POLYMER, BIOORGANIC, AND HYBRID NANOMATERIALS

Nanostructuring Polystyrene in a Melt

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Abstract—The melts of four fractions of polystyrene are investigated by the method of electric birefringence. It is found that the electro-optical properties of the melt greatly depend on the length of the polymer chain. The fractions with the highest molecular weight showed an increase in the Kerr constant K at temperatures above 120°C. The anomalous nature of the temperature dependence of the form $K \propto T$ is explained by the fact that at high temperatures the flexibility of the polymer chain begins to grow rapidly. This process is called the liquid-liquid transition. As a result, the short-range orientational order increases, which is associated with a change in the mutual orientation of phenyl rings.

INTRODUCTION

Structural transitions of the isotropic phase—isotropic phase can occur in liquids, but until now they have remained a poorly studied phenomenon. The trend in recent years has been the observation of these transitions at extremely high pressures and temperatures in melts of simple substances such as sulfur [1], as well as in melts of binary compounds [2−5]. It was shown that a change in the short-range order in melts can occur under the influence of external conditions not only gradually, but also abruptly. In this case, a change in the structure can be accompanied by a change in a number of physical properties, similar to first-order phase transitions in crystalline substances, and the number of isotropic-liquid states in one substance can reach three [2]. At the same time, even at normal pressure in the isotropic-liquid phase of such complex substances as polymers, strong changes in the structure and short-range order can occur with a change in temperature. The method of electric birefringence (EB, or the Kerr effect) has been used with success for their observation [6]. It was used to detect the transition between two isotropic-liquid states in a polymethacrylate melt with chiral mesogenic side groups, which was confirmed by calorimetry and wide-angle X-ray scattering [7]. A first-order phase transition associated with the microphase segregation of mesogenic and acid side groups was observed in an isotropic melt of statistical comb-like copolymers [8, 9]. Finally, in many flexible-chain polymers, a phenomenon called the liquid−liquid transition (LL transition) has been studied by various experimental methods [10−14]. It manifested itself in both equilibrium and dynamic properties. The transition was explained by the fact that, upon heating and reaching the LL-transition temperature, the cooperativity of the movement of monomer-chain links decreases, the movement disappears, and the monomer unit of the macromolecule becomes the main kinetic unit. This transition was also studied in polystyrene [10, 12, 14]. The results of this work show that this kind of transition in polystyrene leads to the appearance of an anomalous temperature dependence of the EB in a polystyrene melt at a high temperature, which is associated with an increase in short-range orientational order in the system of phenyl rings.

RESULTS

The electro-optical properties of melts of four fractions of polystyrene, including oligomer P-5 with a mass of $M_W = 504$ and three polymers P-25, P-45 and P-88 with masses of 2.63×10^3, 4.65×10^3 and 9.1×10^3 respectively. The designation of the type P-n indicates the number of monomer units in the chain (Fig. 1), where $n = 5, 25, 45$ or 88. The polymers are produced by the company Tosoh Corp. (Japan) by anionic polymerization and have a narrow molecular weight distribution; the polydispersity coefficient M_W/M_N is in the range from 1.02 to 1.14.

An experimental technique was used that was previously applied when working with polymer melts [6−9, 15]. The electric birefringence Δn was measured in a pulsed electric field with the strength E up to 2.5×10^3 V/cm with a pulse duration up to 100 ms. The duration of rectangular pulses was chosen such that it was sufficient to establish an equilibrium electro-optical effect. The Kerr constant K was calculated from the ratio $K = \Delta n / E^2$. Kerr's law was fulfilled in all cases; the relative measurement error did not exceed 10%.
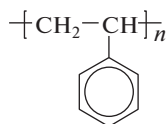
Fig. 1. Structure of the monomer unit of polystyrene. The phenyl rings of atactic polystyrene are statistically distributed on both sides of the chain.

For measurements, a rotary elliptical compensator, an elliptical light-polarization modulator [15], and an electro-optical cell with an optical-path length of 10 mm and a volume of 10 mm³ were used. The measurements were carried out in the range of the glass transition temperature T_g up to 200°C. A systematic study of the electro-optical properties of the melts of a number of polystyrene fractions, depending on the length of the macromolecule, was carried out for the first time.

The measurement results are shown in Fig. 2. We note, first, the significant dependence of the average value K on the number of monomer units in the polymer and, secondly, the existence of two fundamentally different types of temperature dependence TO, which was previously revealed in one of the fractions [16]. The same figure shows the Kerr constants of benzene C_6H_6 and toluene $C_6H_5CH_3$ at a temperature of 20°C. The structure of these molecules is similar to the structure of polystyrene monomer units.

The polymer melt is a condensed phase. Polymer chains in a closely packed molecular system are intertwined. At the same time, they have individual charac-teristics, such as coil size and chain stiffness, which can affect the physical properties of the medium as a whole. This circumstance is directly indicated by the strong dependence of the electro-optical properties on the number of monomer units in the macromolecule discovered in the work. In polystyrene, as in other flexible-chain polymers, when the number of links in the chain changes from several units to tens of n the formation of a polymer coil occurs. The ability of a macromolecule to form a coil depends on the rigidity of the chain, the measure of which is the Kuhn segment: a kinetically independent section of the chain, consisting of several monomer units. The more monomer units included in one segment, the more rigid the chain and therefore the chain is less coiled. For polystyrene, the Kuhn segment corresponds to eight monomer units [17]. Therefore, the P-5 oligomer molecule consisting of five units is smaller than the Kuhn segment and has the shape of a rod, while the P-25 polymer molecule is a slightly curved rod. Coil formation occurs in polymers P-45 and P-88. As follows from the data obtained, a change in the chain conformation is accompanied by a change in the value K. The polymer P-25 has a Kerr constant 1.5 times greater than the oligomer P-5, and more than 2 times for P-45 and P-88.

The Kerr constant in the Langevin−Born theory is expressed in terms of the molecular parameters of a substance as follows:

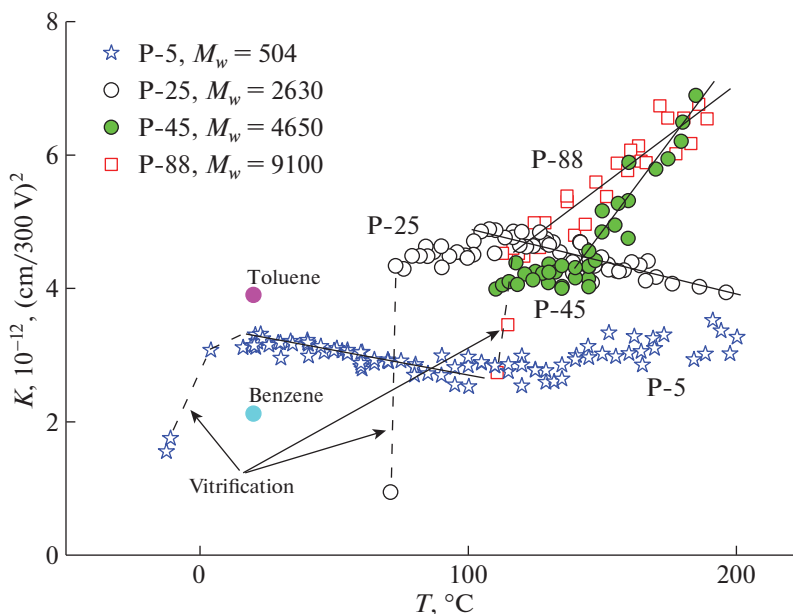$$K = A \frac{\Delta b}{kT} \left[2\Delta\alpha + \frac{\mu^2}{kT}(3\cos^2\beta - 1) \right].$$

Fig. 2. Temperature dependences of the Kerr constant $K(T)$ in the melt of oligomer P-5 and polymers P-25, P-45, P-88. Solid lines in the graphs show the dominant temperature dependence of the form $K \propto (1/T)$ in samples P-5 and P-25 and the type $K \propto T$ for samples P-45 and P-88. The dashed lines indicate a drop in the value of the electro-optical constant in the glass-transition region. The values K for benzene and toluene at 20°C are noted.

Here, Δb and $\Delta\alpha$ are the anisotropy of the optical and electric polarizabilities, μ is the dipole moment, β is the angle between the dipole moment and the longitudinal axis of the molecule, k is the Boltzmann constant, T is the temperature, and A is a numerical coefficient. The monomer unit of polystyrene consists of a non-polar phenyl ring with high electrical and optical anisotropy, as well as the $-CH_2-$ and $-CH-$ groups with a dipole moment of $\mu < 0.2D$. Therefore, at 20°C, the constant K of the oligomer equal to 3.3×10^{-12} (cm/300 V)^2, turns out to be between the values $K = 2.1 \times 10^{-12}$ (cm/300V)^2 of benzene with zero dipole moment and $K = 3.9 \times 10^{-12}$ (cm/300 V)^2 of toluene with $\mu = 0.37D$ (Fig. 2). Thus, the electro-optical effect of polystyrene is determined by the presence of both anisotropic cycles and weakly polar groups.

Phenyl rings are capable of mutual ordering due to the aromatic $\pi-\pi$ interaction between them [18]. There are several basic configurations in which rings can be found in close-packed conditions [18, 19]. The arrangement of the rings in the T-type configuration (Fig. 3a), which is energetically most favorable, leads to minimization of the local optical and electrical anisotropy. Therefore, in the case of the T-type configuration, the Kerr constant will be minimal. In the other two options shown in Figs. 3b and 3c, a large local anisotropy is created, which significantly increases the constant K of the melt.

In order to determine which configurations correspond to the obtained experimental data to a greater extent, we simulated liquid benzene as an analogue of phenyl cycles of polystyrene. The molecular-dynamics method was used in the AKMD program [20]. In this case, they were limited to a temperature of 20°C, at which the experimental values K for benzene and polystyrene can be compared. From the graph in Fig. 2 it can be seen that the addition of a dipole moment to the benzene molecule corresponding to a monomer unit of polystyrene should lead to a good agreement of the values K of the two substances. Consequently, their closeness gives reason to believe that under these conditions the result of benzene modeling can be transferred to short-range order for rings in one of the studied samples, i.e., in oligomer P-5.

The modeling used the full-atomic model of a molecule with the parameters of the atom-atom interaction OPLS-AA [20]. The simulation was carried out in the NpT ensemble using a Nosé barostat/thermostat with periodic boundary conditions and using the Ewald method to calculate electrostatic interactions. To maintain the length of chemical bonds unchanged, the SHAKE algorithm was used; in this case, the simulation step was 2 fs. There were 2700 molecules in the system. The equilibration time of the systems was 4 ns, and the trajectory analysis time was 1 ns, which was sufficient to obtain the equilibrium distributions of molecules relative to each other. As a result of calcula-
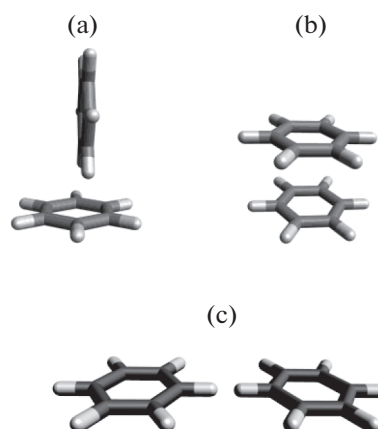

Fig. 3. Possible configurations of the mutual arrangement of molecules in liquid benzene: (a) T-type configuration; (b) "sandwich" configuration; (c) planar configuration.

tions, the distribution of the centers of mass of benzene molecules was obtained as a function of the cylindrical distribution [22] around the central molecule, Fig. 4.

It turned out that the distance to the maximum density distribution of the centers of mass of the surrounding molecules above the plane of the central molecule is 4.9 Å, which is close to the distance 5.1 Å between the centers of mass of molecules in the T-type configuration. The probability density of the planar configuration of molecules turned out to be noticeably lower. In the "sandwich" configuration, for which the distance between the centers of mass should be 4.0 Å, there is an even smaller fraction of molecules. Consequently, most benzene rings are in the T-type configuration, which is partially blurred by the thermal motion of the molecules. The calculation performed by the Monte Carlo method [23] and the experiment on X-ray scattering [24] also showed the presence of all configurations in liquid benzene; however, the T-type configuration dominated among them. In its pure form, the T-type configuration is implemented in crystalline benzene [25, 26], under conditions of maximum coordination and orientational orders.

Based on the data obtained, the relationship between the chain length and the behavior of the EB of the melt can be represented as follows. The Kerr constant K for oligomer P-5 has the lowest average value among the measured samples and at room temperature is close to the constant K of benzene. Under these conditions, the orientational order values for phenyl rings in oligomer P-5 and for benzene molecules are comparable, and the fraction of phenyl rings in the T-type configuration for both substances is sufficient to maintain the values of Δb and $\Delta\alpha$ at a low level. The formation of a coil in polymer P-25 leads to the fact that the polymer chain begins to restrict the freedom of orientation of the rings due to steric interactions. As a result, the distribution of rings over possible config-
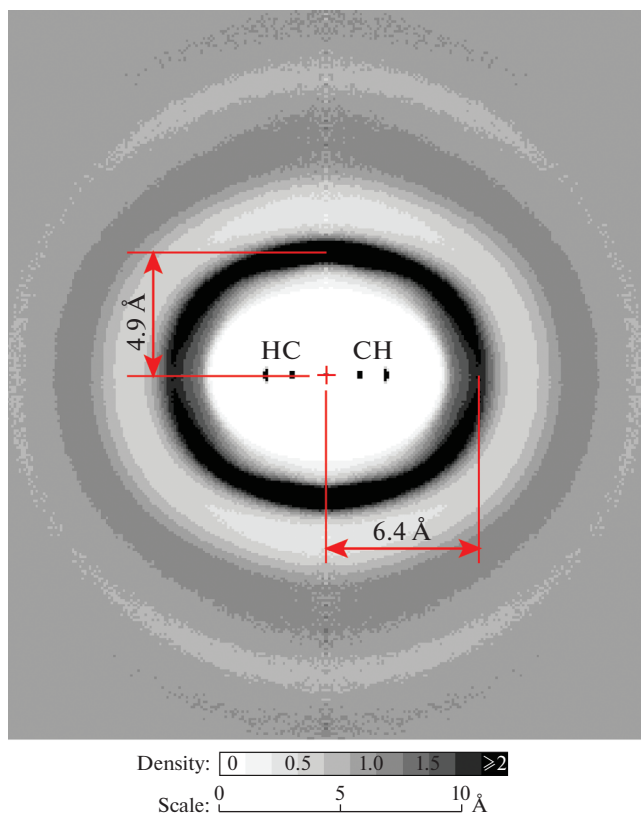
Fig. 4. Cylindrical distribution function of the centers of mass of benzene molecules. The axis of the cylindrical coordinate system is directed upward and coincides with the symmetry axis of the molecule C_6. The center of mass (origin) is marked with a cross. At the center of the distribution, the position of the carbon and hydrogen atoms of the central molecule is shown. On the scale of the probability density and image scale, gray corresponds to the average density of benzene molecules and white indicates the excluded volume of the molecule.

urations changes, and the proportion of rings in the T-type configuration decreases due to those rings that have acquired a "sandwich" and planar configuration. Therefore, the local anisotropy in polymer P-25 increases, and the average value K becomes 1.5 times more than that of the oligomer. At the same time, for samples P-5 and P-25, the temperature dependence retains the classic form $K \propto (1/T)$. However, in samples P-45 and P-88, in which the coil conformation was formed, at $T > 120°C$, the temperature dependence changes to the opposite, namely, to the dependence $K \propto T$. This may be the result of "melting" of the polymer chain during the isotropic phase—isotropic phase transition [13]. As a result, with increasing temperature, the freedom of rotation of monomer units around the simple (single) bonds of the main chain connecting them increases. The micro-Brownian thermal motion of the monomer units is enhanced and averages the probabilities of different configurations for the phenyl rings. As a result, the contri-

bution of the dominant T-type configuration continuously decreases with increasing temperature, while the contribution of the "sandwich" and planar configurations increases. This leads to an increase in the local optical and electrical anisotropy and, accordingly, the appearance of an anomalous (inverse) temperature dependence of the Kerr constant K.

CONCLUSIONS

The observed nanostructuring of polystyrene, which manifested itself in a sharp increase in local anisotropy at high temperatures, is due to a combination of several factors. The most important of them: the aromatic $\pi-\pi$-interaction between phenyl rings, a strong influence of the polymer chain on the orientation of the rings, and the isotropic phase—isotropic phase transition occurring at elevated temperatures, as a result of which the micro-Brownian motion of the polymer-chain links increases.

ACKNOWLEDGMENTS

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