result of bringing ion pairs closer to one another. If we deal with multiply charged ions characterised by stronger coordination ability, polymer chains can approach one another in the course of the synthesis of ionomers with the formation of salt ionic cross-links (Fig. 19 *b*) or more complex aggregates (Fig. 19 *c*). Indeed, an increase in the molecular mass of such ionomers in solution was detected by gel-permeation chromatography and by light scattering. During removal of the solvent the aggregates formed in the stage of ion exchange can lead to a sterically unfavourable arrangement of macromolecules and induce the appearance of defects in the packing of the side mesogenic fragments, thus leading to destabilisation of the mesophase formed. Mutual compensation of the stabilising contribution of ionic aggregates (due to the microphase separation and chain stiffening mechanism) on the one hand and an increase in the number of defects on the other hand corresponds to reaching a plateau in the clearing point plot of ionomers containing Ca^{2+} cations (see Fig. 19 *a*).

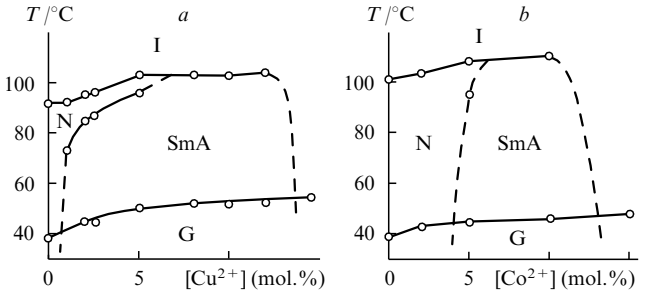


Figure 20. Phase diagrams of LC ionomers containing transition metal ions: **4c**-Cu (*a*) and **4b**-Co (*b*).[61–63]

c. Liquid-crystalline ionomers containing transition metal ions

The temperature dependences obtained for the liquid-crystalline ionomers containing doubly charged transition metal ions (Fig. 20) are in general similar to those found for Ca^{2+}-containing ionomers.[60] At the same time, optical polarisation microscopy and microcalorimetry data revealed breakdown of the liquid-crystalline phase at a concentration of M^{2+} (M = Co, Ni or Cu) ions of nearly 12 mol.%. This is probably due to the formation of coordination bonds between the M atom and oxygen atoms and terminal CN groups in the mesogenic fragments of the copolymer. A trend towards an increase in the coordination numbers of Co^{2+}, Ni^{2+} and Cu^{2+} ions to 4–6 was confirmed by the UV spectra of films and solutions of the corresponding ionomers.

Strong coordination bonds between transition metal atoms and the polymer matrix can cause a considerable increase in the concentration of defects in the matrix and produce steric strain. If the formation of an ionic cross-link involving a Ca^{2+} ion leads to fixation of two COO^- groups (and corresponding polymer chains), a transition metal atom can form additional bonds with a number of neighbouring mesogenic groups. At a sufficiently high concentration of transition metal ions (from 10 mol.%–15 mol.% in the compounds we have studied), enhanced defect formation in the mesophase leads to complete disordering.[61–64]

Important experimental information on the supramolecular organisation of comb-shaped LC ionomers, the state of charged groups in them and the influence of such groups on the polymer matrix can be obtained by studying the magnetic properties of corresponding derivatives containing Cu^{2+} ions.

The energy of exchange interaction between metal atoms in ferromagnets and antiferromagnets is known to be comparable with the thermal energy, which gives rise to co-operative magnetic phenomena.[72, 73] (In ferromagnets, the atomic magnetic moments are directed parallel to one another, while in antiferromagnets they are directed antiparallel and compensate one another.) A measure of the degree of correlation of the atomic magnetic moments is the exchange parameter *J*. Note that isolated transition metal atoms (*e.g.*, in a dilute solution) are not involved in the exchange interactions and, hence, can not induce co-operative magnetic phenomena.

Undoubtedly, investigations of the magnetic properties of LC ionomers are of considerable interest, because this makes it possible to establish the spin state of their metal atoms. The magnetic properties of compounds are described using a number of models of interacting metal atoms.[73] The simplest dimer model allows for the magnetic exchange between two metal atoms, while a more complex one-dimensional (1D) model considers infinite chains of interacting particles.

The temperature dependences of the magnetic susceptibility of LC ionomers **4c**-Cu in the temperature range 4.2–300 K (Fig. 21) revealed the absence of a maximum value and a low room-temperature magnetic moment characteristic of antiferromagnets. The experimental values of the magnetic susceptibility were approximated using the dimer model and the 1D Heisenberg model.

Table 2. Results of approximaton of the data on the magnetic susceptibility of LC ionomers **4**-Cu using the 1D Heisenberg model and the dimer model.[62]

Ionomer	Model	σ^2	$-J$ /cm^{-1}	C_m (%)	C_j (%)	$-\theta$ /K
4-Cu(9.9%)	1D	0.8	178	3.6	96.4	2.9
	dimer	28.0	349	15.3	84.7	26.0
4-Cu(5.0%)	1D	0.9	148	5.3	94.7	5.0
	dimer	20.5	265	12.7	87.3	16.3
4-Cu(2.5%)	1D	1.5	116	4.7	95.3	4.1
	dimer	1.8	264	22.2	77.8	−28.0

Note. Notations are as follows: σ^2 is the root-mean-square deviation of experimental data from the dimer model and 1D Heisenberg model; J is the magnetic exchange parameter; C_m and C_j are the concentrations of isolated and magnetically coupled copper ions; and θ is the Curie–Weiss constant.

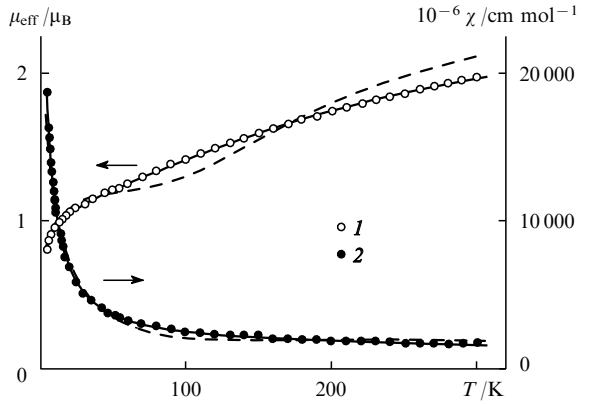


Figure 21. Magnetic moment (*1*) and magnetic susceptibility (*2*) of LC ionomer **4c**-Cu(9.9%) plotted *vs.* temperature .[61]
Full and open circles denote experimental data. Solid and dashed lines denote fits of experimental data by the 1D Heisenberg model and the dimer model, respectively.

Analysis of the approximation parameters (Table 2) showed that LC ionomers **4c**-Cu containing 2.5 mol.%–9.9 mol.% of copper atoms are antiferromagnets with high exchange parameters. At Cu^{2+} content from 5.0 mol.% to 9.9 mol.%, the temperature dependence of the magnetic susceptibility of ionomers is correctly described by the 1D Heisenberg model, whereas the use of the dimer model leads to marked deviations from the experimental curve. This unambiguously indicates that copper ions exist in LC ionomers in the form of complex aggregates.[62]

Low concentration (< 15%) of the Cu^{2+} ions not involved in the magnetic exchange should be pointed out. In the model of structural organisation of LC ionomers shown in Fig. 22 these ions correspond to isolated ionic cross-links. This fact is very important because it shows that steric hindrance in comb-shaped polymers with bulky side fragments (including the systems under study) does not preclude a trend towards formation of multiplets by the charged groups. At the same time it was impossible to propose an accurate structural model for magnetically interacting centres because of a limited number of compounds. Probably, copper atoms in the polymer matrix can be involved in both direct (if brought to close proximity) and indirect exchange through oxygen bridges of the ester groups.[74]

The magnetic properties of the LC ionomer **4**-Cu(2.2%) with low metal content are somewhat different from those considered above. This ionomer is also an antiferromagnet, but the root-mean-square deviations of the experimental data from both the Heisenberg model and the dimer model in this case are the same.

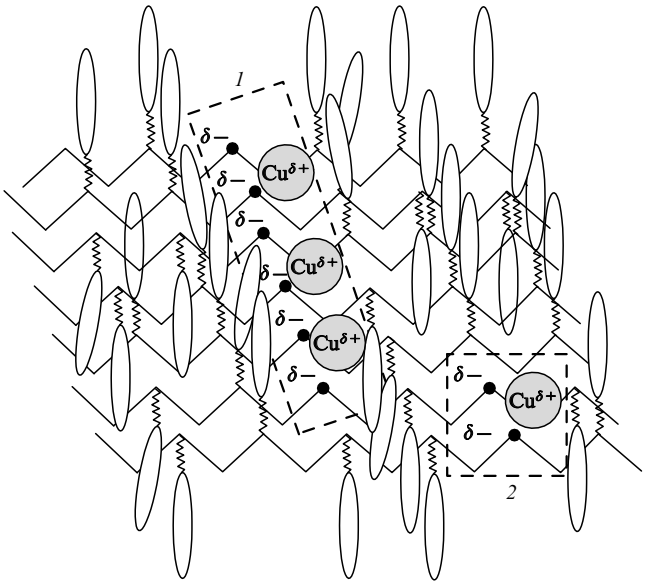


Figure 22. Model of LC ionomers containing Cu^{3+} ions (see Ref. 61). Multiplet (*1*) and isolated cross-link (*2*).

Thus, none of the models provides a correct description of the magnetism of compound **4**-Cu(2.2%). But it should be noted that manifestation of the antiferromagnetic properties at so low a copper content confirms the ability of charged groups to form aggregates (multiplets), because isolated copper atoms are not involved in co-operative magnetic interactions (see above).

Yet another approach to the synthesis of LC ionomers containing ferrocene in the side groups (**11a–c**) was reported in studies by Zentel *et al.*[50–55] (Scheme 1). The oxidation of ferrocene fragments to give cationic ferrocenium groups leads to some broadening of the interval of existence of the SmA phase and to a slight increase in the clearing points (Table 3). This can be explained by ordering of the mesogenic groups in the backbone (for details, see Section IV). The introduction of bulky isometric ferrocene fragments into the LC copolymer must lead to defect formation in the packing of the anisometric mesogenic groups. At the same time the oxidation of ferrocene groups produces ion pairs which tend to form aggregates that in turn form corresponding microphases. Thus, bulky ferrocene fragments can be treated as excluded from the mesophase and thus can affect its liquid-crystalline characteristics to a much lower extent.[55]

The formation of ionic aggregates in the ferrocene-containing LC ionomers investigated by the Zentel group was confirmed by the results of dynamic mechanical measurements, small-angle X-ray scattering and by the orientation features of nematic samples in electric field.[54] The temperature dependences of the mechanical loss factor tan δ and the elastic modulus showed that the LC ionomers studied obey the regularities known for weakly cross-linked polymeric systems. At the same time studies on the orientation of samples in electric field revealed an interesting feature that is atypical of conventional LC polymers, *viz.*, the Frederix transition threshold ¶ was almost independent of the presence of charged groups.[54] These experimental results were explained by the possibility of breakdown of ionic aggregates and formation of new aggregates in other domains of the polymer matrix upon the motion of the polymer chains under the action of external field. At the same time the influence of the multiplet structure manifests itself as a considerable (by an order of magnitude) increase in the reorientation time of the LC ionomers.

Dielectric spectroscopy studies and thermodepolarising current measurements were carried out to obtain information on the molecular mobility of copper-containing LC ionomers and to establish how ionic aggregates influence the local and segmental motions of the polymer chains and side mesogenic groups.[65] The incorporation of copper ions into the LC copolymer **4** led to a slight decrease (by 3–4 °C) in the temperatures of co-operative α- and δ-processes (Fig. 23), which respectively reflect the segmental mobility of the backbone and the reorientation of the side

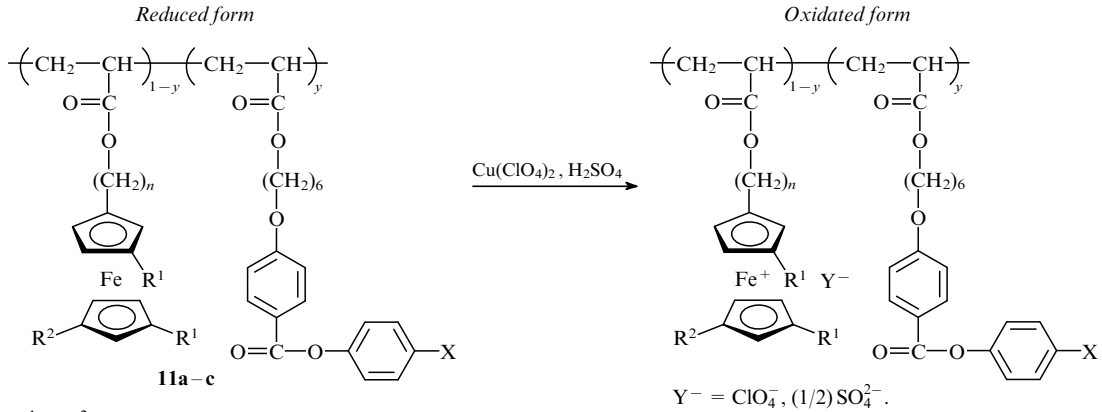
Table 3. Compositions and transition temperatures of comb-shaped ferrocene-containing LC polymers according to ^{1}H NMR data (see Ref. 54).

Polymer	*y* (mol.%)	Phase transitions	
		reduced form	oxidated form [a]
11a	4.3	G 28 SmA 82 N 108 I	G 32 SmA 84 N [b] (ClO_4^-)
11a	9.5	G 26 SmA 66 N 96 I	G 36 SmA 97 N I [b] (ClO_4^-)
11a	13.2	G 32 SmA 67 N 100 I	G 35 SmA 74 N 106 I (SO_4^{2-})
11b	2.7	G 28 SmA 85 N 110 I	G 32 SmA 87 N 105 I (SO_4^{2-})
11b	4.4	G 35 SmA 75 N 98 I	G 29 SmA 81 N 100 I (SO_4^{2-})
11c	2.3	G 30 N 115 I	G 32 N 118 I (SO_4^{2-})
11c	7.5	G 26 N 106 I	G 33 N 106 I [b] (ClO_4^-)
11c	8.3	G 30 N 94 I	G 37 N 95 I [b] (ClO_4^-)

[a] The counterion is given in parentheses. [b] With decomposition.

¶ The critical strength of external field at which the orientation of mesogenic fragments (direction of director) in liquid crystal sample changes.

Scheme 1



11a: $R^1 = R^2 = H$, $n = 2$; X = OMe;
11b: R^1 = Me, $R^2 = (CH_2)_2CH=CH_2$, $n = 4$, X = OMe;
11c: $R^1 = R^2 = H$, $n = 2$, X = CN.

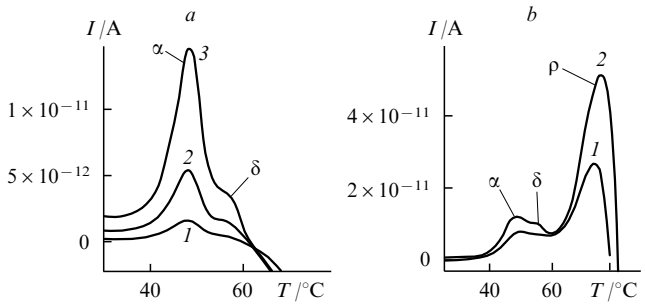


Figure 23. Depolarisation current plotted *vs*. temperature for copolymer **4** (*a*) and ionomer **4**-Cu(2.5%) (*b*).[65]
Polarisation temperature is 60 °C and the electric field strength is 50 (*1*), 100 (*2*) and 300 V mm^{-1} (*3*).

mesogenic groups of the copolymer, which proceeds at higher temperatures. At the same time studies of LC ionomer **4**-Cu(2.5%) at 74 °C revealed yet another intense co-operative ρ-process (also dipole in nature), which was characterised by significantly restricted molecular mobility compared to the α- and δ-processes.

The results obtained are consistent with the Eisenberg model of amorphous ionomers (see above), according to which the polymer chains in the multiplet shell are characterised by restricted mobility (see Fig. 5). The high-temperature process detected in the thermodepolarising current curves seems to correspond to the dynamics of the polymer chains in the regions of restricted segmental mobility in the multiplet shell. The temperatures of the local processes associated with the rotational mobility of the side mesogenic groups along the long axis and with the mobility of the methylene spacers are almost independent of the content of copper ions in the **4**-Cu ionomers.

All the LC ionomers discussed above belong to the acrylic and methacrylic series with nearly the same type of molecular architecture. Information on the systems with polysiloxane backbone [75] and comb-shaped LC ionomers with the charged groups localised within the backbone [76] is scarce. It is interesting that in last case the glass transition temperature and the clearing point of the liquid-crystalline phase depend only slightly on the structure of the side mesogenic fragments. This may be due to strong microsegregation of charged mesogenic fragments and poly(ethylene oxide) blocks incorporated into the backbone.

The results obtained in studies of comb-shaped metal-containing LC ionomers were analysed by the Zhao [45–48] and Zentel [50–55] groups and by the authors of this review. It was unambiguously shown that correct prediction of the physicochemical properties and structure of these compounds requires taking into account not only the concentration of charged groups but also some additional factors, *e.g*., the chemical structure of macromolecules, the structure of functional (ionogenic) fragments, methods of synthesis, *etc*. The phase state and the structure of this class of comb-shaped polymers are primarily determined by competition between such processes as the formation of mesophase due to the dispersion interactions of mesogenic fragments, the ionic aggregation of charged groups and the microphase separation of the backbone and the side fragments.

We believe, and this was confirmed by the results of investigations of LC ionomers of different chemical nature (see Table 1), that prediction of the structural features and phase behaviour of these compounds first of all requires taking into account positions of the charged groups relative to the backbone and the ability of the starting polymer to form a smectic order (so named smectogeneity). For instance, the formation of smectic packing is characteristic of comb-shaped ionomers with high content of acrylic acid units (> 30 mol.%) and cyanobiphenyl mesogenic fragments because of (i) the microphase separation between the polar chains and nonpolar side groups and (ii) ionic aggregation. At the same time a decrease in polarity of the backbone makes this tendency much less pronounced.

A fundamentally different situation occurs for those LC ionomers in which functional groups are distant from the backbone. Irrespective of the phase character of the initial copolymer these compounds exhibit a decrease in the clearing point with an increase in the content of the charged groups owing to the disordering effect of ionic aggregates on the surrounding mesogenic fragments.

The phase behaviour and structure of the systems with multiply charged metal ions depend on the structure of the polymer matrix in a more complex fashion. This is associated with the possibility of formation of ionic cross-links or coordination bonds. It seems to be that the most important feature of such compounds is breakdown of the mesophase (amorphisation) at high concentrations of transition (or rare-earth) metals. This imposes limitations on the design of functional materials or composites based on LC ionomers containing multiply charged metal ions.

2. Comb-shaped liquid-crystalline ionomersc containing organic counterions

A conventional method of preparation of thermotropic comb-shaped LC polymers involves the chemical addition of mesogenic groups to the side aliphatic branchings of comb-shaped polymers (Fig. 24 *a*).[3–5,7] At the same time an approach to the design of comb-shaped LC copolymers by electrostatically binding diphilic molecules to the polymer chain with the formation of polycomplexes (Fig. 24 *b*) has been intensively elaborated in the last decade. Research groups headed by Paleos,[77,78] Ujiie,[79,80] Bazuin [81–83] and Talrose [84–88] contribute largely to the development of this avenue. Physicochemical studies of various aspects of the structure formation and lyotropic mesomorphism in solutions of such polycomplexes can in fact be treated as a specific, important field of polymer science. It is necessary to emphasise that the subject of investigations carried out by all the research groups mentioned above is thermotropic mesomorphism, *i.e*., the ability of polymeric systems to form LC phases in a particular temperature range under solvent-free conditions.

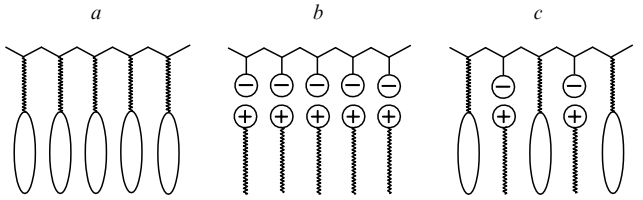


Figure 24. Schematic representation of the molecular structure of comb-shaped LC polymers with covalent (*a*), electrostatic (*b*) and mixed (*c*) type of addition of side groups.

Considerable advances in the design and synthesis of a novel class of thermotropic liquid-crystalline ion-containing polymers have been made by Russian scientists.[84–88] Polycomplexes obtained *via* molecular self-organisation of a polymer matrix and a low-molecular-mass amine form a smectic-type LC phase. It should be noted that the individual components of the complexes form no thermotropic mesophases. Conventionally used polymer matrixes include amorphous polyacids (polyacrylic acid, polymethacrylic or polymalonic acid) and polyvinylsulfonates. Amines can be chosen from a broader range of compounds, namely, from primary to quaternary amines with various structures of the lyophobic molecular fragment. The reaction between the polyacid and amine usually results in proton-transfer complexes.

It should be noted that basic to the mesomorphism revealed is the marked diphilicity of the polycomplex and the corresponding

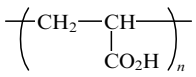
microsegregation processes rather than the rigidity or geometric anisotropy of the side groups. Such ionic complexes represent microheterogeneous systems in which the layered structures formed due to packing of the side chains are 'reinforced' with a network of electrostatic interactions and hydrogen bonds.[85] If one uses linear long-chain aliphatic amines, crystallisation of the complex involving the formation of crystalline or rotationally-crystalline phases is highly possible. At the same time it is assumed that incorporation of one or two aromatic or cyclohexane rings into the amine molecule must cause appreciable changes in the symmetry of the alkyl fragment, thus making crystallisation of the polycomplex less probable.[84]

Ion-containing polymeric LC systems obtained by non-covalent binding of the polymer chains to low-molecular-mass compounds are of considerable interest. Investigations of the properties of comb-shaped LC polymers of mixed structure (one type of the side groups of a macromolecule are covalently bonded while the other type of the side groups are attached through electrostatic interactions; Fig. 24 *c*)[89–92] are also of great importance. Polymeric systems containing relatively low concentrations of charged groups can be considered as a specific class of LC ionomers with organic counterions.

Mesomorphous ion-containing polycomplexes and comb-shaped LC ionomers with organic counterions exhibit a number of salient features distinguishing them from the metal-containing ionomer systems considered above. If the phase states and the structure of metal-containing ionomers depend on the chemical nature and concentration of metal ions and on the structure and mesomorphous characteristics of the polymer matrix, in the case of ionomers with organic counterions one should also allow for the concentration and structure of low-molecular-mass complexant. As will be shown below, long aliphatic or aromatic fragments of counterions can be involved in the formation of mesophase and also act as bulky packing defects of the side mesogenic groups.

a. Synthesis of liquid-crystalline ionomers containing organic ions

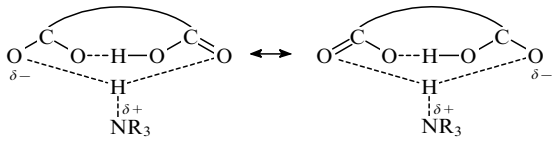
Ion-containing complexes of polyacids with low-molecular-mass amines are obtained by mixing the initial components in the same solvent (ethanol, chloroform, pyridine) followed by concentration of the mixture or by the deposition of the polymer complex in an appropriate solvent (ethyl acetate, diethyl ether).[83] For instance, the reaction between amines and polyacrylic acid



12

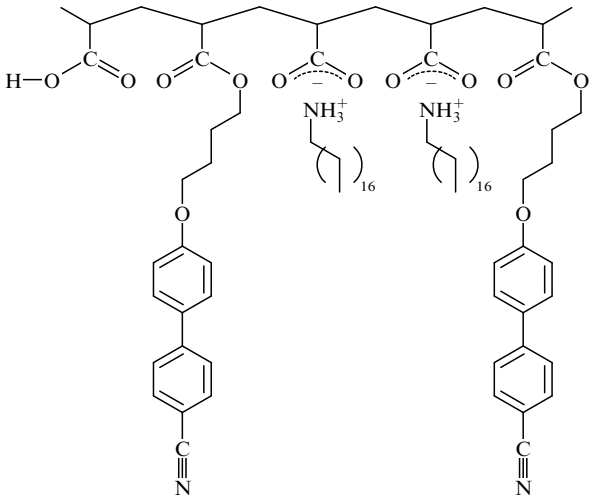
was detected[84–88] from opalescence and precipitation on mixing transparent solutions of the initial components in ethanol. Even at a large excess of amine in the initial solutions the characteristic composition of the solid complex corresponds to a 2 : 1 polyacid : amine ratio (two carboxyl groups per amino group).[84] At the same time for mixtures of polymethacryloyl-ω-aminocarboxylic acids with cetylamine $CH_3(CH_2)_{15}NH_2$ (see Ref. 88), complexes of all polyacids studied contain 60 mol.% – 70 mol.% of amine. Thus, the degree of substitution of carboxyl groups in these compounds depends only slightly on such characteristics of the polymer matrix as the distance between the COOH groups and the polymer chain.

Based on the results obtained in studies of model compounds (malonic and glutaric acids), it was proposed that non-stoichiometric complexes of polyacids are essentially stabilised by the intermolecular hydrogen bonds.[84] Seemingly, the case in point is the formation of a Y-shaped bond, because the proton involved in the strong hydrogen bond can form an additional H-bond with strong acceptors.



The reactions between polyacids and low-molecular-mass amines in a medium with low dielectric constant (THF) were also studied.[89–94] Good solubility of the polymer complex formed allowed complexes of controllable (stoichiometric) composition to be synthesised. The character of the polyacid – amine bond was studied in detail taking complexes of polymers **4d** and **10** with low-molecular-mass primary and tertiary amines as examples.

Analysis of the IR spectra of the products of the reaction between a nematic copolymer **4d** (based on acrylic acid and units containing mesogenic cyanobiphenyl groups) and octadecylamine $CH_3(CH_2)_{17}NH_2$ (**13**) revealed[89] the absence of the antisymmetrical and symmetrical vibrational bands of NH_2 groups (at 3340 and 3260 cm^{-1}, respectively) characteristic of the spectrum of the low-molecular-mass amine (Fig. 25). The spectrum of ionomer **4d**·**13** exhibited reduced intensities of the $\nu_{C=O}$ stretching bands of carboxyl groups. These data unambiguously point to the formation of an ionic complex *via* protonation of the amine NH_2 groups by the carboxyl groups of copolymer **4d**. A polymer chain fragment of ionomer **4d**·**13** is schematically shown below for the case of incomplete substitution of carboxyl groups of the copolymer **4d**.



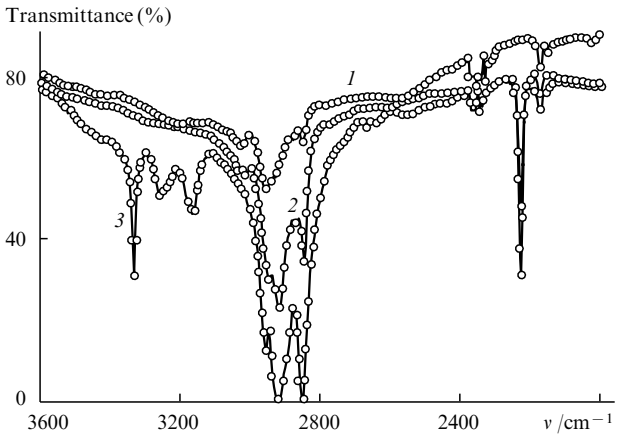
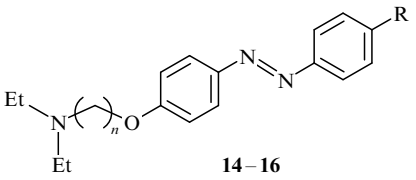


Figure 25. IR spectra of LC copolymer **4d** (*1*), ionomer **4d**·**13** (9%) (*2*) and low-molecular-mass amine **13** (*3*).[89]

In order to compare the ratios of the carboxyl groups involved and not involved in the formation of hydrogen bonds, differential IR spectra of mixtures containing different amine concentrations were studied.[89] A greater decrease in the band intensity of H-bonded carboxyl groups (at 1704 cm^{-1}) means that they are more accessible to complexation. An analogous conclusion was drawn [84] for the complexes of compound **12** with salts of tertiary amines (**14**–**16**) differing in the structure of the lyophobic fragment of the molecule.



14–**16**

14: R = CN, n = 10;
15: R = H, n = 10;
16: R = CN, n = 4.

The reaction between polyacid **12** and photochromic tertiary amine **15** was confirmed by IR spectroscopic data (Fig. 26).[92] An increase in the concentration of tertiary amine **15** in the mixture of compounds **12** and **15** leads to a decrease in the intensities of the ν_{O-H} and $\nu_{C=O}$ stretching bands in the regions 3100–3700 and 1650–1750 cm^{-1}, respectively. These changes are due to the decrease in the amount of carboxyl groups of polyacid **12** with an increase in the concentration of tertiary amine. The spectra of the complex obtained exhibit no intense ν_{C-H} band of the methylene group at the nitrogen atom of the initial amine (at 2788 cm^{-1}). The formation of a proton-transfer complex is also indicated by the appearance of the N–H stretching bands at 2505 and 2610 cm^{-1}. A similar character of products of the reaction between acid **12** and a tertiary amine was revealed in studies.[85–87]

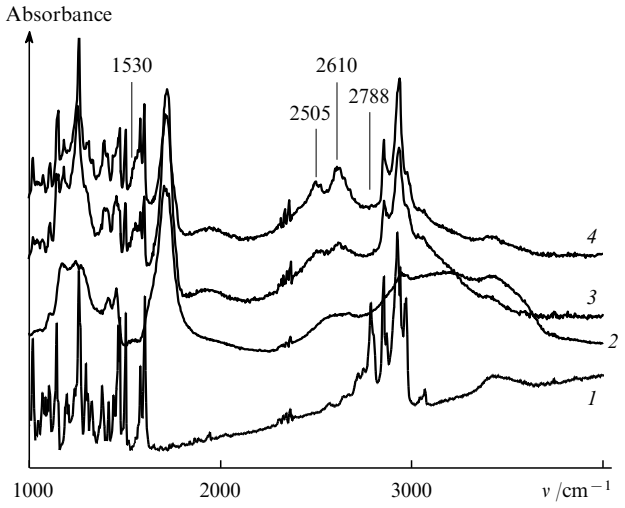


Figure 26. Fragments of IR spectra of polymer **12**, photochromic tertiary amine **15** and their mixtures with different content of amine **15**.[92]
Content of amine **15** (mol.%): 100 (*1*), 0 (*2*), 29 (*3*) and 44 (*4*).

b. Structural organisation of liquid-crystalline ionomers containing organic ions

We will consider salient features of the phase behaviour of LC ionomers containing organic ions taking ionic complexes of nematic copolymer **4** with primary amine **13** [59, 89, 90] as examples. Mixtures with octadecylamine concentrations from 6 mol.% to 29 mol.% were obtained in THF solutions for this system. Investigations of samples with different concentrations of amine **13** allowed us to establish how sequential 'build-up' of a comb-shaped polymer by non-mesogenic low-molecular-mass amine molecules (see Fig. 24 *c*) affects the state and thermal stability of the mesophase. This approach provides an effective method of

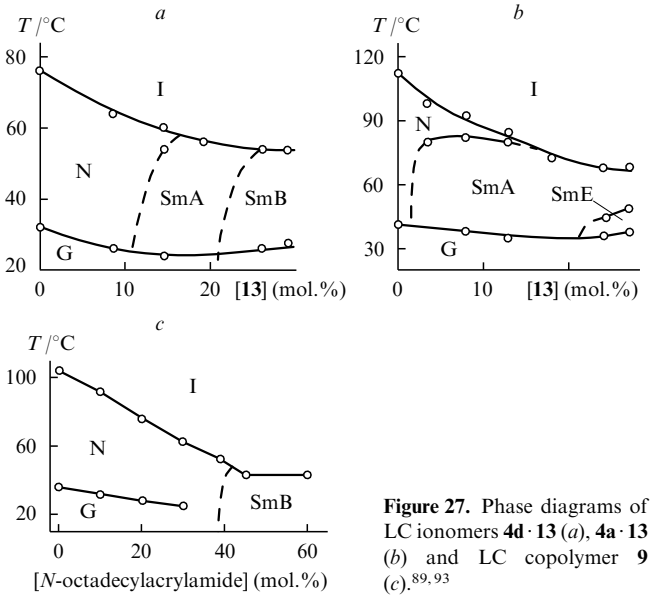


Figure 27. Phase diagrams of LC ionomers **4d**·**13** (*a*), **4a**·**13** (*b*) and LC copolymer **9** (*c*).[89, 93]

structure modification of comb-shaped LC copolymers and opens prospects for additional functionalisation of these compounds.

The phase diagrams of the LC ionomers **4**·**13** obtained using fractions of copolymer **4** with different molecular masses are shown in Fig. 27.[89, 90] Noteworthy is the disappearance of the nematic phase characteristic of the initial ionogenic copolymer and the formation of the SmA phase at concentrations of amine **13** of 5 mol.%–14 mol.%. Thus, the phase states of LC ionomers containing organic ions and metal cations obey similar patterns, namely, an increase in the content of charged groups is accompanied by an increase in the ordering of the side mesogenic fragments.

With allowance for the (i) phase transformations and structures of metal-containing LC ionomers (see above) and (ii) model concepts proposed for their interpretation, the formation of the smectic mesophase in the systems based on copolymers with organic counterions seems to be quite reasonable. Indeed, the formation of supramolecular aggregates and microphase separation, which plays a key role in the formation of mesophase, are primarily governed by the presence of ion pairs rather than the nature of the functional groups and counterions they are comprised of. Hence, all considerations concerning the character of the effect of the concentration of charged groups, the composition of the polymer matrix and the distance between functional groups and the backbone must also hold for the complexes of polymers with organic amines. The correctness of this approach is apparently confirmed by the features of the phase diagrams in the systems **4**·**13** (see above). However, the nature of the counterion can also influence the phase state of the complexes obtained and impart them in some cases the properties characteristic of the organic amine added.

Thus, the formation of the SmA phase in the LC ionomers **4**·**13** is governed by ionic aggregates. The effect of the aliphatic groups of octadecylamine manifests itself at high concentrations of this compound, which is associated with manifestation of the effects of microphase separation in the side groups of the comb-shaped polymer. If the concentration of amine **13** exceeds 24 mol.%, more ordered smectic mesophases (SmB, SmE) are formed. Samples with the degree of polymerisation P_w = 25–59 form the smectic B phase while those characterised by P_w = 100 form the smectic E phase. Apparently, the formation of these ordered mesophases is due to the microsegregation of long methylene chains of amine **13**.

This assumption was tested taking copolymers **9** of a mesogenic monomer 4-[(4′-cyano-1,1′-biphenyl-4-yl)oxy]butyl acrylate with *N*-octadecylacrylamide as examples. In these copolymers, the

octadecylamide fragment is chemically bonded to the polymer chain (Fig. 27 *c*). Microcalorimetric and X-ray diffraction studies showed that copolymer **9** forms an ordered mesophase with hexagonal packing of the side groups. However, this occurs at a much higher content of non-mesogenic monomer units (> 40 mol.%) compared to the series **4**·**13** (25 mol.% of amine **13**). An increase in the content of aliphatic units in LC copolymers **9** leads to a faster (compared to ionomers **4**·**13**) decrease in the clearing points. A broad range of the nematic phase (> 40 mol.%) and the absence of induction of the SmA phase in copolymers **9** should also be pointed out.

In a continuation of these investigations, comb-shaped functionalised LC complexes containing tertiary amine molecules **14**–**16** with azobenzene fragments were obtained.[91,94] Photochromic organic counterions were chosen to attain two goals, *viz*., the incorporation of ion-containing groups simulating the structure of low-molecular-mass liquid crystals and the use of the ability of *para*-substituted azobenzene derivatives to undergo *cis*–*trans*-isomerisation and photo-orientation on exposure to polarised laser light.[95] The LC ionomers obtained are light-sensitive materials and can be used for recording and storage of optical information. A study of the kinetic curves of growth and of the relaxation of photo-induced birefringence revealed the influence of the electrostatic binding of the photochromic molecules with the polymer matrix on the character of photo-optical processes.[91,92]

The phase diagrams of the mixtures based on nematic compound **4c** and smectic compound **10** with low-molecular-mass components **14** and **15** are shown in Fig. 28. Irrespective of the phase state of the initial copolymer an increase in the concentration of dye in the mixture causes a monotonic decrease in the clearing point and the glass transition temperature; at a content of the photochromic component in the 15 mol.% – 34 mol.% it undergoes partial crystallisation. All the mixtures based on the ordered smectic phase retain an orthorhombic pattern of packing of the side mesogenic groups in the smectic layer. An increase in the content of amine **16** only leads to thickening of the smectic layer due to the 'build-up' of the copolymer by photochromic amine groups, which are longer than the biphenyl mesogenic groups of the initial LC copolymer **10**. It should be emphasised that the addition of amine **15** (5 mol.%) to nematic polymer **4c** is accompanied by a change in the phase state, *viz*., the formation of smectic phase and complete disappearance of nematic phases.

In these LC ionomers photochromic amines are not only involved in microphase separation and ionic aggregation but also induce the formation of defects during the ordering of side fragments, which governs the formation of mesophase. The role of defects can be played by bulky fragments of quaternary ammonium cations arranged near the polymer chain. Besides, long aliphatic bridges between the azobenzene fragment and the tertiary amino group hamper simultaneous packing of the photochromic and mesogenic groups of LC copolymers, which manifests itself in a decrease in the clearing point and the enthalpy of melting of the LC phase with an increase in the content of amine. The use of amine **16**, containing a shorter spacer, is accompanied by a slight decrease in this negative influence. For example, an increase in the amine content in smectic ionomers **10**·**16** is accompanied by a much lower decrease in the clearing temperatures than in ionomers **10**·**14** (Fig. 28 *b*).

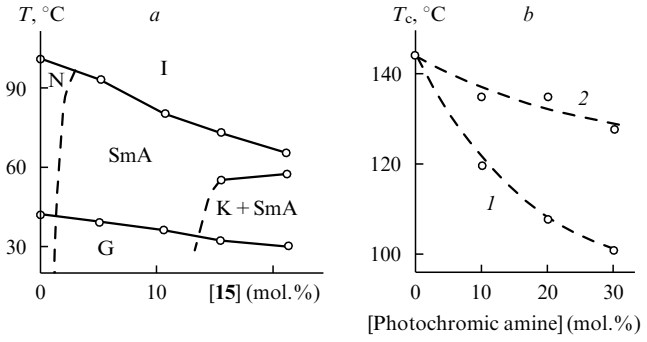
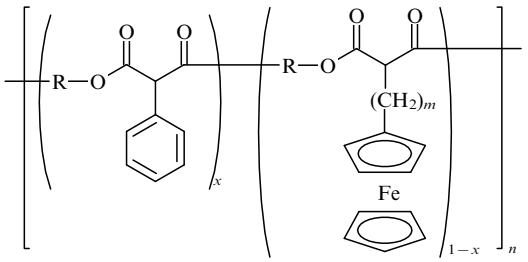


Figure 28. Phase diagram of LC ionomers **4c**·**15** (*a*) and dependence of clearing point an concentration of photochromic component for LC ionomers **10**·**14** (*1*) and **10**·**16** (*2*) (*b*).[91,94]

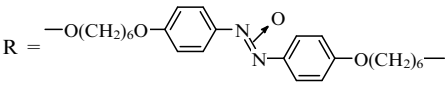
IV. Liquid-crystalline ionomers with mesogenic groups in the main chain

A significant role in the development of approaches to the synthesis of ferrocene-containing LC ionomers has been played by the studies of Zentel *et al*.[55,96–99] who showed that incorporation of ferrocene fragments into the polymer backbone followed by their oxidation produces no pronounced changes in the phase state of the systems under study.[97,98] This may be due to considerable steric hindrance to the formation of ionic aggregates in related polymeric systems. It is known that the macromolecules of LC polymers with mesogenic groups in the backbone adopt extended conformations. Due to the entropy and steric factors, this can be a possible reason for hindered interaction of charged groups, resulting in the formation of multiplets.

In order to reduce steric hindrance in the formation of ionic aggregates, a series of linear LC copolymers **17a**–**f** was obtained[98] by polycondensation. In these macromolecules, the ferrocene fragments were separated from the backbone through a flexible aliphatic bridge $(CH_2)_m$.



17a–**f**



The ferrocene groups were oxidised by mixtures of *p*-benzoquinone with sulfuric or methylsulfonic acids or by a mixture of copper(II) perchlorate and perchloric acid.

The effect of the nature of the oxidant counterion Ox on the phase behaviour, structure and thermal stability of LC ionomers (**17a**–**f**)·Ox can be followed from the data listed in Table 4. In the case of the hydrosulfate and methylsulfonate counterions the compounds obtained are stable on heating above the clearing point, whereas systems with the perchlorate counterions slowly decompose under identical conditions. Irrespective of the nature of the counterion incorporation of charged groups into the macromolecule leads to some increase in the glass transition and clearing temperatures. If an increase in T_g is typical of ionomers, an increase in T_c is associated with microsegregation of the ferrocene fragments (see above), which facilitates packing of the mesogenic groups in the linear polymer (Fig. 29).

For the systems with charged groups smaller than ferrocene ions one can expect the formation of more stable ionic aggregates. Sulfite and phosphate groups were chosen[99] as candidates. The initial LC polymer **18**, to which charged groups were attached, forms a nematic rather than smectic mesophase unlike the derivatives **17a**–**f**. With allowance for this fact it was proposed that the formation of ionic aggregates in this polymer matrix will be associated with lower steric constraints and smaller entropy limitations.

Table 4. Phase transition temperatures of ferrocene-containing LC polymers **17a**–**f** and LC ionomers (**17a**–**f**)·Ox with mesogenic groups in the backbone.[55,97]

Polymer	*m*	Phase transitions in polymer	Phase transitions in oxidised LC ionomer **17**·Ox		
			Ox = $MeSO_3^-$	Ox = HSO_4^-	Ox = ClO_4^-
17a	2	G 20 SmA 120 I	G 20 SmA 121 I	G 20 SmA 121 I	G 21 SmA 121 I
17b	3	G 17 SmA 111 I	G 18 SmA 115 I	G 17 SmA 115 I	G 24 SmA 119 I
17c	4	G 18 SmA 102 I	G 22 SmA 107 I	see [a]	G 27 SmA 112 I
17d	5	G 14 N 83 I	G 22 SmA 81 N 105 I	see [a]	see [a]
17e	7	G 20 SmA 110 I	G 23 SmA 115 I	see [a]	see [a]
17f	8	G 15 SmA 105 I	G 18 SmA 108 I	see [a]	see [a]

[a] Compound was not obtained.

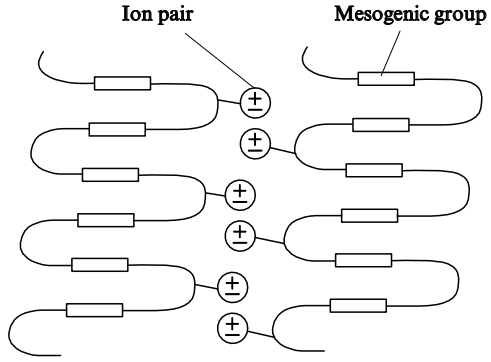
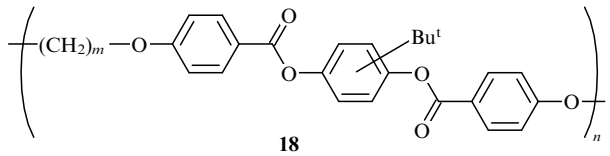


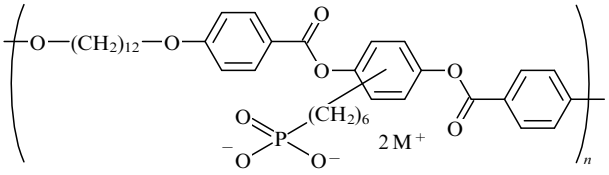
Figure 29. Schematic illustration of microsegregation of ionic multiplets and mesogenic groups in linear ferrocene-containing LC ionomers.[97]



18

Experiments showed that the LC ionomers **19** and **20** with sulfite ions exhibit a monotonic increase in the clearing point and a decrease in the glass transition temperature with an increase in the content of charged units. This was explained by the impossibility of efficient formation of ionic clusters in the absence of a spacer connecting the charged groups to the polymer backbone (reduction of T_g) and by an increase in the anisometry of macromolecules upon incorporation of charged fragments (increase in T_c), because these fragments are more anisometric than the mesogenic groups themselves.

The opposite was observed for LC ionomers **21a**,**b** with the phosphate charged groups separated from the backbone by flexible spacers. The glass transition temperatures of ionomers considerably increase compared to the T_g value of the uncharged polymer. This was associated with the formation of ionic clusters. At the same time the clearing point of compound **21a** somewhat decreases while ionomer **21b** forms no LC phase at all, which can be explained by the undesired steric effect of the bulky counterion.[99] However, since these polymers contain charged groups in all monomer units, the interpretation of their properties based only on the model of random ionomers may be to some extent incorrect.

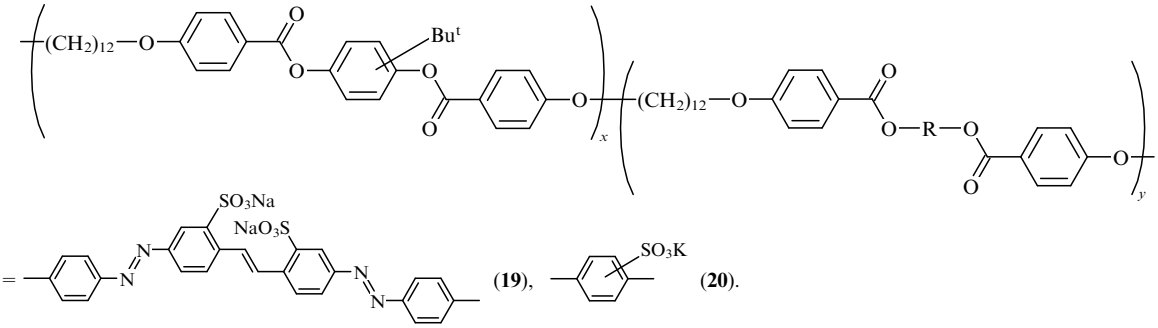


21a,**b**

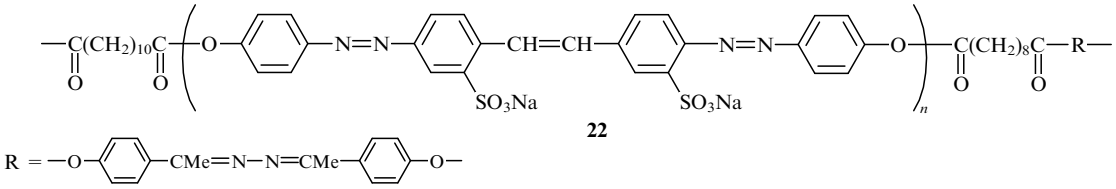
$M^+ = (1/2)\,Ba^{2+}$ (**21a**), $NH_2(C_6H_{12})_2^+$ (**21b**).

The phase behaviour of structurally similar LC ionomers **22** was also studied.[100] It was established that an increase in the content of charged groups in these systems is accompanied by a decrease in the glass transition and clearing temperatures and the systems become more prone to thermal degradation. The decrease in T_g was associated with a decrease in the molecular mass of ionomers on an increase in the content of charged groups. At the same time, the overall narrowing of the temperature range of the existence of mesophase is due to undesired influence of ionic aggregates which play the role of packing defects in the mesogenic fragments. An additional confirmation of this conclusion is provided by the fact that the temperatures of transition to the isotropic phase for a number of ionomers with similar molecular masses decreased to a greater extent as the proportion of charged groups increased.[100] Thus, the model assuming the formation of microphases comprising ionic aggregates and corresponding improvement of packing of mesogenic groups (see above)[55] is inapplicable to these ionomers.

Important information on the ionic dissociation in LC ionomers **22** was obtained in solution studies of the behaviour of macromolecules. The solubility of samples of compounds **22** in chloroform decreased in a regular fashion with an increase in the content of charged groups and the concentration dependence of



R = (**19**), (**20**).



22

the reduced viscosity was strongly different from the linear dependence characteristic of the initial polymer. Additional experiments showed that at low concentration of ionomer **22** in solution intramolecular ionic interactions favour a decrease in the size of the polymer coil, whereas at high concentrations of the ionomer the interaction of macromolecules is accompanied by a dramatic increase in the reduced viscosity. Thus, solutions of these LC ionomers excellently obey the regularities established in studies of amorphous random ionomers.[16]

Analysis of the data on the LC ionomers with mesogenic groups in the backbone provides an additional confirmation of the occurrence of ionic association in mesomorphous polymeric systems. However, a correct interpretation of the changes in the phase behaviour and structure, induced by the incorporation of charged groups in the polymer, requires taking into account a number of factors similarly to the case of comb-shaped ionomers.

V. Thermotropic liquid-crystalline chelato-telechelic polymers

The so-called LC chelato-telechelic polymers (see Fig. 1 *c*) represent a specific class of liquid-crystalline ionomers with unusual chemical structure and a vast variety of supramolecular structures. These are ionic complexes of anisometric low-molecular-mass compounds (mesogenic groups) with terminal functional groups of the polymer chains (Fig. 30). Intensive studies of these compounds have been carried out in a research group headed by Jerome.[101–105]

Liquid-crystalline chelato-telechelic ionomers are usually characterised by a low content of charged groups. The SAXS diffraction patterns of these compounds exhibit a characteristic 'ionic peak' (Fig. 31). Possible types of structural organisation [105] of these compounds are schematically shown in Fig. 32.

As mentioned above, the ionic peak is a direct indication of the formation of ionic aggregates (multiplets and clusters) responsible for specific features of the structure and physicochemical properties of ionomers. At the same time, microcalorimetric, polarisation microscopy and X-ray scattering data unambiguously confirm the possibility for mesophases to exist in such polymeric systems. The formation of smectic mesophases only was observed for all studied compounds as a result of combination of ionic interactions and microsegregation. It should be noted that the ionic and mesogenic (*i.e.*, corresponding to the packing of mesogenic groups) reflections can appear in the diffraction patterns of LC chelato-telechelic polymers together or separately, which points to a complex character of supramolecular organisation of this type of compounds.[105]

According to Gohy and Jerome,[105] the key factors responsible for the supramolecular structure of LC chelato-telechelic polymers are the tendency of mesogenic fragments to form a liquid-crystalline order and the ionic aggregation of charged groups precluding this ordering (see Fig. 32). Some other factors, *e.g.*, the character of the bonds between functional groups of the polymer and mesogenic fragments, the glass transition temperature of the polymer (*i.e.*, the backbone flexibility), the molecular mass of the polymer and the mass fraction of mesogenic groups in the polymer matrix should also be taken into account. Let us consider them in more detail.

Let a terminal group of a polymer be connected to the mesogenic fragment owing to the formation of an ion pair with large dipole moment. In such polymeric systems, one should first of all expect the formation of ionic aggregates, which can suppress the structural organisation of mesogenic fragments, all things being equal.[105] This is characteristic of, *e.g.*, LC chelato-telechelic polymers with terminal sulfonic acid groups, whereas typical of

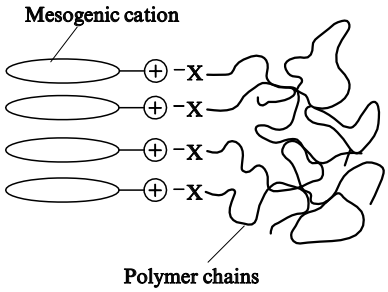


Figure 30. Chemical structure of linear LC chelato-telechelic polymers containing carboxyl groups ($X^- = COO^-$) and sulfonic acid groups ($X^- = SO_3^-$).[105]

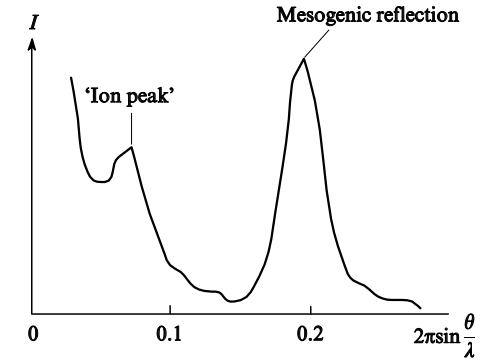


Figure 31. SAXS diffraction pattern of LC chelato-telechelic polymers.[105]

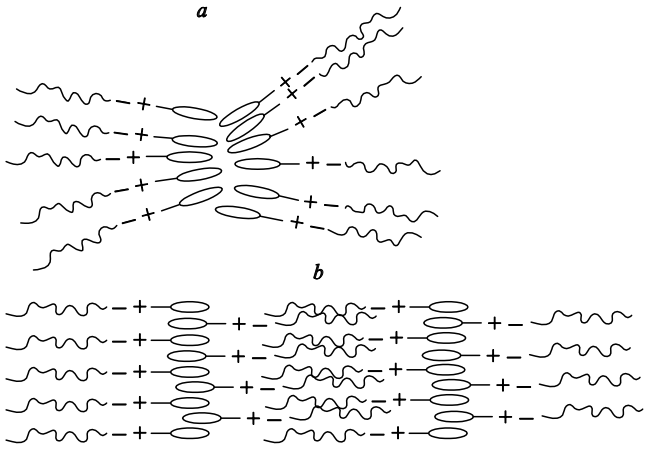


Figure 32. Supramolecular organisation of LC chelato-telechelic polymers according to SAXS data.[105]
Multiplets (*a*) and layered organisation in the smectic mesophase (*b*). For notations, see Fig. 30.

carboxylate ions is full suppression of ionic association in favour of mesophase formation or coexistence of both these types of supramolecular organisation. In polymers with terminal carboxyl groups, the average distance between mesogenic groups is, for steric reasons, shorter than in the polymers containing sulfonic acid groups. This can facilitate effective side interactions resulting in liquid-crystalline ordering.[103, 105]

X-Ray diffraction patterns exhibiting ionic peaks are more typical of ionomers containing sulfonic acid groups bonded to polystyrene chains, whereas for more flexible polyisoprene macromolecules the formation of mesophase becomes possible. By decreasing the molecular mass of the polymer one can attain the appearance of an ionic peak, but this will lead to a regular decrease in the glass transition temperatures.

At very low concentration of mesogenic groups dispersed in the polymer matrix, they can no longer interact in a co-operative fashion and the formation of mesophase becomes impossible. In the case of LC chelato-telechelic polymers the content of mesogenic groups is unambiguously related to the molecular mass of the polymer chains and the amount of terminal functional groups per chain. In order to estimate the upper limit of the molecular mass at which the mesophase can still be formed, one should take into account the size of smectic layers formed by the mesogenic groups. Gohy and Jerome [105] believe that if the chain length is such that the polymer coil can not be effectively arranged within the layer of mesogenic groups, their coexistence is impossible. Clearly, the critical length depends on the chemical nature of the polymer used.

The dependence of the ionic peak position on the molecular mass of the polymer chains provides with information on the structure of ionic aggregates. In LC chelato-telechelic polymers the multiplets are cylindrical particles of radius $\sim$3.5 nm and a shell (region of restricted mobility of polymer chains [17]) size of $\sim$5.5 nm rather than spherical or lamellar entities.[105] Unfortunately, the length of such aggregates was not reported in the review cited.[105]

It is noteworthy that mesophase formation in the classical comb-shaped LC polymers is usually possible at a content of mesogenic groups of at least 50 mass% – 80 mass% (this value decreases to 5 mass% – 40 mass% for LC chelato-telechelic polymers [101 – 105]). Unusually low content of mesogens necessary for mesophase induction in such polymeric systems was explained [101 – 105] by strong microsegregation of charged mesogenic groups and the main polymer chains.

VI. Conclusion

Analysis of the published data and the results obtained by the authors permits a step forward in the development of model concepts of the structure and physical chemistry of LC polymers and amorphous ionomers and their use for the description of specific features of the phase behaviour of comb-shaped LC ionomers. Using the methods of synthesis of LC ionomers considered in the review and the laws of mesophase formation, one can obtain novel metal-containing mesomorphous polymers and predict possible changes in the phase behaviour and structure of these compounds due to electrostatic interactions between charged groups. The review can be useful for those researchers who work in the field of design of new-generation LC polymers and materials based on them, *i.e.*, films, coatings, membranes, *etc.*

Investigations of LC ionomers containing transition metal ions make it possible to synthesise polymeric materials with controllable magnetic properties and to obtain mesomorphous nanocomposites which can find application as catalysts, nonlinear optical media, anisotropic conducting films and coatings. These fields are quite promising, as shown by studies on specific features of the state, structure and physicochemical properties of LC ionomers in the condensed phase.

Of considerable interest also are investigations of dilute solutions and gels of LC ionomers. In the text above we have pointed to the dual nature of these macromolecules, which is due to the presence of hydrophobic mesogenic fragments responsible for the formation of the LC phase and hydrophilic functional groups, which are prone to form ionic multiplets. The diphilic nature of macromolecules predetermines an increased ability of a polymer to microsegregation, which leads to formation of a complex hierarchy of liquid-crystalline structures in the condensed phase. In solutions of LC ionomers the conformational state of macromolecules can be controlled by choosing particular solvent/precipitant ratios for selective solvation of functional groups. It is quite interesting to specify a conformation in solution by fine adjustment of hydrophobic – hydrophilic balance and then to try to 'solidify' it in the condensed state of the polymer by gradually removing or slowly displacing a certain solvent. This approach seems to be highly efficient for control of the character of packing and the size of liquid-crystalline nanostructures formed.

Unfortunately, such experiments have not been reported so far. However, similar, in some sense, investigations have long and successively been carried out by researchers from the Netherlands and Finland.[106] The focus of these studies has been design of self-organised supramolecular structures as a result of hydrogen bonding between block copolymer polyelectrolytes and low-molecular-mass non-mesogenic amphiphilic compounds. In such systems, phase separation due to variation of temperature causes the formation of optically anisotropic films comprising a number of types of lamellar nanostructures of different size (50 to 350 Å). These films closely resemble smectic mesophases of LC compounds and some block copolymers. Transitions between different structural types cause considerable (up to two orders of magnitude) changes in the electrical conductivity of the films. This offers interesting perspectives for the design of conducting polymer membranes in which the type of supramolecular organisation responsible for conductivity can be specified in solution.

Probably, an analogous approach can also be realised in the case of comb-shaped LC copolymers bearing functional groups by employing hydrogen bonding between these groups and corresponding dopants and introduction of charges into the polymer chain. Such ternary copolymers could also serve as models for some complex bioactive systems combining the ability of self-organisation and molecular recognition mechanisms.

In Japan, Prof. Osada and his collaborators do research in a related field. They design and study gel-like mesomorphous systems taking gels of comb-shaped LC polymers with mesogenic side fragments and functional carboxyl groups in the backbone (acrylic acid) or in side branchings as examples.[107 – 109] Strictly speaking, these compounds are not LC ionomers because the backbone contains no charged groups, but they belong to an interesting class of mesomorphous systems potentially capable of forming ionomers. Such copolymers readily form various types of mesophases and at low concentration of hydrophobic mesogenic groups some of them can dissolve in water giving anisotropic gels. Combination of the anisotropy of properties (in particular, birefringence) with a rather high molecular mobility allows LC gels to behave similarly to conventional low-molecular-mass liquid crystals and produce a fast response to the action of external (electric, magnetic, mechanic) fields accompanied by a change in the shape and size of the initial sample. Great prospects for the use of such systems in the design of novel 'smart' materials and possible fields of application have been outlined.[110]

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