

# Simulation of Structural Transition in an Isotropic Melt of Nematic and Smectic Polymers

V. B. ROGOZHIN, S. G. POLUSHIN, A. A. LEZOVA, G. E. POLUSHINA, A. S. POLUSHIN

Department of Physics,  
St. Petersburg University,  
7-9 Universitetskaya Embankment, 199034, St Petersburg,  
RUSSIA

*Abstract:* - The isotropic phases of four fractions of a mesogenic comb-shaped polymer were studied using the electric birefringence method. The fractions have either nematic – isotropic melt, or smectic-A – isotropic melt phase transition, depending on the degree of polymerization. All samples showed a structural transition in isotropic phase. Mathematical modeling of the electro-optical properties was performed based on the modified Landau-De Gennes theory using three- order parameters. The reason for the transition in the isotropic phase is the mutual rearrangement of the polar side groups of the polymer as a result of dipole-dipole interaction.

*Key-Words:* - comb-shaped polymer, short order, Kerr effect, iso - iso transition, mathematical modeling, dipole - dipole interaction.

Received: June 16, 2023. Revised: November 27, 2023. Accepted: January 2, 2024. Published: February 12, 2024.

## 1 Introduction

Structural transitions in the isotropic phase (iso-iso) are an interesting but insufficiently studied phenomenon. They are found in simple substances, [1], [2], [3], [4], in low molecular weight liquid crystals, [5], [6] and in flexible chain polymers, [7], [8], [9], [10]. Such transitions have also been found in liquid crystalline polymers. Liquid crystal polymer materials are widely used nowadays. It is important to understand the physical properties of their isotropic melts to use them, since the isotropic state is used in production process technologies. Furthermore, structural transitions in the isotropic phase can affect the properties of the liquid crystalline phase of a polymer material. This has been shown in works, [11], [12], [13]. The P8\*NN comb-shaped chiral LC polymer was found to have bistable phase behavior. It forms either a smectic-A phase or a TGB phase upon cooling. This depends on the cooling rate of the isotropic melt. A follow-up study of P8\*NN using the electro-optic (the Kerr effect) and X-ray scattering methods has shown that there is a structural transition in the isotropic phase. The transition is apparently associated with chirality of the polymer, since the same effects were found in the isotropic phase of chiral low molecular weight liquid crystals. The presence of such a transition in P8\*NN made it possible to explain the reason for the existence of two alternative liquid crystalline phases, [13]. In [14], two comb-shaped copolymers were studied by electro-optic methods. They

contained both mesogenic side groups and isophthalic acid groups in their structure. The isotropic phase was conventional for a sample with a fraction of acid groups of 18 mol %. The iso-iso transition appeared after increasing the proportion of acid groups to 37 mol %. In this case, the transition is caused by microphase separation due to a significant difference in the physicochemical properties of the monomer units of the copolymer, [15]. It should be noted that iso-iso transitions also exist in conventional flexible chain polymers that do not have a mesophase, such as polystyrene, [7], [8], [9], [16]. They are caused by a change in the cooperativity of the segmental thermal motion of macromolecules in a narrow temperature range near the temperature of the structural transition. As temperature rises, kinetic flexibility or “chain melting” increases. This is a common phenomenon for polymer melts. Thus, we can conclude that iso-iso transitions in various polymers are not uncommon. Their appearance is due to the structural features of macromolecules. And the nature of the transition can be associated with a number of reasons, such as temperature changes in dynamics of the main chain, chirality of the molecular system, heterogeneity of its chemical composition, and so on.

This work is a continuation of studies of iso-iso transitions in polymers. In this regard, we have selected a series of liquid crystalline comb-shaped polymers of the same structure, differing from each

other in the length of the main chain and the type of liquid crystalline phase.

## 2 Problem Formulation

The choice of research objects is due to the fact that we have discovered signs of a structural transition in an isotropic melt of one of these polymers previously, [17]. The selected polymers do not have chirality; the side groups have the same chemical nature. It follows that in this case a new version of the iso-iso structural transition is observed. Presumably, it is associated with the dipole-dipole interaction of polymer molecules. This work is devoted to the experimental and theoretical study of a new short-range order effect.

We use a conceptually new approach to study the electro-optical effect in the isotropic melt. Previously, the properties of the isotropic phase of low- and high-molecular mesogens have been studied in the range from the temperature of the isotropic melt-LC phase transition,  $T_C$ , to temperatures that are no more than 20-30 degrees higher. Both the value of the Kerr constant and its relative change are maximum under these conditions. In addition, the physical effects in this temperature range are well described by the Landau-De Gennes theory of phase transitions. We have expanded the research area. The properties of the isotropic phase were studied over the entire temperature range available for measurements. Mathematical modeling was performed for the same temperatures.

Polymer fractions with an acrylic main chain and mesogenic side groups were studied. The molecular weights of the fractions are in the region of transition from oligomers to polymers. For this reason, phase properties vary significantly with changes in molecular weight. We have set the following tasks:

1. The study of polymer fractions where different types of transition are realized: nematic-isotropic melt and smectic-A-isotropic melt.
2. The measurement of the Kerr effect in the isotropic melt over a wide temperature range and with an accuracy sufficient to detect possible structural transitions.
3. The modeling of electro-optical properties of the isotropic phase of liquid crystalline polymers based on the obtained experimental data.

## 3 Problem Solution

### 3.1 Material and Method

The four fractions studied are designated as P-15, P-86, P-200, and P-572, where the numbers correspond to the degree of the sample polymerization. The structure of the monomer unit is shown in Figure 1. The polymer synthesis and the phase behavior of the fractions were described in [18]. The samples have either a nematic and smectic-A phase (P-15, P-86 samples), or only a smectic-A phase (P-200 and P-572 samples), depending on the degree of polymerization. Thus, P-15 and P-86 polymers undergo a nematic – isotropic phase transition, while P-200 and P-572 polymers undergo a smectic-A – isotropic phase transition.

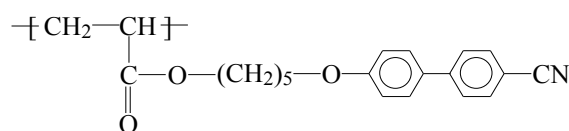


Fig. 1: Structure of a monomer unit

The isotropic melt was studied by the Kerr effect method. The magnitude of birefringence  $\Delta n_E$  induced by an electric field is related to the Kerr constant  $K$  and the electric field strength  $E$  by the relation  $\Delta n_E = KE^2$ . The value of  $K$  is calculated from this. The measurements were carried out using a pulsed rectangular field with a strength  $E$  of up to  $1.5 \times 10^3$  V/cm. The duration of each pulse did not exceed 100 ms, the interval between pulses reached several seconds. A highly sensitive compensation method for measuring birefringence was used with the application of an elliptical light polarization modulator, [19]. This made it possible to measure induced birefringence of less than  $10^{-9}$ . Measurements of the Kerr constant  $K$  were made both when the temperature increases and when it decreases. Thermostatting was performed at each temperature point with an accuracy of 0.1 degrees for 15-20 minutes, followed by measurements. The temperature dependence of  $K$  was completely reproducible, that is, temperature hysteresis of  $K$  or polymer destruction was not observed.

### 3.2 Experimental Results

The results of measurements in the isotropic phase over a wide temperature range are presented in Figure 2. An important feature is the division of the general dependence  $1/K = f(T)$  into two straight segments with different slopes. Apparently, this is due to changes in molecular packing and short-range order. On this basis, we can talk about the

presence of two isotropic phases and the transition between them.

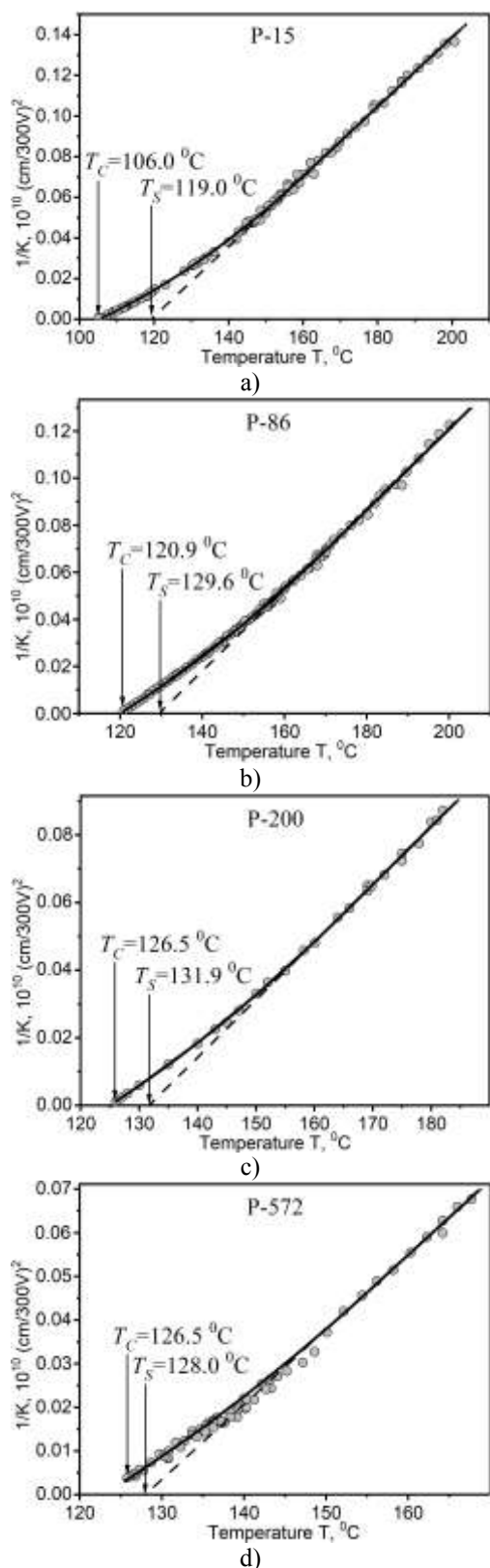


Fig. 2: Temperature dependences of the inverse Kerr constant for samples P-15 (a), P-86 (b), P-200 (c), and P-572 (d). Experimentally obtained inverse values of the Kerr constant are indicated by points,

theoretically calculated values are shown by solid lines.

We can assume the following mechanism of structural transition in these polymers. The side groups have a dipole moment. Its magnitude is approximately 5 D, and the dipole is directed along the axis of the group. The architecture of the comb-shaped macromolecule forces neighboring side groups, and hence their dipoles, to be oriented parallel to each other. The energy of the dipole-dipole interaction is high, therefore, such an arrangement is energetically unfavorable for them. They strive to take an antiparallel position whenever possible. The temperature rise increases the flexibility of the polymer chain by rotating the units around single bonds. As a result, when the critical temperature is reached, some of the side groups are rearranged into a more stable antiparallel orientation, [20]. Consequently, the molecular effective dipole moment decreases, which manifests itself in a change in the temperature dependence of the Kerr constant.

The strong dipole interaction of alkoxy-cyanbiphenyl molecules, which are used as side groups in the polymer, is confirmed by experiments and calculations. In [21], it was found that most of the neighboring 8CB molecules are oriented antiparallel using the molecular dynamics method. This pattern is performed in all phases, including isotropic. Neutron and X-ray scattering methods showed that the layered structure is formed in alkyl- and alkoxy-cyanbiphenyls by a double molecular layer with partial overlapping of the layers, [22]. This also means a predominantly antiparallel orientation of the polar mesogenic groups.

### 3.3 Modeling

The Landau-De Gennes theory, which was originally developed for nematics, is successfully used to describe the electro-optical properties of the isotropic phase in the region of transition to the liquid crystalline phase, [23], [24]. Later, versions of this theory were extended to the case of isotropic phase – smectic-A phase transitions, in the description of which it is necessary to use both orientational and translational order in calculations, [17], [23], [24], [25], [26]. Further complications of the theory were associated with the fact that structural transitions were discovered in polymer melts, at which a sharp change in the temperature dependence of the electro-optical constant  $K$  was observed. The reason for this behavior of the melt was different, including microphase separation of molecular fragments with different chemical natures and chirality of the molecules, [14]. In these works,

another, third order parameter was introduced in addition to the orientational and translational order parameters. It was used in work [14], where microphase separation in a copolymer that had chemically dissimilar side groups was discussed. The parameter was called “microphase”, and we will use the term in this work, but its meaning is much broader. It is responsible for rearrangements at the molecular level. Electro-optical measurements, which were carried out in our work, also demonstrate a complex dependence of the Kerr constant on temperature (Figure 2). This is due to the dipole-dipole interaction of the polar side groups of the polymers. The change in the mutual orientation of such groups should be especially considered in the calculations, since they, unlike the units of the main chain, form short-range order in the melt. Therefore, to describe the experimental results, we use the theoretical model of the electro-optical effect that we have developed, which also includes the third order parameter.

The electro-optical properties of liquid crystalline polymers in the vicinity of the isotropic liquid – liquid crystal phase transition temperature can be described using the Landau-De Gennes phenomenological approach. According to this approach, the Helmholtz energy of the polymer melt ( $F$ ) is expanded into a series of powers of the orientational ( $S$ ) and translational ( $\varphi$ ) order parameters. The presence of fragments with different chemical natures in the composition of macromolecules can lead to the appearance of a large number of disordered microdomains in the melt. Such a microstructured phase can exist even in the absence of orientational ( $S = 0$ ) and layer ( $\varphi = 0$ ) ordering, [27] and is characterized by the microphase separation parameter  $\psi$ . The measured quantity in experiments to determine the electro-optical properties of copolymer melts is the Kerr constant  $K = \Delta n/E^2$ , where  $\Delta n$  is the birefringence. To calculate the value of  $K$ , it is necessary to add the  $WS$  summand to the expression for calculating the Helmholtz energy, considering the influence of the electric field, [24], where  $W = \frac{1}{12\pi}\Delta\varepsilon_0 E^2$ ,  $\Delta\varepsilon_0$  is the dielectric anisotropy of the melt at  $S = 1$ . Due to the smallness of the orientational ordering induced by a weak electric field, the expansion of the Helmholtz energy can be limited to summands of no higher than the second degree in  $S$ , [24].

In this case, the energy of the melt  $F$  can be expanded into a series in powers of  $S$ ,  $\varphi$ , and  $\psi$  parameters as follows:

$$F = F_0 + \frac{1}{6}k\varphi^6 - \frac{1}{4}\beta\varphi^4 + \frac{1}{2}\alpha\varphi^2 - \frac{1}{2}\eta\varphi^2\psi^2 - \frac{1}{2}\delta\varphi^2S^2 + \frac{1}{2}\gamma\psi^2S^2 - \frac{1}{2}e\psi^2 - \frac{1}{3}b\psi^3 + \frac{1}{2}AS^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 - WS \quad (1)$$

where  $A$ ,  $e$ , and  $\alpha$  coefficients depend on the melt temperature  $T$ :  $A = A_0(T - T_S)$ ,  $e = e_0(T - T_P)$ ,  $\alpha = \alpha_0(T - T_f)$ , while  $A_0$ ,  $e_0$ ,  $\alpha_0$ ,  $T_S$ ,  $T_P$ , and  $T_f$  have a positive value. The remaining expansion coefficients are assumed to be independent of temperature.

The choice of degrees of expansion parameters in relation (1) is determined by the necessity to comply with experimental data. It allows one to describe the behavior of the melt in the vicinity of first kind phase transitions into nematic and smectic states with discontinuous changes in  $S$  and  $\varphi$  parameters. The summands proportional to the first powers of the expansion parameters are absent in expression (1), since they exclude the possibility of the existence of an isotropic phase, where  $S$ ,  $\varphi$ , and  $\psi$  are equal to zero. We can leave only summands with even degrees to describe layer ordering in equation (1), since  $F(\varphi) = F(-\varphi)$ , [24], [25]. The summands containing  $\varphi^2\psi^2$ ,  $\varphi^2S^2$ , and  $\psi^2S^2$  products are introduced to consider the mutual influence of these parameters.

Minimization of the Helmholtz energy (1) according to  $dF/d\varphi = 0$ ,  $dF/d\psi = 0$ , and  $dF/dS = 0$  expansion parameters allows us to determine the conditions for the equilibrium existence of the smectic, microstructured and nematic phases, respectively (2-4):

$$\varphi(k\varphi^4 - \beta\varphi^2 + \alpha - \eta\psi^2 - \delta S^2) = 0 \quad (2)$$

$$\psi(-b\psi - e - \eta\varphi^2 + \gamma S^2) = 0 \quad (3)$$

$$AS - BS^2 + CS^3 - W - \delta\varphi^2S + \gamma\psi^2S = 0 \quad (4)$$

Thus, the parameter values of  $\varphi > 0$  in (2) correspond to the presence of layer ordering and, accordingly, the presence of the smectic phase. Wherein:

$$\varphi^2 = \frac{\beta}{2k} \left[ 1 + \sqrt{1 - \frac{4k}{\beta^2}(\alpha - \eta\psi^2 - \delta S^2)} \right] \quad (5)$$

The parameter  $\psi$  corresponding to this state in this case is expressed as:

$$\psi = P(1 + \sqrt{1 - Q/P^2}) \quad (6)$$

where:

$$P = \frac{b(e+\beta\eta/2k-\gamma S^2)}{b^2-\eta^3/k}$$

$$Q = \frac{(e-\gamma S^2)^2 + \frac{\beta\eta}{k}(e-\gamma S^2) + \frac{\eta^2}{k}(\alpha-\delta S)}{b^2-\eta^3/k}$$

The simultaneous solution of the system of equations (4-6) by numerical methods makes it possible to determine the equilibrium values of the order parameters at a given temperature in the smectic phase.

The trivial solution (2)  $\varphi = 0$  corresponds to the absence of layer ordering and, accordingly, the smectic phase. For this case, we obtain expression (7) from condition (3) for  $\psi > 0$ . Expression (4), which meets the condition of equilibrium existence of the nematic phase at  $\varphi = 0$ , is transformed into (8), from which the value of the orientational order  $S$  can be calculated considering (7):

$$\psi = -\frac{1}{b}(e - \gamma S^2) \quad (7)$$

$$AS - BS^2 + CS^3 - W + \gamma\psi^2 S = 0 \quad (8)$$

The parameter  $\psi$  cannot take negative values; its smallest value is  $\psi = 0$ . In this case, expansion (1) takes the form (9), and expression (4) transforms to the form (10):

$$F = F_0 + AS^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 - WS \quad (9)$$

$$AS - BS^2 + CS^3 - W = 0 \quad (10)$$

Thus, in the temperature region where microstructuring is absent ( $\psi = 0$ ), expression (9) fully corresponds to the expansion of the Helmholtz energy in the Landau-De Gennes form for nematics, [23], [24].

Finally, let us consider two possible states of the melt, where the orientational ordering parameter is  $S=0$  in the absence of an electric field ( $W=0$ ). The state in which  $\varphi = 0$ ,  $S = 0$ ,  $\psi > 0$  can be considered as a separate microstructured phase, consisting of microdomains randomly distributed throughout the entire volume of the melt. Expression (7) in this case takes the form (11):

$$\psi = -\frac{e}{b} \quad (11)$$

Coefficient  $e$  depends on temperature as  $e = e_0(T - T_P)$ . Respectively, (11) is chosen as a solution when  $T < T_P$ , and when  $T > T_P$ , the second case is realized from the non-negativity condition of  $\psi$ , when  $\psi = 0$  corresponds to the solution to

equation (3). This case corresponds to an isotropic state. That is why  $T = T_P$  value can be considered as the temperature of transition from the isotropic phase to the microstructured one. There is no jump in the microphase ordering parameter at  $T = T_P$ , and such a transition can be considered a second kind phase transition.

Turning to a discussion of the electro-optical properties of isotropic copolymer melts, it should be emphasized that the appearance of even a very weak electric field ( $W > 0$ ) inevitably induces long-range orientational ordering  $S_E > 0$  in the temperature range, where there is no long-range orientational ordering in the absence of a field. This is due to the partial orientation of mesogenic fragments of macromolecules by the electric field. Such ordering is extremely small due to the smallness of the electric field in comparison with the orientational ordering in the nematic or smectic phases. The value of  $S_E$  directly depends on the field and is determined by the shift of the minimum Helmholtz energy from the position  $S=0$  at  $W=0$  to the region of positive values  $S_E > 0$  at  $W > 0$ . The position of this minimum is determined directly by formulas (1), (7)-(11).

One of the main measured quantities in electro-optical experiments is the Kerr constant  $K = \Delta n_0 S_E / E^2$ , where  $\Delta n_0$  is the birefringence in a fully oriented phase ( $S=1$ ),  $S_E$  is the orientational order parameter in the presence of an external electric field with strength  $E$ , [19], [23], [24].

The expansion of the Helmholtz energy  $F$  can be limited to summands of no higher than the second degree according to [23], [24], due to the smallness of the orientational ordering induced by a weak electric field.

In the isotropic phase, where there is no microphase separation, the expression for  $S_E$  coincides with that obtained in the Landau-De Gennes theory for isotropic nematic melts, [23], [24]:

$$S_E = W/A_0(T - T_S) \quad (12)$$

In the microstructured phase, the parameter  $S_E$  is determined by the relation:

$$S_E = W/\{A_0(T - T_S) + \gamma \frac{e_0^2(T - T_P)^2}{b^2}\} \quad (13)$$

The inverse value of the Kerr constant of the melt  $1/K$  for an isotropic phase, considering (12), is determined by relation (14), and for a microstructured phase, considering (13), by relation (15):

$$1/K = \frac{12\pi}{\Delta n_0 \Delta \varepsilon_0} A_0 (T - T_S) \quad (14)$$

$$1/K = \frac{12\pi}{\Delta n_0 \Delta \varepsilon_0} \left\{ A_0 (T - T_S) + \gamma \frac{e_0^2 (T - T_P)^2}{b^2} \right\} \quad (15)$$

The temperature dependence of the inverse value of the Kerr constant is thus linear (14) in the isotropic phase at temperatures  $T > T_P$ , while in the microstructured phase at  $T < T_P$  this dependence is nonlinear (15).

To analyze the obtained relationships, numerical calculations of the temperature dependences of the inverse value of the Kerr constant  $1/K$  were carried out in the MatLab package under conditions when a microstructured state appears in the melt. The temperature of the phase transition from microstructured to nematic (samples P-15 and P-86) or smectic state (sample P-200 and P-572) was determined based on the condition of coincidence of the Helmholtz energy minima for states with  $S=0$  (microstructured state) and  $S>0$  (nematic or smectic state).

Table 1 and Table 2 show the values of coefficients calculated for the indicated samples, as well as the calculated phase transition temperature  $T_C$ . The values of some coefficients remained constant:  $\beta = 72$  kJ/mol,  $\eta = 1$  kJ/mol,  $\delta = 1$  kJ/mol,  $b = 24$  kJ/mol,  $C = 5$  kJ/mol,  $a_0 = 2$  kJ/(K×mol),  $A_0 = 0.295$  kJ/(K×mol).

Table 1. Values of coefficients that were used in modeling

| Fraction | $k$ ,<br>kJ/mol | $\gamma$ ,<br>kJ/mol | $B$ ,<br>kJ/mol | $W$ ,<br>J/mol |
|----------|-----------------|----------------------|-----------------|----------------|
| P-15     | 60              | 4.90                 | 2.00            | 0.43           |
| P-86     | 60              | 3.45                 | 2.25            | 0.43           |
| P-200    | 90              | 2.35                 | 2.71            | 0.43           |
| P-572    | 90              | 2.35                 | 2.71            | 0.43           |

Table 2. Values of coefficients defining the temperature dependence during modelling

| Fraction | $e_0$ ,<br>kJ/(K×mol) | $T_f$ ,<br>°C | $T_P$ ,<br>°C | $T_S$ ,<br>°C | $T_C$ ,<br>°C |
|----------|-----------------------|---------------|---------------|---------------|---------------|
| P-15     | 0.40                  | 95.0          | 160           | 119.0         | 106.0         |
| P-86     | 0.42                  | 110.0         | 172           | 129.6         | 120.9         |
| P-200    | 0.56                  | 124.7         | 165           | 131.9         | 126.5         |
| P-572    | 0.60                  | 123.0         | 155           | 128.0         | 126.5         |

### 3.4 Discussion

Low-temperature segments of the  $1/K$  versus  $T$  curves occupy intervals of the order of 25 – 40 °C, depending on the fraction, Figure 2. High-temperature segments are more extended, since on

the side of maximum temperatures they are limited only by the temperature of polymer destruction. Thereby, it was possible to observe the properties of the isotropic phase from 106 to 200 °C in the P-15 oligomer. The wide temperature range distinguishes the present work from earlier works, [19], [28], [29] and from our previous results, [13].

The nature of the dependence of  $1/K$  on  $T$  for fractions P-15, P-86, P-200, and P-572 is independent of the type of phase transition to the LC phase. Therefore, the electro-optical properties were described using a general theoretical approach.

The macromolecules of acrylic homopolymer are polar. The electro-optical effect in a melt is determined by optically and electrically anisotropic side cyanobiphenyl groups. In addition, the electro-optical effect depends on the short-range order in the arrangement of these groups. They can change their mutual orientation relatively freely due to long aliphatic spacers connecting them to the main polymer chain of the molecule.

The electro-optical constant  $K(T - T^*)$  is used to quantify the electro-optical effect. Here  $T^*$  is the temperature of the imaginary second order transition. In this work, the dependence of  $1/K$  on  $T$  is not linear. Thus, the values of this constant for different segments of the experimental dependence in Figure 2 can be found as  $ctg\alpha$ , where  $\alpha$  is the slope of the experimental curve. A change in the slope in the region of the structural transition indicates a change in the electro-optical constant. For example, for the P-572 fraction the ratio is  $ctg\alpha_2/ctg\alpha_1 = 0.71$ , where indices 1 and 2 correspond to the low- and high-temperature segments of the curve. This is a big change. The effective dipole moment is greatly decreased as a result of the reorientation of side groups from parallel to antiparallel orientation while the temperature is increased.

## 4 Conclusion

The temperature dependence of the inverse Kerr constant in the region of the phase transition from the isotropic to the liquid crystalline phase should be linear according to the theory of electro-optical properties of mesogens. The experimentally discovered nonlinearity of the temperature dependence does not fit into these theoretical concepts. The nonlinearity arises from the dipole-dipole interaction of the side cyanobiphenyl groups. The groups are partially reoriented when the temperature changes, and a structural transition occurs with a change in short-range order.

Therefore, the Landau - De Gennes phenomenological approach was modified. The contribution of an additional parameter responsible for the dipole rearrangement is considered in the expansion of the Helmholtz free energy. It is shown that varying the expansion parameters makes it possible to obtain temperature dependences for the inverse Kerr constant that correspond to the experimental ones.

The measurements performed made it possible to observe the iso-iso transition in four fractions using the electro-optic method. Other methods are also necessary to characterize the transition properties, changes in structure, and physical properties of polymer melts. The list of possible methods includes X-ray diffraction analysis, precision calorimetry, dielectric spectroscopy, and so on.

The study of short-range order effects in the isotropic phase of polymers is a general trend of our research. The orientational short-range order in comb-shaped polymers is formed by anisometric side groups. They are connected to the main chain through flexible spacers and are capable of self-organization. A short-range order depends on the degree of freedom of mesogenic groups, the nature of intermolecular interactions, and temperature. The combination of these factors, as well as their changes, determine the properties of the isotropic phase, including, among others, the appearance of iso-iso transitions. Interesting objects for future research may be comb-shaped polymers, in which side mesogenic groups are connected to the main chain through short spacers. Such spacers limit the freedom of orientation of side groups [30], [31]. A polymer may lose its ability to form the LC phase. Under these conditions, the short-range order among mesogenic groups can be quite perfect, but at the same time the polymer chain will have a strong effect on it. The competition of various factors can lead to the appearance of previously unknown nanostructural effects. Thus, new opportunities are opening up for the creation of promising polymer materials.

#### References:

[1] L. Henry, M. Mezouar, G. Garbarino, D. Sifré, G. Weck and F. Datchi, Liquid-Liquid Transition and Critical Point in Sulfur, *Nature*, Vol. 584, 2020, pp. 382 -386.  
 [2] V. V. Brazhkin, Y. Katayama, M. V. Kondrin, T. Hattori, A. G. Lyapin and H. Saitoh, AsS Melt Under Pressure: One Substance, Three

Liquids. *Phys. Rev. Letters*, Vol. 100, 2008, pp. 145701[1]-145701[4].  
 [3] Paul F. McMillan, Mark Wilson, Martin C. Wilding, Dominik Daisenberger, Mohamed Mezouar and G. Neville Greaves, Polyamorphism and Liquid-Liquid Phase Transitions: Challenges For Experiment And Theory, *J. of Physics: Condensed Matter*, Vol. 19, 2007, p. 415101 (41pp).  
 [4] Paul F. McMillan, Polyamorphic Transformations in Liquids and Glasses, *J. Mater. Chem.*, Vol. 14, 2004, 1506- 1512.  
 [5] I. Nishiyama, J. Yamamoto, J. W. Goodby, H. Yokoyama, Ferrielectric and Antiferroelectric Chiral Twin Liquid Crystals Showing a Stable Chiral Nematic Phase, *Mol. Cryst. Liq. Cryst.*, 2005, Vol. 443, No.11, pp. 1409-1423.  
 [6] J. W. Goodby, A. Petrenko, M. Hird, R. A. Lewis, J. Meierb and J. C. Jones, Liquid-Crystalline Abrikosov Flux Phase with an Antiferroelectric Structure, *Chem. Commun.*, Vol. 13, 2000, pp. 1149-1150.  
 [7] C. A. Glandt, H. K.Toh, J. K. Gillham and R. F. Boyer, Effect of Dispersity on the  $T_{II}$  ( $> T_g$ ) Transition in Polystyrene, *J. of Appl. Polym. Sci.*, Vol 20, 1976, pp. 1277-1288.  
 [8] R. F. Boyer, Pressure Dependence of Secondary Transitions in Amorphous Polymers. 1.  $T_{II}$  for Polystyrene, Poly(vinyl acetate), and Polyisobutylene, *Macromolecules*, Vol. 14, No. 2, 1981, pp. 376-385.  
 [9] S. J. Stadnicki, J. K. Gillham, R. F. Boyer, The  $T_{II}$  ( $T > g$ ) Transition of Atactic Polystyrene, *J. of Appl. Polym. Sci.*, Vol. 20, 1976, pp. 1245-1275.  
 [10] R. F. Boyer and R. L. Miller, Correlation of Liquid-State Compressibility and Bulk Modulus with Cross-Sectional Area per Polymer Chain, *Macromolecules*, Vol. 17, 1984, pp. 365-369.  
 [11] M. Kozlovsky, B.-J. Jungnickel, H. Ehrenberg, Bistable Phase Behavior and Kinetics of Nonisothermal Mesophase Formation in a Chiral Side Chain Polymethacrylate, *Macromolecules*, Vol. 38, 2005, pp. 2729-2738.  
 [12] M. V. Kozlovsky, Influence of Chirality on the Mesophase of Side Chain Polymers with Phenyl Benzoate Pendant Groups, *Liq. Cryst.* Vol. 32, No.3, 2005, pp. 401-406.  
 [13] S. Polushin, V. Rogozin, I. Beloborodov, E. Rjuntsev and M. Kozlovsky, Existence of Two Different Isotropic Phases as a Reason for Bistable Phase Behavior of an LC Side-

- Chain Polymethacrylate, *Macromol. Rapid Commun.*, Vol. 29, 2008, pp. 224-228.
- [14] V. B. Rogozhin, A. V. Lezov, S. G. Polushin and E. I. Ryumtsev, Effect of the Microphase Separation on the Electro - Optical Properties of Isotropic Melts of Thermotropic Liquid Crystals, *Russian J. of Phys. Chem. A*, Vol. 85, No.11, 2011, pp.1867-1871.
- [15] L. Leibler, Theory of Microphase Separation in Block Copolymers, *Macromolecules*, Vol. 13, No.6, 1980, pp. 1602-1617.
- [16] S. Shuying, Z. Zhenguang, L. Zaijun and Z. Guangzhao, Liquid-to-Liquid Relaxation of Polystyrene Melts Investigated by Low-Frequency Anelastic Spectroscopy., *J. Phys.: Condens. Matter*, Vol. 19, 2007, pp. 416107-416116.
- [17] S. G. Polushin, V. B. Rogozhin and E. I. Ryumtsev, Kerr Effect in the Isotropic Melt of Smectic Polymer, *Doklady Phys. Chem.*, Vol. 465, Part 2, 2015, pp. 298-300.
- [18] S. G. Kostromin, V. P. Shibaev, U. Geßner, H. Cackovic, Separation and Study of Oligoacrylates with 4-Cyanobiphenyl Mesogenic Groups, *Springer, J. Polym. Sci., Ser. A.*, Vol. 38, No.9, 1996, pp. 1039-1047.
- [19] N. V. Tsvetkov and E. I. Rjuntsev, Kerr Effect in the Isotropic Phase of Nematogens, *Mol. Cryst. and Liquid Cryst.*, Vol. 133, 1986, pp. 125-134.
- [20] S. J. Cowling, A. W. Hall, J. W. Goodby, Effect of Terminal Functional Group Size on Ferroelectric and Antiferroelectric Properties of Liquid Crystals, *Liq. Crystals*, Vol. 32, No.11, 2005, pp. 1483-1498.
- [21] M. F. Palermo, A. Pizzirusso, L. Muccioli and C. Zannoni, An Atomistic Description of the Nematic and Smectic Phases of 4-n-Octyl-4 Cyanobiphenyl (8CB), *J. of Chem. Phys.*, Vol. 138, 2013, pp. 204901[1]-204901-[16].
- [22] S. Urban, J. Przedmojski and J. Czub, X-Ray Studies of the Layer Thickness in Smectic Phases, *Liq. Cryst.*, Vol. 32, No.5, 2005, pp. 619-624.
- [23] P. G. de Gennes., J. Prost, *The Physics of Liquid Crystals*, Oxford, Clarendon Press, 1993.
- [24] S. Chandrasekhar, *Liquid Crystals*, Cambridge: Cambridge Univ. Press, 1992.
- [25] P. K. Mukherjee, H. Pleiner and H. R. Brand, Simple Landau Model of the Smectic-A-Isotropic Phase Transition, *Europ. Phys. J. E.*, Vol. 4, 2001, pp. 293-297.
- [26] P. K. Mukherjee, The Kerr effect and Nonlinear Dielectric Effect in the Vicinity of the Isotropic to Anti-Ferroelectric B2 Phase Transition in Banana Shaped Molecules, *Chemical Physics*, Vol. 405, 2012, pp. 67-70.
- [27] P. K. Mukherjee and S. J. Rzoska, Pressure Effect on the Smectic-A-Isotropic Phase Transition, *Phys. Rev. E*, Vol. 65, 2002, pp. 051705[1]-051705[4].
- [28] M. Eich, K. Ullrich, J. H. Wendorff and H. Ringsdorf, Pretransition Phenomena in the Isotropic Melt of Mesogenic Side Chain Polymer, *Polymer*, Vol. 25, 1984, pp. 1271-1276.
- [29] Th. Fuhrmann, M. Hosse, I. Lieker, J. Ruebner, A. Stracke and J. H. Wendorff, Frustrated Liquid Crystalline Side Group Polymers for Optical Storage, *Liq. Cryst.*, Vol. 26, No.5, 1999, pp. 779-786.
- [30] V. P. Shibaev, Liquid-Crystalline Polymer Systems: from the Past to the Present, *Polymer Science A*, Vol. 56, 2014, pp. 727-762.
- [31] H. Finkelmann, H. Ringsdorf, J. Wensdorff, Model Considerations and Examples of Enantiotropic Liquid Crystalline Polymers, *Makromol. Chem.*, Vol. 179, No.1, 1978, pp. 273-276.

#### Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

- V. B. Rogozhin: investigation, theory, modeling, writing original draft.
- S. G. Polushin: conceptualizing, data curation, writing original draft.
- A. A. Lezova: modeling, writing - review and editing.
- G. E. Polushina: writing - review and editing.
- A. S. Polushin: data curation.

#### Sources of Funding for Research Presented in a Scientific Article or Scientific Article Itself

No funding was received for conducting this research.

#### Conflict of Interest

The authors have no conflicts of interest to declare.

#### Creative Commons Attribution License 4.0 (Attribution 4.0 International, CC BY 4.0)

This article is published under the terms of the Creative Commons Attribution License 4.0

[https://creativecommons.org/licenses/by/4.0/deed.en\\_US](https://creativecommons.org/licenses/by/4.0/deed.en_US)