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Thermotropic Liquid Crystal Polymers with Mesogenic Groups in the Main Chain

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The present state of the synthesis and studies of the structure and properties of thermotropic liquid crystal polymers and copolymers with mesogenic groups in the main chain is examined and the thermodynamic and structural principles of the identification of the polymeric mesophases as well as the influence of the chemical structure of the mesogenic blocks and flexible spacers on the mesomorphic properties of the polymers are discussed.
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I. INTRODUCTION

The interest in the liquid crystal state of polymers which has arisen in the last decade is due to a large extent to the possibility of obtaining ultrastrong highly modular fibres based on polymers exhibiting mesomorphic properties.[1-9] In addition, the study of the nature of the polymeric liquid crystal (LC) state is of independent interest. The lyotropic mesomorphism of polymers has long been known and has been thoroughly investigated; the principal results obtained during the last 20 years in this field have been surveyed in a monograph.[1] Thermotropic LC polymers have been discovered recently and the main direction of studies in this field has been associated with the investigation of the LC state of polymers with mesogenic groups in the side branches.[5,6-8,10] The main idea underlying the creation of such polymers has been the combination of properties characteristic of polymers (including their ability to form films and fibres) with the properties of low-molecular-weight LC compounds. The LC properties were manifested only when the behaviour of the side chains is relatively autonomous. This means that the structural transformations occurring in such polymers at the level of mesogenic groups need not necessarily be associated with the behaviour of the main chain. The mesomorphic properties of such polymers can be in many respects similar to the properties of low-molecular-weight liquid crystals: indeed it has been found that the differences between the electro-optical properties over a wide range of polymers are quantitative but not qualitative.[10]

When the mesomorphic properties of polymers are determined by the structure of the main chain, the differences between the low-molecular-weight liquid crystals and polymers are qualitative, since the structure of the mesophase is found to be related to the macroconformations of the molecules. The LC state of linear polymers is directly related to the anisotropy of the properties induced by the chain structure of the molecules. It would seem that the presence of long chain molecules should give rise to the possibility of the appearance of the LC state in the majority of polymeric systems. Nevertheless the existence of structures exhibiting order intermediate between the types of order which obtain in the crystalline and isotropic states does not always justify the inclusion of such structures among LC structures. Such structures obtain in polyphosphazenes, in polytetrafluoroethylene, in polyethylene at a high pressure, and also on fusion of orientationally-crystallised flexible-chain polymers.[11] A common feature of such structures is a pseudo-hexagonal packing of the chains arising as a result of the appearance of the rotational degree of freedom around the long molecular axis. It is known that such "rotational-crystalline" states occur in many low-molecular-weight compounds[12] (for example, in normal hydrocarbons), and yet such compounds are not classified as liquid crystals. According to Wunderlich's classification, the mesomorphic structures occurring in flexible-chain polymers belong to the category of crystals with elements of conformational disorder.[11]

Thus the chain structure of polymeric molecules is not a sufficient condition for the manifestation of LC properties characterised by the presence of a high degree of orientation order in combination with total or partial absence of positional order.[13]

Orientational order occurs to the maximum extent in complex aromatic polyethers containing only *para*-substituted benzene rings. However, the high anisometry of the molecules increases the stability of the crystal lattice, so that the region in which the mesomorphic properties are manifested lies above the chemical decomposition temperature. One of the ways of reducing the melting point involves the introduction of asymmetric groups or substituents in the *ortho*- and *meta*-positions in the polymer chain,[14] which hinders the packing of the macromolecules in the crystal and lowers appreciably the melting point. The occurrence of mesomorphism in such systems is caused by the rigidity of the polymer chain, which in many respects engenders a similarity between the aromatic polyethers and lyotropic LC polymers such as aromatic polyamides. The high equilibrium rigidity of such polymers results in the appearance of the isotropic state only in the presence of a solvent, i.e. for truly rigid-chain polymers thermotropic mesomorphism is impossible.

According to Flory's theory,[15] which describes the orientational ordering of solutions of rigid-chain polymers, there is a maximum critical axial ratio $p = l/d$ (where l is the length of the molecule and d its diameter) above which the isotropic phase is absolutely unstable in the absence of solvent. The concept of the critical axial ratio, introduced for absolutely rigid rodlike molecules, retains its significance in the description of the ordering in a solution of freely jointed chains,[16] and the quantity $p = A/2d$ represents the anisometry of the

Kuhn segment having a length A. Thus the anisometry of a section of the chain with a length of the order of A is a criterion of the possibility of the appearance of thermotropic mesomorphism: thermotropic behaviour is observed for sufficiently flexible chain polymers for which the condition $A < 2pd$ holds. The increase in the molecular diameter by the introduction of asymmetric substituents or benzene rings in the *ortho*- and *meta*-positions can entail the complete loss of capacity for crystallisation and also the suppression of LC properties.

One of the most convenient methods of regulating the mesomorphic properties involves the introduction of flexible sections (spacers) into the mesomeric skeleton of the macromolecule. Thermotropic LC polymers, whose mesomorphic properties are determined by the structure of the main chain consisting of rigid mesogenic (R = rigid) and flexible (F = flexible) fragments (RF-polymers) constitute systems with a specific combination of the properties of flexible-chain polymers and low-molecular-weight liquid crystals. The synthesis of RF-polymers has given rise to a series of fundamentally new problems for both the physics of liquid crystals and for the physics and chemistry of polymers.

The principal problem among those described involves the elucidation of the relation between the thermotropic mesomorphism of polymers and the LC state of low-molecular-weight compounds, whose nature has been fairly thoroughly investigated.

This problem has the following aspects: is there a possibility of the classification of a structural type of polymeric mesophases on the basis of the classification of low-molecular-weight compounds; how are the properties of the polymers related to the properties of low-molecular-weight model compounds and how does the molecular-weight (MW) of the polymer influence its mesomorphic properties and for what values of MW are the specific features of the LC state realised; to what extent can the ideas and methods of study traditional in the physics of polymers be applied to thermotropic LC polymers.

This review analyses the studies of the synthesis and properties of RF-polymers in which the questions formulated above have been reflected; important fields such as electrooptics,[17] rheology, mechanical properties,[18,19] and dielectric properties have remained outside the framework of the review, since the study of these aspects of the thermotropic mesomorphism of RF-polymers is only just beginning.

II. CLASSIFICATION AND IDENTIFICATION OF THERMOTROPIC LIQUID CRYSTALS

Liquid crystals can be divided into three main types: nematic, cholesteric, and smectic.[20] In nematic liquid crystals the centres of gravity of the molecules are distributed at random and long-range order is observed only with respect to their orientation (Fig. 1*a*). The cholesteric mesophase is illustrated schematically in Fig. 1*b*. The centres of gravity of the molecules lie in layers without any order and in each layer, the director (i.e. the vector characterising the preferential direction of the long molecular axes) is located in the plane of the layer. On passing from one layer to the next, it rotates by a small angle and a structure with a helical order is formed overall. Smectic liquid crystals, where the centres of gravity are located in layers but the director is no longer in the plane of the layer, forming an angle with the latter, are the most ordered (Fig. 1*c*). The thermodynamic and structural aspects of smectic mesomorphism have been described in two communications.[21,22]

The knowledge of the type of mesophase makes it possible to infer the behaviour of the substance as a function of the external conditions (temperature, pressure, and external field strength). The main question which arises in the study of newly synthesised LC compounds is therefore related to the elucidation of the type of mesophases formed by the given compound and also to the determination of the temperature limits of their existence.

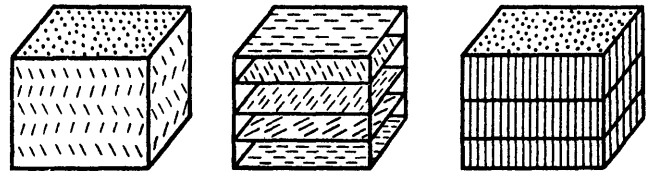


Figure 1. Structural types of mesophases: *a*) nematic; *b*) cholesteric; *c*) smectic.[20]

One of the commonest methods for the determination of the type of mesophase involves the observation of the optical textures of the liquid crystals in polarised light. A specific type of optical texture is associated with the behaviour of the director in the layer of the preparation, which is specific to the given type of liquid crystal. All the textures of LC compounds observed hitherto have been compiled in an atlas.[21] The most reliable identification method is X-ray diffraction, whose foundations in relation to low-molecular-weight liquid crystals have been described in a review;[23] the application of the diffraction methods in the study of mesomorphic polymers has been described by Blumstein.[3] The use of the given method for the identification of mesophases formed by RF-polymers is limited owing to the difficulty of obtaining specimens with a homogeneous orientation in a magnetic field.[24–26]

The foundations of the classification of the structural types of mesophases based on calorimetric data have been laid by Barall and Jonson,[27] who examined the ratio of the entropy of their transition from the LC state to the isotropic liquid melt (LC–I) ΔS_i to the overall entropy change in all the transitions undergone by the liquid crystal ΔS_T (this includes the polymorphic transformations in the crystalline phase). It was found that this quantity ($\Delta S_i/\Delta S_T$) is usually small for the nematic phase (of the order of 10^{-2}), while for the smectic phase it is an order of magnitude higher. Analysis of the thermodynamic parameters of the transition showed that calorimetric data can be used for the identification of liquid crystals.

The study of the phase equilibria in mixtures of LC compounds is an extension of the identification method. It is based on the hypothesis that two components can be infinitely miscible when their mesophases are isomorphous. For low-molecular-weight liquid crystals, there are extensive theoretical and experimental data concerning the character of the coexistence of the phases in binary mixtures.[28] The application of the given method to the investigation of polymers has been described in a series of recent studies.[29–31]

For polymeric mesomorphic systems, the problem of identification is greatly complicated, because so far there have been no classifications of polymeric liquid crystals which could satisfy investigators. For this reason, in most studies the

authors either use the existing classification for low-molecular-weight compounds or they refrain from any definite conclusions about the type of mesophases. Furthermore, in the identification of polymeric liquid crystals there is a possibility that complications may arise due to kinetic causes, because observations are carried out under conditions remote from thermodynamic equilibrium. Thus the principal concepts accumulated in the study of low-molecular-weight compounds can be applied to the study of the mesomorphism of polymers only with caution since the nature of the polymeric mesophases may differ greatly from that of the low-molecular-weight liquid crystals.

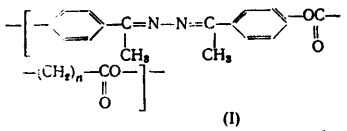
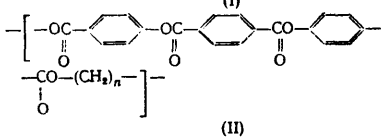
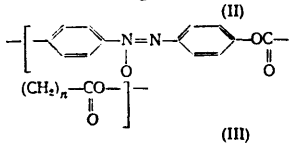
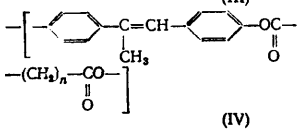
III. THE ROLE OF FLEXIBLE SPACERS IN THE ORDERING OF LIQUID CRYSTAL POLYMERS

In 1975 de Gennes predicted the possibility of the existence of an enantiotropic nematic phase in polymer systems formed by linear flexible macromolecules containing mesogenic groups in the main chain.[32] The synthesis and mesomorphic properties of such polymers were reported at the same time.[33] Subsequently the above investigations developed in the USA, France, the USSR, and the Federal Republic of Germany, which led to the synthesis of tens of *RF*-polymers.[4,34]

According to Flory's theory,[35] for any flexible chain polymer the first (formal) crystallisation stage consists in the cooperative orientational ordering of the polymer chain. This state of orientational order can, however, be thermodynamically unstable in relation to the crystalline phase, which leads to spontaneous crystallisation. This process, leading to a "parallel arrangement" of the chains, corresponds to monotropic LC behaviour. The polyesters synthesised by Roviello and Sirigu are capable of forming an enantiotropic LC phase.[33,36]

The method of synthesis of *RF*-polymers is distinguished by an appreciable flexibility, since wide-scale variation of the chemical nature and molecular parameters of the spacers and mesogenic blocks has been postulated. Aliphatic polyenes of 4,4'-dihydroxy-αα'-dimethylbenzylideneazine with $n = 8$, 10, and 12 carbon atoms in the spacers [Table 1, compound (I)] have been investigated.[33] X-Ray diffraction studies have shown that these polymers are partly crystalline. With the aid of differential scanning calorimetry (DSC) and optical studies, it has been established that the polymers exhibit a first-order transition, which may be associated with the fusion of the crystal structure and also a transition from the LC state to the isotropic state. Comparative studies on the thermodynamic properties of polymers of different chemical nature and model low-molecular-weight compounds demonstrated an appreciable difference between the molar entropies of the LC–I transition.[36,37] For the low-molecular-weight models, this quantity was $\Delta S_i \cong 3$ J mol^{-1} K^{-1}, while for the polymers $\Delta S_i = 13$–16 J mol^{-1} K^{-1}. It has also been observed that ΔS_i is almost independent of the length of the flexible fragments, which has been attributed to the use of the representation of the nematic phase where the disordered flexible part of the chains behaves like an isotropic liquid, i.e. the chains are not involved in the formation of orientational order and can be regarded as solvent molecules. The same conclusions have been reached by other investigators[38] in the study of the temperature dependence of the molar volumes of a series of polymers with flexible spacers of different lengths. The contribution of aliphatic chains to the molar volume proved to be close to the molar volume of amorphous polyethylene, which supports the hypothesis of a disordered conformation of flexible spacers in the nematic phase. However, this conclusion must be made with caution, since the molar volume is not very sensitive to small conformational changes. The conformational state of spacers in different phase states for polymers based on terephthaloylbis(4-hydroxybenzoic) acid [Table 1, compound (II)] has been determined by IR spectroscopy.[39,40] Despite the fact that the conformational composition of the polymers in the LC and isotropic states is almost the same, the flexible-chain spacers in such polymers are partly oriented, i.e. play a definite role in the establishment of the LC order. The orientational order of the flexible sections Q_F is probably related to the redistribution of the rotational-isomeric forms in the LC state compared with the isotropic state. The parameter of the orientation of the mesogenic sections Q_R † is different from Q_F and $Q_R > Q_F$. When the length of the spacer is altered, Q_F hardly changes, which indicates a decisive contribution of the intermolecular interactions in the mesogenic sections of the macromolecule. It has been shown that Q_R and Q_F change in the temperature range corresponding to the existence of LC order; under these conditions, Q_R diminishes faster than Q_F, which is due to the temperature dependence of the intermolecular interaction in the mesogenic sections of the macromolecule.

Table 1. Chemical structures and transition temperatures of certain types of *RF*-polymers.

Structure of monomeric unit	n	Transition temperature, °C*	Refs.
 (IV)	10	*C* 208 *N* 322 *I*	[33]
 (I)	10	*C* 223 *S* 297 *I*	[34]
 (II)	10	*C* 119 *N* 165 *I*	[41]
 (III)	12	*C* 200 *I* (on heating), *I* 177 *N* 172 *C* (on cooling)	[49]

*C = crystalline phase, N = nematic phase, S = smectic phase, I = isotropic phase; the corresponding transition temperatures are shown between two symbols representing the phases.

† The order parameter $Q = \langle(3\cos^2\theta - 1)/2$, where θ is the angle between the rigid section of the chain (or a segment of the flexible fragment) and the anisotropy axis.

The temperature dependence of the order parameter of the polymer based on 4,4'-dihydroxy-2,2'-dimethylazoxybenzene and decamethylene glycol [Table 1, compound (III)] has been determined.[41] The authors note the unusually high order parameter in the transition to the isotropic state for the polymer compared with the low-molecular-weight nematic compound having the initial structure. For the given polymer, Q_R and Q_F vary in parallel and are almost identical. The transition from the isotropic to the LC state is accompanied by a sharp conformational alteration in the spacers: in the LC phase, they have the straight-chain conformation.

The results presented demonstrate the possibility of the operation of two different mechanisms of the ordering of the *RF*-polymers: in the first case, the stability of the mesophase is determined mainly by the intermolecular interaction of the mesogenic fragment and $Q_R > Q_F$, while in the second $Q_R \cong Q_F$, which indicates the decisive role of the macromolecular order. The second variant presupposes the virtually complete ordering of the flexible fragment.

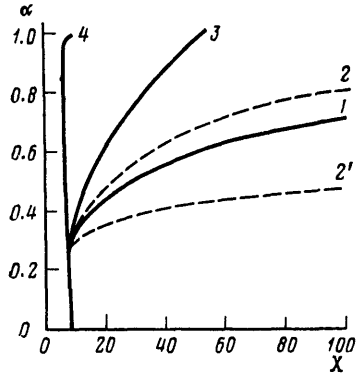


Figure 2. Phase diagram for the system of *RF*-macromolecules; α = volume fraction of flexible fragments; *X* = length of monomeric unit; flexibility parameter f_0; 1) 1.0; 2) and 2') 0.8; 3) 0.6; 4) 0.4.[42]

The role of the flexible spacers in the orientiational ordering has been examined in a number of studies.[42,43] On the basis of the Flory model for *RF*-polymers,[44] account has been taken of tendency of the LC phase for the flexible fragments to become oriented along the anisotropy axis. One of the most interesting results of this investigation is the conclusion that anisotropic phases of two types can exist as a function of the relative length of the flexible spacers and their rigidity. Fig.2 presents the phase diagram. The flexibility of the spacers f_0 is defined by the equation[35]

$$f_0 = \frac{(z-2)\cdot\exp(-\varepsilon/kT)}{1+(z-2)\exp(-\varepsilon/kT)},$$

where *z* is the coordination number of the lattice and ε the difference between the free energies of the *trans*- and *gauche*-conformers. For an undiluted polymer, the conditions governing the stability of the isotropic phase is the inequality $f_0 > 0.63$. Curve *1* has been obtained without taking into account the finite flexibility of the flexible fragment. The nematic phase is thermodynamically stable in the region to the right of curve *1*. Curve *2* consists of two branches (*2* and *2'*), which corresponds to the fact that, for $f_0 = 0.8$ and also for any $f_0 > 0.63$, there is a possibility of an additional phase transition between two anisotropic phases: a highly ordered phase stable for low values of α and a phase with little order, which is stable for high values of α. When f_0 diminishes, the region of stability of the low-order anisotropic phase shifts towards higher values of α, disappearing at $f_0 = 0.63$. According to Flory,[35] when $f_0 < 0.63$, order obtains even for α = 1 (curves *3* and *4*).

Thus, for sufficiently rigid spacers, the behaviour of this system does not differ from that of a melt comprising rigid rods. For fully flexible spacers, there is a possibility of forming a low-order LC phase, and finally, for spacers with intermediate flexibility, either a highly ordered phase in which the flexible spacers participate in the overall ordering process or a low-order phase in which the spacers play the role of a solvent can be formed depending on the length of the spacers.

This result has been obtained in a somewhat different form by Birshtein and Kolegov,[45–47] who showed that, for polymer solutions containing *RF*-macromolecules, anisotropic phases of two types can exist: in the first case the ordering develops at the level of rigid segments and the chain retains overall the structure of a disordered coil (segmental ordering); in the second case the chain as a whole is ordered and intermolecular interactions ensure the loss of internal flexibility (macromolecular ordering). The occurrence of one or other type of ordering depends on the concentration of the rigid blocks in the solution and also on the mechanism of the flexibility. For the intermediate case of non-freely-jointed rigid blocks, an increase in the concentration of the solution initially entails a transition to the LC state by the segmental mechanism and only then, at high polymer concentrations, does macromolecular ordering occur.

Thus the main difference between the mesomorphisms of polymers and low-molecular-weight liquid crystals reduces to the possibility of the cooperative behaviour of the monomeric units, which depends in a specific manner on the chemical nature of the mesogenic fragments, on the length and nature of the flexible spacers, and also on the way in which they are joined to the mesogenic group. For this reason, the identification of the type of polymeric mesophase must include an analysis of the type of ordering on passing from the isotropic to the LC state. The occurrence of a particular type of ordering in the polymer system is, however, inevitably accompanied by the superposition of kinetic effects, which can greatly increase the uncertainty in the interpretation of the experimental results. The separation of the thermodynamic effects in the I–LC transition constitutes an interesting and important problem whose solution would be a major step towards the possibility of the technological use of *RF*-polymers.

The need to take into account the kinetics of the phase transitions of *RF*-polymers follows from ideas common to flexible-chain polymers, according to which there exist appreciable differences between the mechanisms of the fusion of flexible linear macromolecules and small rigid molecules.[48] These differences are associated with the decisive role of the conformational transformations in the phase transitions of flexible-chain polymers. For this reason, the thermodynamic parameters obtained in the study of phase transitions refer in most cases to the so-called irreversible fusion, i.e.

to fusion under conditions different from those in thermodynamic equilibrium.# The polymer (IV) (Table 1, $n = 12$), which exhibits monotropic mesomorphism, has been investigated.[49] Specimens of the polymer which have not undergone a preliminary heat treatment exhibited a "fictitious" enantiotropic mesomorphism. When the specimens were annealed, the melting point approached the equilibrium value, which proved to be higher than the temperature of the transition to the isotropic melt for the non-annealed specimens. Thus the LC behaviour is manifested by this polymer only under conditions remote from thermodynamic equilibrium. The equilibrium melting point of the polymer (II) (Table 1, $n = 10$) has been determined[50] and has been found to be appreciably higher than the observed melting point. Evidently, in order to understand the nature of the mesomorphism of the *RF*-polymers and also to discover a relation between chemical structure and mesomorphic properties, it is essential to know the equilibrium thermodynamic characteristics of the transition from the crystalline to the LC phase and of the LC–I transition.

Studies of the thermodynamic properties of polymers based on terephthaloylbis(4-hydroxybenzoic) acid[51] in dilute solution have shown that the behaviour of their *RF*-polymers is analogous to the behaviour of the usual flexible chain polymers, since the size of the Kuhn segment does not greatly exceed the size of the repeat unit. Studies on the conformations of the *RF*-macromolecules by measuring the magnetic double refraction established that, in a dilute solution and also in an isotropic melt, the molecules exist in coiled conformations.[52] The Cotton–Mouton constants for model low-molecular-weight compounds, *RF*-polymers, and flexible-chain polymers proved to be of the same order of magnitude and at the same time one–two orders of magnitude less than for aromatic *para*-polyamides and DNA.

Studies on the thermodynamic parameters of the I–LC transition of the polymer (III) ($n = 10$) with different molecular weights showed that ΔS_i increases sharply with increase of the MW, which indicates an increase of the contribution of the flexible spacers to the disordering process[53] (Fig. 3). At the same time, the dependence on MW reaches saturation after the attainment of the MW corresponding to approximately 6–8 repeat units, i.e. the cooperative nature of the behaviour of the repeat units does not extend to the entire macromolecule. For high-molecular-weight specimens, the form of the ^{1}H NMR line for the nematic and crystalline phases was the same,[41] while for oligomeric specimens the spectra of the nematic phase were characterised by dipole splitting typical of homogeneously oriented nematic single crystals. For specimens with a high MW, a structural model of the "multidomain" type, postulating the existence of a marked spatial inhomogeneity, whose main source is the breakdown of orientation (disclination), has been proposed. It is natural to assume that the correlation radius of the orientation of the high-molecular-weight specimens does not exceed the length of 6–8 repeat units, which corresponds to the degree of polymerisation for which the dependence of ΔS_i on the MW reaches saturation. On the basis of magnetic double refraction data, thermodynamic studies, and NMR spectroscopy, it has been concluded that the I–LC transition in oligomeric specimens (M_n = 1700–4000) is characterised by a sharp conformational transformation of randomly coiled chains into chains, which are extended to a high degree. In the study of the thermodynamic properties of the *RF*-polymer combined with the measurement of the order parameter in the LC–I transition in the monomer–dimer–polymer series, similar results were obtained[54] (Table 2), and yet the authors nevertheless concluded that the polymeric mesophase has an intermediate degree of order, since, despite the fact that the order parameter of the polymer ($Q = 0.6$) is appreciably higher than for the monomeric compound, it is nevertheless insufficiently high to represent the nematic phase as a set of fully extended chains. The authors assume that, for purely thermodynamic reasons, the system of randomly packed chains undergoes a first-order transition to a nematic phase with an intermediate order.[55]

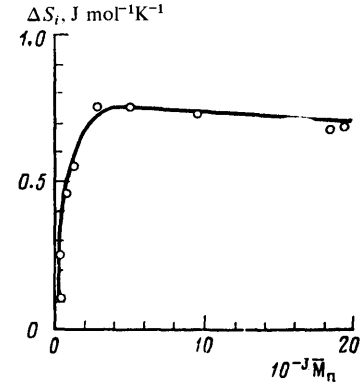


Figure 3. Dependence of the entropy of the LC–I transitions ΔS_i on the molecular weight of the polymers (III) (Table 1); ΔS_i has been referred to the fraction of rigid groups in the main chain.[53]

Table 2. Thermodynamic parameters of the LC–I transition for a nematic polymer, monomer, and dimer.[54]

Specimen*	T, °C	ΔH, kJ mol^{-1}	ΔS_i, J mol^{-1}K^{-1}	Q
Monomer C_5H_{11}—R—C_5H_{11}	79	0.74	2.09	0.37
Dimer C_5H_{11}—R—$(CH_2)_{10}$—R—C_5H_{11}	148	3.52	8.37	0.49
Polymer —[—R$(CH_2)_{10}$—]— (V)	215	6.53	15.4	0.6

*R = –O–C$_6$H$_4$–CO–C$_6$H$_4$–O–

In a study of the thermodynamic properties of the copolymer of ethylene terephthalate with *p*-hydroxybenzoic acid, Krigbaum[56] reached the same conclusions. He showed that, even when, as suggested by Vol'kenshtein,[57] a correction associated with the torsional vibrations (on the assumption that they are fully excited in the nematic and isotropic phases) is introduced into the expression for the free energy, $\Delta S_i/\Delta S_T$ remains approximately 0.45, which is appreciably higher than the experimental value for the polymer investigated ($\Delta S_i/\Delta S_T = 0.11$). It was therefore suggested that

According to Wunderlich's terminology,[48] irreversible fusion is understood as transition from a metastable crystalline phase to a supercooled isotropic or LC phase and also as fusion accompanied by the superheating of the crystal. Here we employ the concept of irreversible fusion in its first meaning.

in the nematic phase the parameter f_0 is non-zero, i.e the mesophase is characterised by the presence of defects in the form of correlated bends in the chain. Thus the ratio $\Delta S_i/\Delta S_T$ deduced from the lattice model of the nematic phase with allowance for the modification mentioned above decreases from 1 to 0.59 or, when the contribution of the torsional vibration approaches the values calculated from polyethylene,[57] from 0.45 to 0.26. Furthermore, in the lattice model no account is taken of the contribution of the entropy change associated with the increase in volume on fusion. Allowance for this contribution should further diminish the $\Delta S_i/\Delta S_T$ predicted by the theory.

The study of Ianelli et al.[58] was devoted to the determination of the ratio $\Delta S_i/\Delta S_T$ for the polymer (IV) (Table 1) with $n = 7$ and 9–12 CH_2 groups in the spacers. The authors began with the hypothesis that the value of ΔS_i determined from direct calorimetric measurements correspond to equilibrium. ΔS_T was determined by studying the melting point depression of the polymers with formation of an isotropic melt in the presence of a low-molecular-weight solvent. The ratio $\Delta S_i/\Delta S_T$ amounted to 0.15–0.17 for even values of n and to 0.07–0.09 for odd values, which implies significant differences between the ordering mechanisms for polymers with odd and even numbers of carbon atoms in the spacers. ΔS_T for polymers is usually represented as the sum of three contributions:[59]

$$\Delta S_T = \Delta S_{pos} + \Delta S_{or} + \Delta S_{conf}$$

associated with the positional, orientational, and conformational disordering. For flexible-chain polymers, ΔS_{conf} exceeds all the remaining contributio s to ΔS_T; thus ΔS_{conf} amounts to 75% of the total entropy change for polyethylene[60] and to 65% for poly(ethylene terephthalate).[61] There are no data at present which would make possible analogous calculations for *RF*-polymers, but it is reasonable to suppose that in this case too the contribution of ΔS_{conf} to ΔS_T is decisive. The quantity ΔS_T calculated for each rigid group in the chain obeys the general rule for linear flexible-chain polymers (Table 3), which means that the nature of the isotropic melt for *RF*-polymers is the same as for flexible-chain polymers, which agrees well with the results of magnetic double refraction measurements.[52] Since ΔS_T calculated for each rigid group of the chain in *RF*-polymers is 6–8 J mol^{-1} K^{-1}, presumably the fusion of flexible-chain polymers and *RF*-polymers has the same character. If the conformational contribution to ΔS_T is decisive, the parameter $\Delta S_i/\Delta S_T$ can be regarded as a structural characteristic reflecting the degree of macromolecular order of the polymer chains in the LC phase.

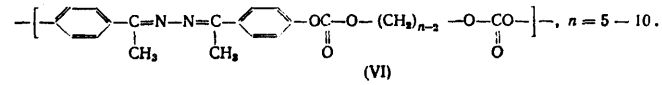
The important role of the macromolecular order is manifested in the change of the thermodynamic properties in homologous series of polymers.§ Differences in the character of the changes in the parameters of the LC–I transition in the homologous series of monomeric, dimeric, and polymeric liquid crystals have been discovered.[62] In the homologous series of monomeric compounds, the usual variation of the mesomorphic properties with increase of the length of the alkyl groups is observed. For certain intermediate lengths, there is a transition from the nematic to the smectic mesophase accompanied by a sharp increase of the clarification entropy; the even–odd effect is most striking for the first homologues and becomes smoothed out with increase of the number of CH_2 groups in the aliphatic components. For the dimer, ΔS_i oscillates about the mean value intermediate between the ΔS_i for the polymer and the monomer and the even–odd alternation becomes more marked on moving from the lowest to the highest homologues (Fig.4). For the polymer, the even–odd alternation is very pronounced and, for all the even and all the odd homologues, the ΔS_i are almost identical. The pronounced even–odd effect for the polymers can be explained by the stronger relation, than in the low-molecular-weight liquid crystals, between the molecular structure of the aliphatic components and the mesomorphic properties. Two different types of ordering, observed for the polymers (III) with aliphatic spacers containing 2–14 carbon atoms, have been described.[63] The first type of ordering has been established for polymers with an even number of carbon atoms (n = 4, 6, 8, 10, 14) and the second for polymers with odd n = 5, 7, 9, 11, 13. The first type is characterised by a higher order parameter $Q = 0.75$ at the clarification point than the second, for which $Q = 0.59$. A high degree of order is achieved as a result of the extension of the spacers, which has been demonstrated by analysing the NMR line form.[41] The corresponding differences between the two types of ordering for polymers with even and odd numbers n are exhibited also in the analysis of thermodynamic data and X-ray diffraction data. The authors explained these features in the following way: the probably of the *trans*-conformation is higher for the first three even bonds, starting from the junction point with the mesogenic component. If both ends of the alkyl chain are fixed, the tendency towards an increase of the number of *trans*-conformers extends along the chain in opposite directions. For an even number of bonds (n is odd), interference results in a decrease of the average ratio of the *trans*- and *gauche*-conformers, while for an odd number of bonds (n is even) the ratio of these conformers actually increases.

Table 3. Thermodynamic characteristics of the C–LC, C–I, and LC–I transitions of flexible-chain and *RF*-polymers*.

Polymer	C-LC			LC-I			C-I				ΔS_T per bond	Refs.
	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS	$\Delta S_i/\Delta S_T$		
(IV), n=7	—	31.7	—	230	2.72	5.44	185	34.4	75.3	0.07	7.5	[58]
(IV), n=10	—	31.8	—	225	7.37	14.8	195	27.3	87.0	0.17	6.2	[58]
Poly(ethylene-terephthalate	—	—	—	—	—	—	280	26.9	48.5	—	9.7	[48]

*T in °C, ΔH in kJ mol^{-1}, ΔS in J mol^{-1} K^{-1}; C–LC and C–I represent transitions from the crystalline to the LC and isotropic states respectively.

The thermodynamic aspects of the even-odd effect for the *RF*-polymers have been investigated in greatest detail by Roviello and Sirigu.[64] Fig.5 presents the dependence of ΔS_i on n for polymers of three types: (I) (Table 1, n = 6–12), (IV) (Table 1, n = 6–12), and



(VI)

In contrast to the polymers (I) and (IV), the polymers of the (VI) series show virtually no even-odd effect. This finding

§ Here and henceforth the concept of "homologous series" is that of a series of compounds (polymeric or monomeric) which differ from one another by the number of atoms in the flexible regions.

indicates the decisive role of the structure of the flexible spacers in determining the thermodynamic parameters of the LC–I transition. The replacement of the methylene groups in the spacers of the polymers (VI) by oxygen atoms probably lowers the conformational limitations imposed on the structure of the spacers by the nematic ordering. The authors assume that the question of the role of the flexible spacers in the LC ordering still remains open. Indeed, the study of the thermodynamic parameters of the LC–I transition in *RF*-polymers has shown that, since ΔS_i is characterised by an appreciable even-odd effect, the description of the LC order as a set of rigid rods connected by spacers, playing the role of a solvent, is illegitimate. On the other hand, the hypothesis of an appreciable role of the conformational transformations in the LC–I transition conflicts with the absence of a dependence of ΔS_i on n for even and odd values of n. If, as follows from the study of Martins et al.,[41] the flexible spacers in the LC phase were almost fully ordered, a marked dependence of ΔS_i on n should have been observed. It is essential to note that the estimation of the structure of the spacers by ^{1}H NMR involves the correct allowance for the dipolar contributions to the broadening of the lines due to the protons in the aliphatic and aromatic component, which can be achieved only on the basis of a more or less legitimate hypothesis about the conformations of the spacers. Recent results[65] have shown that the order parameter of the alkyl chains in the LC phase is not the same for the external and internal methylene groups (0.4 for the external groups and 0.3 for the internal groups). It is necessary to note that the studies were performed for a polymer with deuteriated spacers, which permitted the absolute determination of the order parameter of the spacers not requiring hypotheses about their conformational state. For this reason, the initial hypothesis of the stability of the complete ordering of the spacers is not sufficiently well founded.

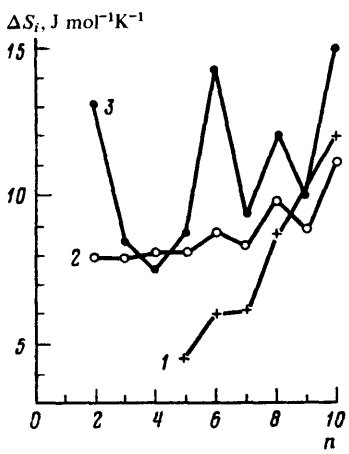


Figure 4. Dependence of the entropy of the LC–I transition ΔS_i on the number of carbon atoms n in the aliphatic components for the monomers (curve *1*), dimers (curve *2*), and polymers (curve *3*).[62]

Thus the nematic ordering of the *RF*-polymers differs greatly from the ordering of low-molecular-weight liquid crystals. The macromolecular ordering of the polymers, whose relation involves the cooperative nature of the dynamic behaviour of the mesogenic groups and depends on the chemical structure of the polymer and also on kinetic factors,¶ greatly complicates the task of identifying the polymeric liquid crystals and apparently entails the need to investigate the supermolecular liquid-crystal morphology of the polymers.

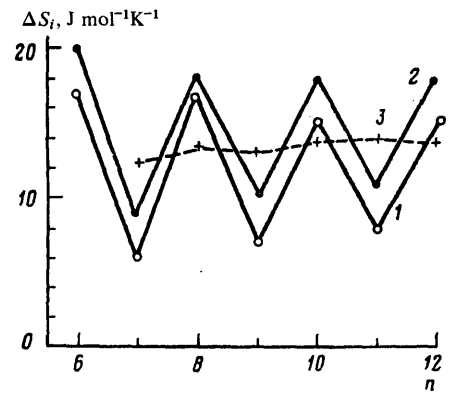


Figure 5. Dependence of the entropy of the LC–I transitions ΔS_i on the number n of atoms in the flexible spacers: 1) polymer (I); 2) polymer (IV); 3) polymer (VI).[64]

IV. THE INFLUENCE OF THE CHEMICAL STRUCTURE OF THE MESOGENIC BLOCKS AND FLEXIBLE SPACERS ON THE MESOMORPHIC PROPERTIES OF THE POLYMERS

There are literature data for the synthesis and properties of polymers with flexible spacers of different chemical nature—aliphatic,[33,34,68,69] oligo(ethylene oxide) (OEO), oligo(propylene oxide) (OPO),[70] and disiloxane spacers.[71] The influence of the structure of the mesogenic blocks has been examined in a number of studies.[68,72,73] However, it is as yet difficult to treat from a general standpoint the extensive experimental data concerning the elucidation of the relation between the mesomorphic properties and the chemical structure of the *RF*-polymers. The difficulties in the interpretation are associated with the fact that the mesomorphic properties are influenced by a series of factors such as the composition, inhomogeneity, MW, and the molecular weight distribution (MWD). In the study of polymers with high clarification temperatures, it is essential to take into account

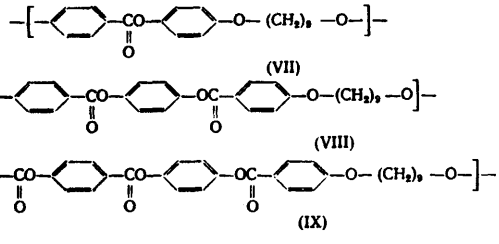
¶ There are no direct indications in the literature that the LC–I transition is non-equilibrium in character. However, certain instances of the monotropic behaviour of the *RF*-polymers have been described.[49,66,67] The occurrence of conformational changes in flexible spacers in the transition to the isotropic melt should lead to the irreversibility of this transition. The small thermal hysteresis and the independence of ΔS_i of the conditions in the heat treatment of the specimens[50] may be a consequence of the kinetic stability of the mesophase and are not an unambiguous proof of its thermodynamic stability.

the possibility of chemical changes which leads to the breakdown of the regulatiry of the chain. Furthermore, the thermodynamic parameters obtained by direct calorimetric measurements do not in most cases correspond to equilibrium, which greatly hinders the elucidation of the relation between the chemical structure and mesomorphic properties.

The influence of the previous history of the polymeric specimens on their mesomorphic properties has been studied in greatest detail by Bilibin et al.,[34] Pashkovskii et al.,[50] Asrar et al.,[74] and Krigbaum and co-workers.[75,76] It has been established that the mesomorphic properties of the polymers depend greatly on the intrinsic viscosity of the specimens $[\eta]$. In the range $[\eta] < 0.4$ dl g^{-1}, the transition temperatures depend greatly on $[\eta]$; the dependence becomes weaker for $[\eta] > 0.4$ dl g^{-1}. Thus, in order to avoid an uncertainty in the interpretation of the experimental data, it is essential to work with specimens having sufficiently high molecular weights. This factor greatly reduces the value of the results obtained in the study of polymers with low $[\eta]$.

The influence of the MWD on the thermal characteristics of the polymers has not been studied in detail, but in a number of communications there are indications that the presence of a broad MWD affects primarily the parameters of the LC–I transition. The synthesis and properties of polymers based on 4-hydroxyphenyl-4-hydroxybenzoate have been described.[77] The transition to the isotropic melt in these polymers is characterised by a broad (50–60 °C) two-phase region, which is a result, according to the authors, of the segregation of the molecules of the specimen with respect to molecular weights in the nematic phase. The influence of the method of synthesis and the purity of the initial components on the properties of the polymers described in the above study[77] has been examined by Krigbaum et al.[76] It was shown that the presence of a broad region in which the isotropic and LC phases coexist is a consequence of the composition inhomogeneity of the polymer specimens, which is caused by the chosen method of synthesis. Krigbaum et al.[76] demonstrated that the correct choice of the methods of polycondensation and purification of the monomers make it possible to synthesise polymer specimens having a narrow two-phase region.

As for low-molecular-weight LC compounds, the mesomorphic properties of *RF*-polymers depend greatly on the chemical structure of the mesogenic blocks. Strzelecki et al.[72] synthesised and investigated the mesomorphic properties of polymers with mesogenic groups containing 2, 3, and 4 benzene rings with nonamethylene spacers:

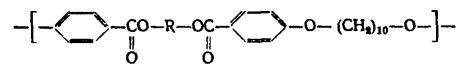


(VII)

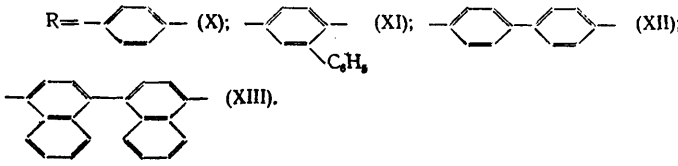
(VIII)

(IX)

The temperatures of the transitions to the isotropic melt for these polymers were respectively 200°, 305°, and 350 °C. The results of the above study[72] have been analysed[74] from the standpoint of the existing theories for low-molecular-weight nematogens, which make it possible to predict the clarification temperature as a function of the chemical structure of the molecules. Using the Flory–Ronca theory,[78] developed for monomeric molecules and taking into account the effects associated with the anisotropy of the molecular shape and with the anisotropy of the intermolecular interactions, the author concluded that the dependence of the clarification temperature T_i on the axial ratio of the rigid blocks is more pronounced for polymers than for the low-molecular-weight liquid crystals. A common conclusion is, however, the claim that existing theories are incapable of predicting the dependence of T_i on the axial ratio of the rigid component of the *RF*-polymers. The influence of the structure of the mesogenic component on the transition temperatures for the polymers (X)–(XIII), having different geometries of the mesogenic blocks and identical structures of the flexible chains, has been studied:[73]



where



It was shown that the clarification temperature and the range of existence of the nematic phase are much higher for the polymers (X) and (XII) than for the polymers (XI) and (XIII) respectively. The changes in the LC properties indicated take place as a consequence of the decrease of the anisometry of the rigid blocks after the introduction of asymmetric substituents.

Thus the character of the influence of the chemical nature of the mesogenic groups on the mesomorphic properties of the polymers is analogous to the influence of molecular structure on the properties of monomeric LC compounds. For low-molecular-weight liquid crystals, there are numerous data describing the relation between the mesomorphic properties and the molecular structure,[79] but there are as yet no criteria which would make it possible to predict the type and range of the existence of the mesophase for substances of a specific chemical nature. One of the most interesting and practically most important is the question of the relation between the structure of the mesogenic blocks and the type of their mesophase. The tendency to generate the smectic phase in low-molecular-weight liquid crystals is associated with the dominant role of the lateral intermolecular interaction compared with the end-face interactions.[5] This postulate is evidently valid also for *RF*-polymers: as can be seen from the data of Strzelecki and Van Lyuen,[80] the increase of the length of the flexible fragments of polymers entails, as for low-molecular-weight liquid crystals, the transition from nematic to smectic mesomorphism. Analogous results have been obtained by Bilibin et al.[81] and it was found that the tendency of polymers to generate the smectic phase is determined in many respect by the tendency of the low-molecular-weight model compounds having an analogous structure to generate this phase. However, the influence of the length of the flexible spacers on the tendency of the *RF*-polymers to generate the smectic phase cannot be explained from the standpoint of the characteristics of the homologous series of low-molecular-weight liquid crystals. A number of polymers based on 4,4'-dihydroxybiphenyl, in which all the even homologues exhibit smectic mesomorphism and the odd homologues exhibit nematic mesomorphism, have been investigated.[74] This indicates the specific role of the flexible spacers in the ordering of the *RF*-polymers.

The most important confirmation of the special role played by the flexible fragments in the generation of LC order in polymers is the marked dependence of the mesomorphic

properties on the chemical nature of the spacers. The flexibility of the latter is a decisive factor influencing their clarification temperature. It has been shown that, for polymers with disiloxane spacers, the range of existence of the mesophase is much narrower and the clarification temperature is lower than for the polymer with decamethylene spacers.[71] Table 4 presents the thermodynamic parameters of the LC–I transition for a series of polymers whose rigid groups consist of aromatic triads and the chemical nature and lengths of the flexible spacers are different. For the polymers with disiloxane spacers (XIV), ΔS_i is greater and T_i appreciably lower than for the polymer with decamethylene spacers (XV), which indicates the decisive role of the entropy jump ΔS_i in the LC–I transition. The introduction of the oligo-oxyethylene spacers does not entail an appreciable decrease of ΔS_i compared with polymers containing oligomethylene spacers [(XIV) and (II), $n = 6$]. However, ΔS_i reflects not only the conformational features of the chains in the isotropic phase but also the structural features of the mesophase and for this reason unambiguous conclusions about the influence of ΔS_i on T_i can be made only on the basis of the knowledge of the structure of the LC and isotropic phases. It is of interest to note that, for polymers having spacers containing asymmetric centres (for example, the OOP spacers[70,81]), calorimetric measurements do not allow the determination of ΔH_i and T_i. Polymers with OOP spacers are non-crystallisable but there are no explicit indications of the suppression of their mesomorphic properties. In a number of studies, it has been reported[74,82,83] that polymers with OOP spacers are capable of forming a cholesteric mesophase. For low-molecular-weight nematic and cholesteric liquid crystals, the ΔS_i are virtually identical[25,26] and the significant difference between the thermodynamic properties of the nematic and cholesteric phases of *RF*-polymers can therefore be accounted for solely by the conformational features of the chains in each phase. The conformation of the chains in the cholesteric phase probably does not differ greatly from the conformation of a statistical coil, which explains the absence of a measurable entropy jump in the LC–I transition in polymers with OOP spacers.

Thus the variation of the chemical nature of the flexible spacers influences decisively the mesomorphic properties of *RF*-polymers. The character of the influence of the nature of the flexible components on the mesomorphic properties of the polymers cannot be understood from the standpoint of the traditional ideas about the mesomorphism of low-molecular weight compounds, since the structure of the polymeric mesophase is determined to a large extent by the conformational state of the macromolecules.

V. COPOLYMERS

The study of the properties of copolymers has attracted investigators for a number of reasons. The nematic states in copolymers have a wider region of stability than in the case of homopolymers.[84] It has been shown that LC polymers based on non-mesomorphic components can be obtained by copolycondensation.[85] The synthesis and properties of copolymers containing aliphatic fragments of different lengths have been reported.[38,84] It has been shown that, in terms of its structural and thermodynamic aspects, the mesophase of the copolymers is virtually identical with the mesophase of the homopolymers, which is indicated by DSC and X-ray diffraction data. The phase diagram for copolymers based on 4,4′-dihydroxy-αα′-dimethylbenzylideneazine, containing octo- and dodeca-methylene spacers, is presented in Fig. 6*a* [Table 5, compound (XVII)]. The solidus lines (which have the form usual for eutectic diagrams) and the line representing the equilibrium between the nematic phase and the isotropic melt indicate the complete compatibility of the copolymer units in the LC phase. It has been established that copolymers with the equimolar composition have a very low degree of crystallinity and that under certain conditions it is possible to obtain specimens in the nematic vitreous state.

Copolymeric systems with one non-mesomorphic component, which, however, is capable of potential mesomorphism have been investigated[86] [Fig. 6*b*, Table 5, compound (XVIII)]. When the content of the non-mesomorphic component is in the range $0 \leq m \leq 75$ mole %, the copolymers exhibit enantiotropic

Table 4. Thermodynamic parameters of the LC–I transitions of *RF*-polymers with different structures of the flexible spacers.

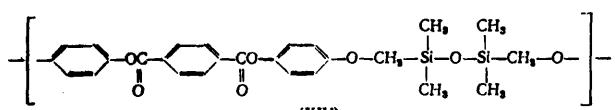
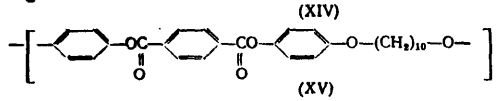
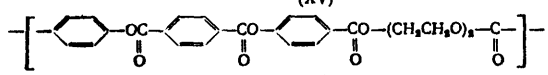
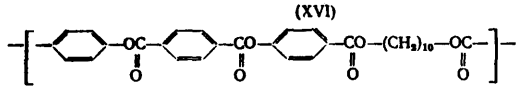
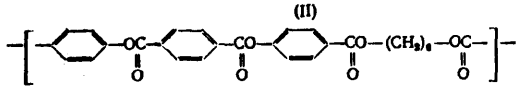
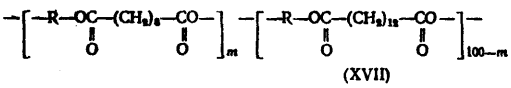
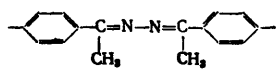
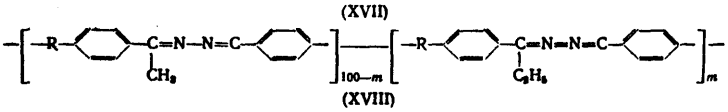
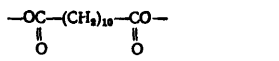
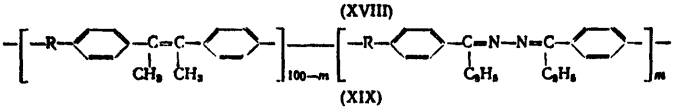
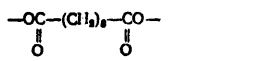
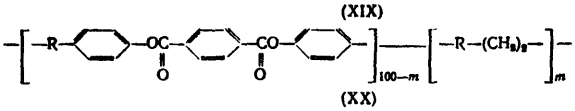
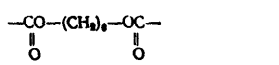
Structure of monomeric unit	T_i, °C	ΔH_i, kJ mol^{-1}	ΔS_i, J mol^{-1} K^{-1}	Refs.
 (XIV)	208	8.0	16.8	[71]
 (XV)	268	2.8	5.0	[71]
 (XVI)	335	7.4	12.2	[81]
 (II)	293	9.3	16.3	[81]
 (II)	347	8.6	13.9	[81]

Table 5. Certain types of mesomorphic *RF*-copolymers.

Structure of copolymer	R	Refs.
 (XVII)		[84]
 (XVIII)		[86]
 (XIX)		[85]
 (XX)		[87]

mesomorphism. When the content of the non-mesomorphic component is greater, there is a possibility of the manifestation of only monotropic mesomorphism in the system. Extrapolation of the thermodynamic parameters for the LC–I transition to the 100% content of the non-mesomorphic component made it possible to determine the "potential" mesomorphic properties of the polymer containing only non-mesomorphic units.† Copolymers with two non-mesomorphic components, exhibiting potential mesomorphism, have been investigated [Fig.6*c*, Table 5, compound (XIX)].[85] Enantiotropic mesomorphism has been observed in the composition range $35 \leq m \leq 60$ mole %. The manifestation of LC properties by copolymers becomes possible by virtue of the significant expansion of the region of stability of the mesophase. In this sense copolymers play the same role as mixtures of low-molecular-weight compounds with potential mesomorphic properties.

The synthesis of copolymers with a single non-mesomorphic component, which does not exhibit potential mesomorphism, has been described[87] [Fig.6*d*, Table 5, compound (XX)]. In contrast to those examined above, copolymers of this type are characterised by a broad two-phase region corresponding to the LC–I transition, which greatly expands with increase in the fraction of the non-mesomorphic component, which implies that there is partial segregation of the non-mesomorphic component.

Despite the outward similarity of the phase diagram presented in Fig.6 and the diagrams for mixtures of low-molecular-weight liquid crystals, the experimental data for copolymers cannot be understood from the standpoint of the characteristics known for low-molecular-weight systems. Furthermore, the study of the copolymers is complicated by the difficulty of obtaining phase equilibria, which greatly limits the progress in this field. Nevertheless, the need for more far-reaching study of the copolymers is evident because of their great practical importance. Copolymerisation is the most effective method of regulating mesomorphic properties and makes it possible to vary parameters important for applications, such as the degree of crystallinity, the glass point, and the mechanical characteristics of the given articles. From the standpoint of the use of *RF*-copolymers in the industrial manufacture of high-strength highly modular articles, systems analogous to that illustrated in Fig.6*d* are of greatest interest, since copolymers of this type make it possible to vary within wide limits the rheological characteristics of anisotropic melts.

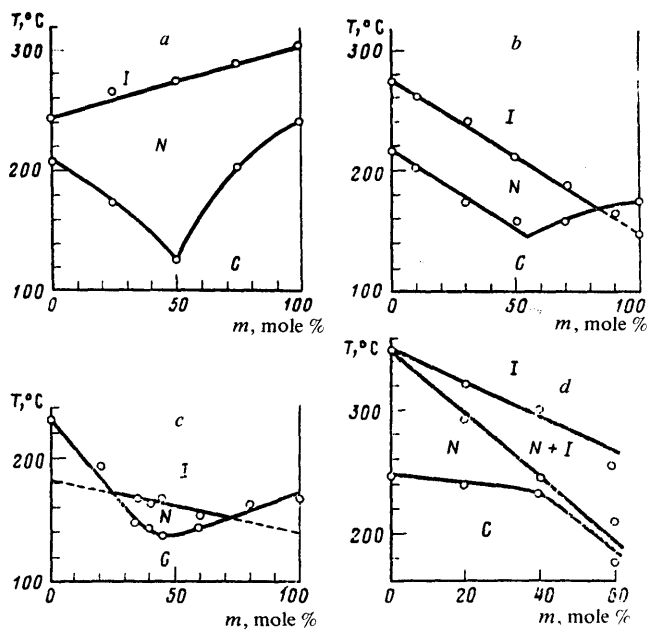


Figure 6. Phase diagrams for the copolymer systems presented in Table 5: *a*) (XVII); *b*) (XVIII); *c*) (XIX); *d*) (XX); *I*, *N*, and *C* = isotropic, nematic, and crystalline phases respectively; *m* = composition of the copolymer; *T* = temperature.[84–87]

† In this case the term "non-mesomorphic component" does not reflect the mesomorphic properties of the monomeric unit and is used in the sense that the homopolymer containing 100% of the non-mesomorphic units is also non-mesomorphic. Compounds for which the temperature of the transition from the crystalline to the isotropic state is higher than the clarification temperature are potentially mesomorphic.

Analysis of the data presented in the review permits the differentiation of three main trends in the study of *RF*-polymers: (1) the elucidation of the character of the influence of the chemical nature of the repeat unit on the mesomorphic properties of the polymers; (2) the study of the structure of the mesophases; (3) the determination of the relation between the molecular characteristics and the LC properties of the polymer. The value of the results obtained in the study of the structural characteristic features of the mesophases or of the influence of chemical structure on the properties of *RF*-polymers is greatly reduced if there are no corresponding data for the dependence of the mesomorphic properties on the molecular characteristics of the polymers. Nevertheless, whereas the first two research trends are fairly widely represented in the literature, the third is only in the initial stage of its development.

Thus an unambiguous interpretation of the experimental data is possible only for polymers with a rigorously defined composition, chemical structure, molecular weight, and molecular weight distribution.

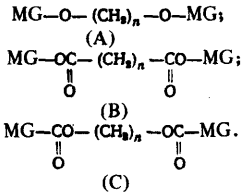
An important feature of *RF*-polymers is the possibility of macromolecular ordering together with the establishment of orientational order at the level of individual segments. This accounts for the interest in the study of the behaviour of the flexible fragments in the I–LC transition. Many experimental data indicate a high activity of the spacers, which is one of the manifestations of the macromolecular ordering process.

Despite the major advances made in the synthesis and study of *RF*-polymers, the problem of the classification of the types of mesophases for the given system remains unsolved. Identification of the low-molecular-weight liquid crystals permits a comprehensive prediction of the behaviour of the given substance as a function of external conditions. The determination of the analogous characteristics of *RF*-polymers should include, apart from the determination of the type of mesophase at the segmental level, the determination of the geometrical characteristics of the chains in the LC phase, since these parameters in fact determine in many respects the macroscopic properties of the polymer. It therefore appears to be essential to develop research directed to the determination of the macroconformations of the chains of mesogenic polymers in the LC phase.

Linear thermotropic polymers capable of existing in the LC state at temperatures ranging from room temperature to 350–400 °C are known. Naturally such a wide range of the thermal stability of the polymeric mesophases gives rise to extensive possibilities for the application of *RF*-polymers in extremely varied fields of science and engineering. Applied studies of *RF*-polymers are directed mainly to the synthesis of fibres and films with improved strength characteristics and a high thermal stability. More far-reaching investigation of the nature of the LC state will undoubtedly open new pathways to the more extensive employment of *RF*-polymers in science and engineering. Furthermore, the interest in thermotropic linear polymers is of fundamental importance: like the study of monomeric liquid crystals, it has expanded our knowledge of the molecular structure of liquid crystals and the study of polymers deepens our understanding of the analogous features of polymer melts and crystals.

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During the preparation of the review for the press, studies of fundamental importance were published. With the aid of the model of rotational-isomeric states,[88] a detailed investigation has been made of the conformational changes in the flexible fragment in the I–LC transition. It has been shown that the behaviour of the spacers during nematic ordering depends on the structure of the groups connecting the flexible fragments to the mesogenic groups (MG). Three types of connection of the spacers to the MG have been examined:



The connections of the (A) and (B) types are preferred for the establishment of the nematic state, since they ensure highly "extended" spacers and a parallel arrangement of the MG without a significant decrease of the configurational partition function for the system. This explains the high conformational contribution to the overall entropy change ΔS_i for *RF*-polymers with connections of the (A) and (B) types and the fact that ΔS_i for polymeric nematic materials is higher by an order of magnitude than for low-molecular-weight materials. In case (C) the extended state of the spacers is unlikely and nematic ordering is therefore unfavourable. If, however, the nematic state does nevertheless obtain, the conformational contribution to ΔS_i is small, since the conformational structure of the spacers in the isotropic and LC phases is virtually the same. The principal conclusions of Yoon and Bruckner[88] have been confirmed experimentally[89] by ^{2}H NMR for a polymer with connections of type (A). The results of the IR spectroscopic study of the structure of the spacers for polymers with type (C) connections[39,40] also confirmed the theory.[88]

Blumstein[90] and Pashkovskii[91] paid particular attention to the study of the dependence of the parameters of the LC–I transition on the molecular weight taking into account the chemical structure of the end groups of the macromolecules. It has been shown that, in the region of low molecular weights, the structure of the end groups influences strongly the properties of *RF*-polymer specimens. This finding demonstrates the difficulty of interpreting the experimental data obtained in the early studies[68,70] for low-molecular-weight specimens.

Volino et al.[92] studied the structure of solutions of an *RF*-polymer in a low-molecular-weight nematic liquid crystal. Relations were obtained between the order parameter of the polymers Q_{RF} and the degree of polymerisation x. It was shown that Q_{RF} increases with increase in the parameter x, tending to the value of Q for a low-molecular-weight nematic material, which indicates the ideal "incorporation" of the polymer chains in the nematic medium. The data of Volino et al.[92] agree with the theory,[93] where it has been shown that flexible *RF*-polymer molecules can be rigid in the nematic phase, in contrast to the usual flexible-chain or comb-shaped LC polymers.

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