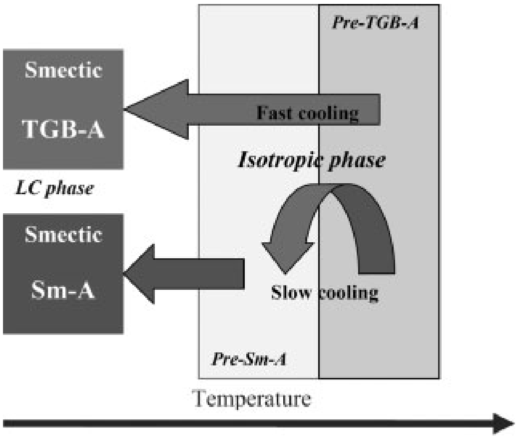
Existence of Two Different Isotropic Phases as a Reason for Bistable Phase Behavior of an LC Side-Chain Polymethacrylate[a]

Sergey Polushin, Viacheslav Rogozin, Ilya Beloborodov, Evgeny Rjumtsev, Mikhail Kozlovsky*

An isotropic melt of a chiral side-chain polymethacrylate was studied by electric birefringence technique. A phase transition between two different isotropic phases was detected by Kerr effect and confirmed by WAXS measurements. The obtained experimental data can explain the previously reported bistable phase behavior of the polymer, as conventional Sm A phase is formed in slow cooling whereas a TGB-like, optically isotropic mesophase in fast cooling.



Introduction

The isotropic phase of mesogenic compounds is characterized by the so-called pre-transitional effects, or short order effects, as numerous physical parameters of the phase change drastically in the vicinity of transition to liquid-crystalline (LC) phase.[1,2] Starting from 2000, a phase transition within the isotropic state (above the clearing point) was reported for several low molar mass liquid crystals.[3–6] Such an Iso–Iso transition is characterized by vanishing low transition enthalpy, $\Delta H \leq 0.2\ \text{kJ} \cdot \text{mol}^{-1}$, but can be detected using X-ray measurements and dielectric spectroscopy. Worth noticing is that the phase transition between two isotropic phases can be observed by chiral compounds only but not for the racemates.

Till date, no phase transformations above the clearing point have been reported for LC polymers. Since chirality should be critical for that phenomenon, one could expect any peculiarities of physical properties for side-chain polymers with chiral mesogenic pendant groups. Among the variety of such materials, the azodye polymethacrylate, P8*NN (Figure 1) was chosen for investigations because of its unusual, "bistable" phase behavior.

The polymer can form at the same temperature two different mesophases depending on the rate of cooling from isotropic melt, r.[7] Slow cooling of the

S. Polushin, V. Rogozin, I. Beloborodov, E. Rjumtsev
V. A. Fock Institute of Physics, Saint-Petersburg State University, Ulyanovskaya 1, Saint-Petersburg, 198504 Russia
M. Kozlovsky
Institute of Physical Chemistry, Darmstadt University of Technology, Petersenstr. 22, D-64287 Darmstadt, Germany
Fax: (+49) 6151 16 46 70; E-mail: mkozlovski@dki.tu-darmstadt.de

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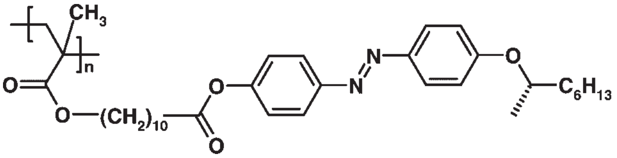

Figure 1. Molecular formula of P8*NN.

polymer ($r \leq 1$ K·min^{-1}) results in the formation of a conventional an LC phase, namely the Sm A phase which is birefringent and scatters visible light due to spontaneously formed polydomain structure. In contrast, fast cooling of a polymer sample at $r > 1$ K·min^{-1} produces an alternative mesophase which appears visually as transparent and optically isotropic but possesses a well developed smectic-like layered structure. That mesophase was attributed as a twist grain boundary (TGB) phase with an extremely short helical pitch.[8] The unique optical properties of the P8*NN films in TGB phase make it promising for applications such as photorecording media.[9,10] A schematic sketch of the short pitch TGB phase is given in Supporting Information (Figure S1), while its structure and properties are reported in detail elsewhere.[8] We should note that both the short pitch TGB phase and Sm A phase are kinetically stable and cannot be transformed to each other without heating above the phase transition point, T_{sm}.

In this work, we attempt to clarify reasons for the unusual, bistable phase behavior of P8*NN. Since isotropic melt of the polymer is a starting point for the formation of either Sm A phase or TGB phase, its properties should be critical for explanation of the bistability.

The isotropic melt of P8*NN was studied using the electric birefringence technique (EB, Kerr effect). This technique allows investigation of near-range ordering of mesogenic molecules in the isotropic state.[1,2] The method has been reported to support such established experimental techniques as DSC and X-ray scattering.[11–16]

Since studies of the Kerr effect gave a hint for possible phase transition between two different isotropic states, a detailed WAXS study of P8*NN in isotropic state was also performed.

Experimental Part

Synthesis of the polymer has been described elsewhere.[7] In this work, the polymer fraction was used with the average molar mass, $\overline{M}_w = 9.3 \times 10^4$ (that corresponds to the weight average degree of polymerization, $X_w = 174$), and the polydispersity index, $\overline{M}_w/\overline{M}_n = 2.0$. The phase transition between the mesophase and isotropic phase can be observed within a wide temperature range, $44\,°C < T_{sm} < 59\,°C$, depending on the heating/cooling rate and on thermal prehistory of the sample.

The polymer appears orange in color because of azobenzene dye moieties, and the laser beam is remarkably attenuated along the used optical path of 4 mm. As the polymer cooled below T_{sm} and Sm A phase formed, no more light came through the cell. Light propagation was therefore indicative for the phase transition directly in the measuring cell.

The EB, Δn_E, was measured by the method of birefringence compensation using mica rotational elliptical compensator and modulator of light elliptic polarization.[17] The method exhibits high sensitivity to induced EB, $\Delta n_E \approx 10^{-9}$.

A self-made Kerr cell was assembled from two parallel 4 mm long flat Al electrodes separated with 0.4 mm spacers. To remove air bubbles, the polymer sample was preliminarily heated in a vacuum oven at 50 Pa. For light source, a 25 mW semiconductor laser was used operating at $\lambda = 655$ nm, and the propagated light was registered by a photomultiplier.

For the EB measurements, rectangular 1–500 ms long voltage pulses up to 600 V were applied with frequency of less than 0.1 Hz. The Kerr cell was kept at a constant temperature with an accuracy of 0.1 °C for 20 min before the measurement for each temperature point, so that the whole experiment continues for about 200 h. The experimental $K(T)$ curves were completely reproducible, neither heating/cooling hysteresis, nor sample destruction was observed.

The X-ray scattering curves from capillary sample of P8*NN (2 mm in diameter) were measured for a broad angle range of $0.9° \leq 2\Theta \leq 27°$, using STADI STOE 2 diffractometer (Germany) at CuK$_\alpha$ radiation. The WAXS curves within the range, $12° \leq 2\Theta \leq 27°$, were then fitted by Lorentz square root function, while scattering within the smaller angle range, $2\Theta \leq 10°$, was used for the detection of a possible phase transition to a smectic phase only.

Results and Discussion

The value of EB, Δn_E, can be written as $\Delta n_E = KE^2$, where K being the Kerr constant and E being the electric field strength. As shown in Figure 2(a), the EB value in P8*NN obeys this relation (the Kerr's law) at all the studied temperatures within the isotropic phase.

Values of the Kerr constant, K, for different temperatures were estimated from the slope of the $\Delta n_E(U^2)$ straight lines. Here, $U = E \times d$, where d is the distance between electrodes (cell thickness). Corresponding reciprocal values, K^{-1}, are plotted in Figure 2(b) versus temperature. As can be clearly seen from the figure, the $K^{-1}(T)$ dependence can be separated onto two straight line sections **A** ($55.6\,°C < T < 70.6\,°C$) and **B** ($T > 70.6$) characterized by different slope parameters, as shown in the figure. Such a behavior has not been reported yet for the isotropic phase of neither low molar mass liquid crystals, nor LC polymers but observed here for the first time.

The electro-optic effect in mesogenic melts was analyzed using the Landau–De Gennes model.[1] According to the model, the expansion for the density of free energy, $F(T)$, as a function of order parameter, S, in electric field, E,

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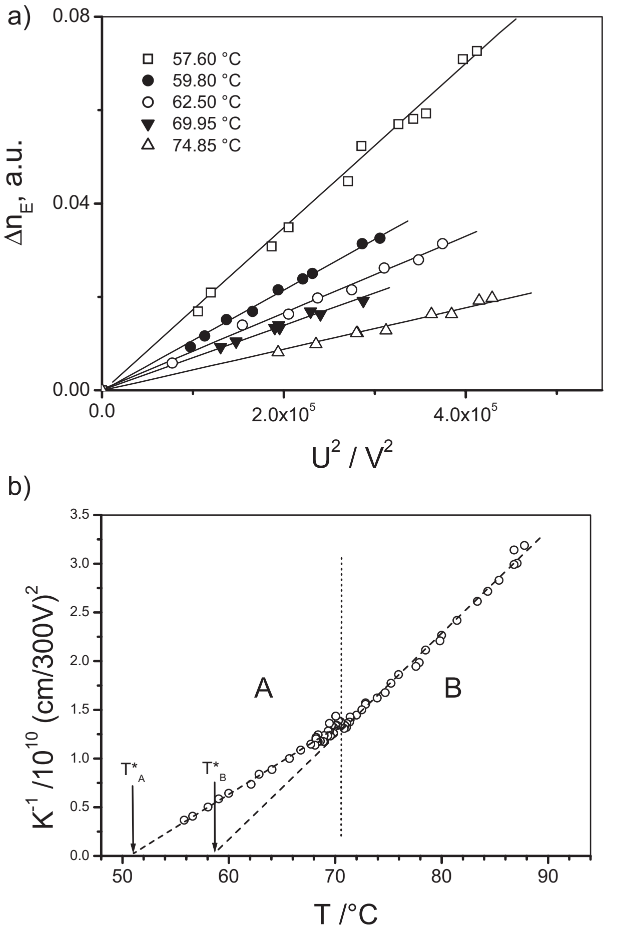

Figure 2. (a) Value of the electrically induced birefringence, Δn_E, versus the squared voltage at the Kerr cell, U and (b) reciprocal Kerr constant, K^{-1}, versus temperature.

can be written as

$$F(T) = F_o(T) + \frac{1}{2}a(T - T^*)S^2 - \frac{1}{12\pi}\Delta\varepsilon_o E^2 \qquad (1)$$

In that expansion, we may neglect all the terms with power of S higher than two. Here T^* is the theoretical temperature of maximum overcooling for the isotropic phase, $a(T - T^*)$ being the expansion coefficient of the quadratic term, and $\Delta\varepsilon_o$ being the dielectric anisotropy of completely ordered LC phase. Using this approach, the following equation can be derived[18] which expresses the Kerr constant using certain thermodynamic and molecular parameters

$$K = \frac{2\pi N^2(b_1 - b_2)(n^2 + 2)^2 Fh^2}{27nVa(T - T^*)^\gamma} \times \left[(a_1 - a_2) - \frac{F\mu^2}{2kT}(1 - 3\cos^2\beta)\right] \qquad (2)$$

Here, F and h are internal field correction factors, μ is the dipole moment of the mesogenic group, β is the angle between that moment and long axis of the mesogenic group, $(a_1 - a_2)$ and $(b_1 - b_2)$ are the electric and optical anisotropy of the group, V is the molar volume, and n is the birefringence index. The expression within the square brackets in (2) is much less dependent on temperature, than the factor before the expression, and it produces a negligible effect only on the $K(T)$ function, as long as angle β is far from the critical value of 56°. Accordingly, the temperature dependence of the Kerr constant (1), can be reduced to the following expression:

$$K = A/a(T - T^*)^\gamma \qquad (3)$$

where A is a constant, and the exponent $\gamma = 1$. Pretransitional behavior of the Kerr constant, K, is analyzed usually with the simplified expression (3). In the literature, the $K^{-1}(T)$ values always fall to a single straight line with slope angle α, where $\cot\alpha = K(T - T^*)$, and a liquid crystal can be characterized by a single limit temperature for the existence of isotropic phase, T^*. It applies for both nematics and smectics.[19]

In contrast, two different values of the slope angle were estimated for the sections **A** and **B** in the Figure 2(b), $K(T - T^*)_A = 1.5 \times 10^{-9}$ and $K(T - T^*)_B = 9.7 \times 10^{-10}$, so that the Kerr constant changes its temperature gradient in about 1.5 times at the point, $T_{ii} = 70.6$ °C. In the similar way, each one of those sections is characterized by its own T^* value: $T^*_A = 50.2$ °C and $T^*_B = 57.7$ °C. Such a phenomenon was never observed earlier and requires a special explanation.

As follows from the expression (2), the value of the Kerr constant, K, is determined by a set of molecular parameters: μ, β, $(a_1 - a_2)$, and $(b_1 - b_2)$ which depend on the molecular structure and, therefore, on possible conformational changes. Smooth character of such changes cannot explain, however, a sharp threshold-like kink in the $K^{-1}(T)$ curve observed for P8*NN. For the same reason, the kink cannot be explained by smectic fluctuations, in contrast to the non-monotonous but smooth $\Delta n_E(T)$ dependence reported for an LC elastomer.[20] We should rather suggest certain changes in the near-range order and/or in the molecular packing of mesogenic groups at a phase transition between two different isotropic phases, IsoA and IsoB, at the T_{ii} point. That should be a second order transition, since DSC data show no peculiarities within the temperature range of 65–80 °C.[8]

The concept of a phase transition between two isotropic phases is supported with the literature data for low molar mass liquid crystals forming a TGB phase. Thus, a similar Iso–Iso phase transition for a TGB/smectic compound was detected by temperature dependence for the time of dielectric relaxation,[5] while a phase transition within the

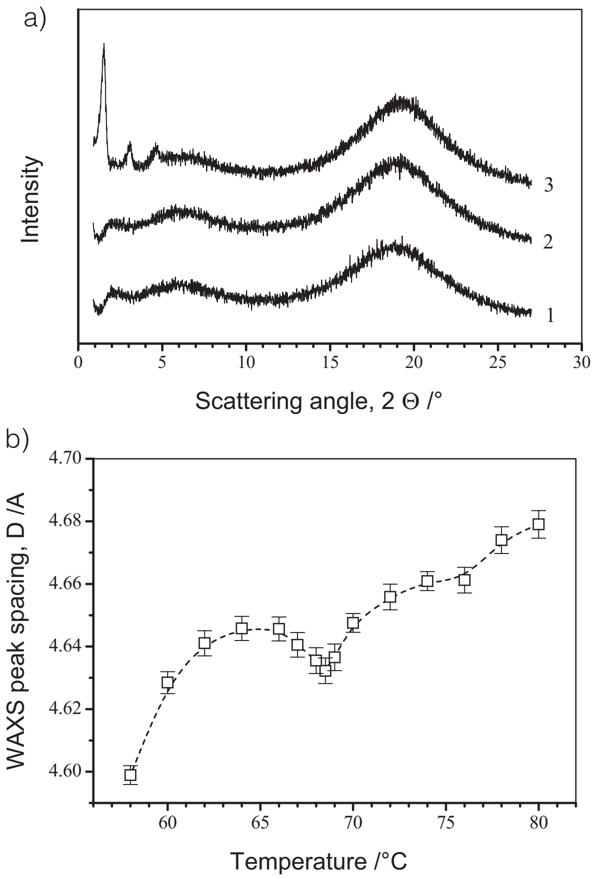

Figure 3. (a) X-ray scattering curves from P8*NN at (1) 80, (2) 66, and (3) 58 °C; and (b) WAXS peak spacing in the isotropic phase, *D*, versus temperature.

isotropic phase for some other TGB compounds was observed using DSC technique.[3,4,21]

A phase transition between two different isotropic phases in P8*NN is also evidenced by detailed X-ray study of the polymer (Figure 3). In the X-ray experiment, the formation of a smectic phase at $T_{sm} \approx 59$ °C (in cooling) was evidenced by a system of small angle peaks [curve 3 in Figure 3(a)]. Above that temperature, all the WAXS curves appear qualitatively similar: neither peak intensity nor its full width at the half-maximum (FWHM) shows any significant changes. However, the WAXS peak spacing, *D* (as estimated by curve fitting), achieves a distinct minimum at 68.5 °C [Figure 3(b)], i.e., at the close to T_{ii}. The *D* value corresponds to the distance between neighboring mesogenic groups. The X-ray data of Figure 3 confirm therefore certain change in molecular packing of the mesogenes at a phase transition between two different isotropic phases, as suggested by the EB data of Figure 2.

It was shown earlier in the literature that some elements of molecular packing of mesogenic groups in liquid crystals can be conserved above the clearing point, especially for the case when the clearing enthalpy is small. Parameters of the isotropic phase, as determined by the EB technique, can be therefore quantitatively correlated with the characteristic of the same mesogenic substance in an LC phase. Thus, value of the Kerr constant, *K*, for the isotropic melt was related to the dielectric and optical anisotropies, $\Delta\varepsilon$ and Δn, of the nematic phase, and the EB relaxation time, τ, was similarly related to rotation viscosity γ_1. Those correlations have been elucidated for both low molar mass liquid crystals[22,23] and LC polymers.[11,13] The literary data prove biunique conformity between the molecular order in the LC phase and the short order in the isotropic melt, which is a precursor of the LC phase. As temperature of the isotropic melt decreases, degree of the short order grows expanding to the whole media at the phase transition point, and long order appears.

Therefore, the bistable phase behavior of P8*NN can be explained by the existence of two alternative LC phases (Sm A or TGB A) at $T < T_{sm}$ along with two different isotropic phases at $T > T_{sm}$. The IsoA phase should be the precursor for the Sm A phase of P8*NN, while IsoB phase should be the precursor for the less ordered TGB phase.

Let us discuss in more detail the low temperature range of the isotropic phase, **A**. Extrapolation of the corresponding straight line in Figure 2(b) gives the value of limit temperature, $T^*_A = 50.2$ °C. During the EB experiment, the phase transition to Sm A phase was observed at 56.2 °C, so that the principal condition $T_{sm} > T^*_A$ is met. The difference between T_{sm} and T^* is known to depend on the type of phase transition: it is within the range of 0.6–1.5 K for transition from isotropic melt to nematic phase but 2–10 K or even more for the formation of a smectic phase.[24] For P8*NN, $T_{sm} - T^* = 6$ K. Thus, the polymer behaves electro-optically above the T_{sm} as an isotropic melt close to the phase transition into a smectic phase.

The transition temperature, T_{sm}, depends remarkably on cooling rate, *r*.[1] As it decreases with increasing *r*, the situation is inverted, so that $T_{sm} < T^*_A$. For the particular case of $r = 20$ Kmin^{-1}, $T_{sm} = 47.9$ °C, whereas $T^*_A = 50.2$ °C.

Generally, phase transformations in polymers are completed in a much longer time, as compared with low molar mass compounds, due to low mobility of polymeric chains and, therefore, to high melt viscosity. As a result, a phase transition at high *r* values occurs in a notably non-equilibrium state, being governed by both a thermodynamic factor (change in enthalpy) and a kinetic factor (mobility of chains). Moreover, the rate of the phase conversion is determined not by temperature itself, but by the overcooling.[24]

Based on the experimental data of this work, we can suggest the following mechanism for the bistable behavior of P8*NN. Properties of its two alternative smectic phases below T_{sm} can be correlated to the short ordering within

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corresponding, also alternative isotropic phases at temperatures above T_{sm}. Let the IsoA have a short-range order corresponding to the Sm A phase but the IsoB an order corresponding to the TGB phase. As being cooled from above 71 °C, the polymer sample passes first the temperature range of IsoB phase and then, subsequently, the range of IsoA phase. If the cooling is sufficiently slow ($r \leq 1$ Kmin^{-1}), the phase transition of IsoB–IsoA is completed, and the Sm A phase will appear at further cooling. In contrast, the IsoA phase has no sufficient time to be formed at higher cooling rates ($r > 1$ K · min^{-1}). For $r = 20$ K · min^{-1}, the sample passes the temperature range of the IsoA phase for about 1 min, while complete formation of the smectic phase in P8*NN takes 24 h and more.[8] Thence, the LC phase grows directly from the IsoB phase, so the short pitch TGB phase will be formed.

Conclusion

A threshold-wise change in temperature dependence of the Kerr constant, $K^{-1}(T)$, has been observed for the first time in the isotropic phase of mesogenic polymer, P8*NN. Two temperature ranges, **A** (55.6 °C < T < 70.6 °C) and **B** (T > 70.6 °C) have been identified; corresponding values of the limit temperature for existence of isotropic phase, T^*, and electro-optic parameter $K(T - T^*)$, have been estimated separately for either temperature range.

Phase transition between two isotropic phases at $T_{ii} = 70.6$ °C is suggested based on the EB data and confirmed by the analysis of WAXS curves from the polymer within the isotropic state. The two isotropic phases, IsoA and IsoB, differ by the average distance between two neighboring mesogenic groups, $D(T)$, which shows a minimum close to the T_{ii}.

The previously reported bistable phase behavior of P8*NN is therefore explained by kinetically governed phase transition between IsoA and IsoB phases, those being precursors for Sm A and short pitch TGB mesophases, respectively.

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