



Peculiarities of δ - and α -relaxations in thermotropic side chain liquid crystalline polymers with and without nematic reentrant phase

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ABSTRACT

We have performed a dielectric spectroscopy study of four homologous cyanobiphenyl polyacrylates with long side chains. The α - and δ -relaxation times were found to be sensitive to the sequential transformations between mesophases. The τ^δ in the isotropic phase exhibits the characteristics that obeys VFT relation and depend strongly on spacer length. The relaxation times, τ^δ , for the crossover from short range intermolecular interactions to long range LC ordering, decreases with increasing side chain length, implying that the cooperative motions of mesogenic dipoles arrange long range order at shorter time scales, as the spacer length is increased. In the SmA mesophases of CBPA n compounds with $n = 8, 9$ and 11 α -relaxation times were found to be nearly temperature independent at high temperatures. Thus, segmental motions take place in the state of diminished dynamical constraints of backbones, which can be attributed to the plasticization effects of polymeric layers in the case of long methylene spacers. In CBPA6 and CBPA8, with even numbers of methylene groups, anomalies of δ -relaxation processes were observed at the nematic reentrant (N_{re}) transitions. The anomalies of α -relaxation processes in the SmA mesophases were found to be precursors of N_{re} transitions as temperature decreases. The changes in backbone conformations of the SmA layers with decreasing temperature create the conditions for molecular corrugations of the side chains leading to the formation of the nematic order of N_{re} phases.

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1. Introduction

Thermotropic cyanobiphenyl polyacrylates (CBPA) constitute an interesting group since, below the isotropization temperature (T_i), they exhibit various phase sequences and reentrant topologies depending on the number methylene groups $[-CH_2-]_n$ in the side chain [1]. In CBPA n compounds with short methylene spacers ($n \leq 5$) only one type of mesophase, namely the nematic (N) or the smectic A (SmA) exists between the isotropic (I) phase and the glass transition (T_g) while for long methylene spacers ($n \geq 6$) the nature of the liquid crystalline (LC) ordering between the I phase and the glassy state changes considerably with increasing n [2]. For instance, while CBPA6 exhibits the nematic phase contiguous the isotropic phase, in the other members of the homologous series, CBPA n ($n = 7-11$), the SmA ordering appears below the isotropic state. The LC ordering of the phases that is adjacent to the glassy state depends on side chain length and the parity of the number of

methylene spacer, odd or even. In CBPA6 and CBPA8 compounds the transition from the reentrant nematic phase (N_{re}) to the glassy state takes place upon cooling. On the other hand CBPA7, CBPA9, and CBPA10 compounds exhibit the SmA to glass transition while the transition from the smectic C (SmC) to glassy state in CBPA11 is seen as temperature decreases. Since polyacrylate main chain and cyanobiphenyl mesogenic group, with CN terminator, are the same in these homologous, the crucial role of side chain length on the phase sequence is obvious.

The first evidence on the decoupling processes of polymeric backbone and the mesogenic group with long alkyl spacers were given by Shibaev and Finkelman [3–6]. The segmental and side chain dynamics were argued in a series of side chain liquid crystalline polymers (SCLCP) based on poly(vinyl methyl ether), poly(methyl methacrylate), poly(methyl acrylate), poly(dimethyl siloxane) by Ngai et al in the framework of the coupling theory as well [7]. From the analysis of the coupling parameter, namely n_c , using the cooperativity plot for a series of SCLCP in the vicinity of T_g , the authors concluded that the interaction between the main chain and the mesogenic group motion decreases due to the flexibility of methylene chains. Recently, Mano et al., using dielectric spectroscopy,

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mechanical analyzer and DSC techniques in combination have pointed out a decrease in the degree of cooperativity of the relaxation processes by long methylene groups in side chains [8–10]. The evolutions of the α - and δ -relaxation processes have been mostly investigated as temperature approaches to the glass transition. Indeed, for SCLCP having relatively short methylene spacers the temperature dependence of α - and δ -relaxation times converges smoothly to the Vogel–Fulcher–Tammann (VFT) relation as the temperature approaches to T_g [11,12].

On the other hand, in polymethacrylates with (*p*-alkoxyphenyl) benzoate as mesogenic unit for long methylene groups ($n = 6, 8, 10$) a crossover behavior from Arrhenius to VFT type in the evolution of α -relaxation rates was also reported [13]. It was observed that the curvature and steepness of the slope of α -relaxation rates gradually increases with the number of methylene groups in the side chains. Imrie has further pointed out the plasticization effects of the backbone by the side chains in thermotropic SCLCP [14,15]. Decoupling of the motions of the mesogenic units from the polymeric backbone due to flexibility of the spacers results in self-assembly of the mesogenic groups and random coil configuration of the polymeric backbone [16].

In general, it is well known that δ - and α -relaxation processes exhibit anomalies at isotropic phase transition in SCLCP having various polymeric backbone and mesogenic unit compositions [17,18]. Rearrangement of the mesogenic dipoles about the director causes mesophase transformation above T_g and, hence leads to an anomalous evolution of the segmental and side chain relaxation times with temperature [19]. In our recent dielectric study we have shown that δ -relaxation time exhibits sensitivity to the SmA–N_{re} transition in CBPA6 polymer. The evolution of this relaxation with temperature is given by overlapping VFT fitting curves [20]. In the present work it is our aim to focus on how the phase transformations of the mesophases influence the cooperative processes of molecular motion in the presence of flexible spacers of various lengths. In order to get deeper insight into the effect of the spacer length we have further proceeded with the synthesis and the dielectric spectroscopy study of CBPA n homologous series with various lengths, $n = 6, 8, 9$, and 11.

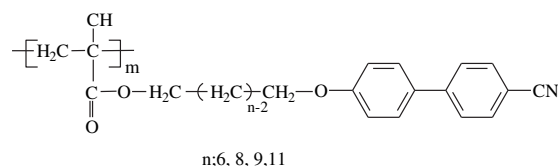
As long methylene groups cause plasticization of the polymeric backbone [14–16], so one can anticipate an unusual behavior of α -relaxation mode in the case of diminished environmental constraint of the segmental motion. Furthermore, we have demonstrated that the temperature dependence of δ -relaxation time of CBPA6 in the isotropic phase obeys the VFT relation [20]. This reflects the rise in the viscosity of the polymer in the isotropic phase due to the evolution of short-range interaction between the mesogenic dipoles as the temperature approaches to the isotropization temperature, T_i , from above. Hence, it is reasonable to assume that the number of methylene groups in the side chain has a strong influence on $\tau_1^\delta(T)$ near T_i during the formation of interdigitated structure of LC mesophases. Therefore our other aim is to investigate the influence of viscosity on α - and δ -relaxation processes at the sequential phase transitions. In order to reveal the “virgin” states of the relaxation processes near the mesophase transformations of CBPA n compounds with long methylene spacers unaligned samples were used.

2. Experimental

2.1. Materials and characterization

Liquid crystalline polyacrylates under investigation were prepared by free-radical polymerization of the corresponding acrylate monomers using 2-2'-azo-bis-isobutyronitrile (AIBN) as

initiator according to the method reported in Ref. [21]. General formula of CBPA n polymers is given below.



As a typical example, the preparation of poly(9-(4-Cyanobiphenyl-4'-oxy) nonyl acrylate) (CBPA9) was as follows: in this reaction 0.5 g (1.4 mmol) of CBA9 and 8.2×10^{-4} g (5×10^{-3} mmol) AIBN were dissolved in chloroform. The reaction mixture was introduced in a Pyrex glass tube, thoroughly freeze-thaw degassed and the sealed under vacuum. After reacting for 4 days at 70 °C, the polymer was precipitated by addition of a ten-fold excess of methanol, filtered and purified by reprecipitation into methanol. The polymer was then dried in vacuum for 18 h. Conversion was 21%. The proposed structures of the monomers and polymers were verified using ^1H NMR.

^1H NMR (CDCl_3): δ (ppm): 1.2–2.0(m, 14H, $-(\text{CH}_2)_7$), 2.29 (1H, $-\text{CH}$), 3.9–4.0 (t, 2H, $\text{O}-\text{CH}_2$), 4.1–4.2 (t, 2H, CH_2-OAr), 6.9–7.0 (m, 2H, aromatic), 7.4–7.5 (m, 2H, aromatic), 7.6–7.7 (m, 4H, aromatic).

Thermal properties of the polymers and their T_g temperature were measured by a Perkin Elmer Diamond DSC in the flowing nitrogen atmosphere at a heating rate of 10 K/min. The structures of the mesophases were identified by an Olympus BHSP polarizing microscope equipped with a hot stage and with a EMKO ESM 9320 temperature controller in a wide temperature range.

2.2. Dielectric measurements and data treatment

Dielectric measurements were carried out in the frequency range of 30 Hz–13 MHz using an HP-4192A impedance analyzer. The impedance analyzer automatically sweeps 48 frequencies in this interval at approximately every 60 s. The measurements were performed over the temperature range of 100–470 K. The temperature scanning rate was about 0.2 K/min especially near the phase transition regions. The surfaces of the electrodes were polished up to “optical” quality, using in the final stage 0.5 μm diamond polish paste, and then coated with gold. The dielectric cells with teflon spacers of thickness 0.1 mm and electrodes of 12 mm in diameter were used as capacitor.

The probability of planar orientation of CN terminated side chains near the electrode surface was discussed for unaligned CBPA n samples in Ref. [22]. However, the δ -relaxation peaks are approximately 2.5 times more pronounced than the α -relaxation peaks in the dielectric loss spectra for all CBPA n ($n = 6$ –11) compounds investigated. This means that, in the interdigitated structure of the mesophases, the orientation of the mesogenic dipoles parallel to the measuring field takes place in the unaligned bulk polymer.

The conductivity contribution to the low-frequency dielectric loss was subtracted using the linear fit to $\varepsilon'' \approx \omega^{-s}$ ($s \approx 1$). Subsequently the data were fitted to two Havriliak–Negami (HN) relations corresponding to overlapping δ - and α -processes,

$$\varepsilon^*(\omega) - \varepsilon_\infty = -\frac{i\sigma}{\varepsilon_0\omega^s} + \sum_k \frac{\Delta\varepsilon_k}{[1 + (i\omega_k\tau_{0k})^{a_k}]^{b_k}} \quad (1)$$

where the first term indicates the contribution of the ionic conductivity, τ_{0k} is the relaxation time, $\Delta\varepsilon_k$ is the relaxation strength of the k -th relaxation process, namely α - and δ -processes, a_k and b_k are the shape parameters ($0 \leq a_k, b_k \leq 1$) representing the degree

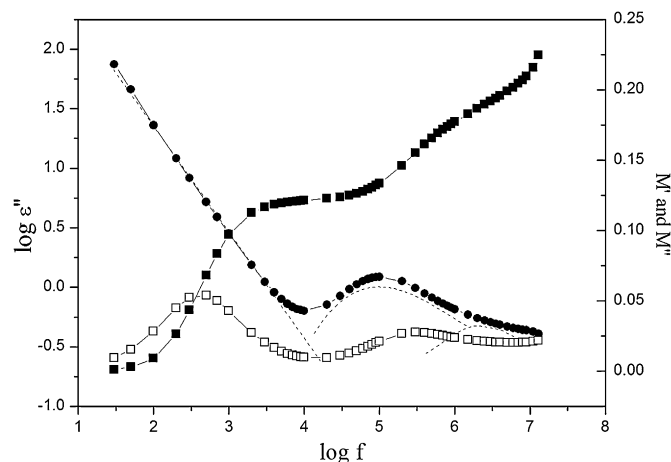


Fig. 1. Dielectric loss and electrical modulus versus frequency for CBPA9 at 385 K. ● – $\epsilon''(\omega)$, ■ – $M'(\omega)$, □ – $M''(\omega)$. Solid lines are guides to the eye. The dash lines describe the separation of conductivity contribution to low frequency dispersion, δ - and α -relaxation according to the HN relation.

of asymmetric broadening of the absorption peak. The δ - and α -relaxation maxima were fitted using the nonlinear least square method. In Fig. 1 we present the examples of the fits to $\epsilon''(\omega)$ data of CBPA9 compound. Temperature dependence of the relaxation times obtained from the dielectric measurements for each process was found to be non-Arrhenius type and then fitted to the VFT relation given by

$$\tau^k = \tau_0^k \exp\left(\frac{A^k}{T - T_{VFT}^k}\right), \quad (2)$$

where τ_0^k , A^k and T_{VFT}^k are the fit parameters.

As temperature increases, the ionic conductivity turns out to dominate in the SmA phase of CBPA9 compounds having long side chains. Temperature evolution of the ionic conductivity was analysed via the Arrhenius relation,

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (3)$$

where E_a is the activation energy of the ions. Besides, in order to analyze the relaxation of the conductivity due to ionic motion, the electrical modulus formalism, $M^* = 1/\epsilon^*$, was used [23]. The electrical modulus method permits to suppress a conductivity contribution in the linear part of low frequency dielectric dispersion and to reveal $M''(\omega)$ relaxation peak. The relaxation times of the conducting ions were estimated by fitting the peaks in the imaginary part of the dielectric modulus, $M''(\omega)$, in the appropriate temperature ranges. As seen from Fig. 1 at low frequencies $M'(\omega)$ approaches to zero indicating that the contribution of the electrode polarization to electrical modulus is quite negligible.

3. Results and discussion

In CBPA8, CBPA9, and CBPA11 compounds we have observed that low frequency ϵ' vs T data undergo maxima at the isotropization transition, which can be attributed to the long range LC ordering below T_i . Additionally the temperature positions of these maxima, ϵ'_{\max} corresponding to T_i , are compatible with the literature data [2]. Although the glass transition temperature obtained from dielectric data were confirmed by DSC thermograms with good accuracy, the endothermic minima in the region of the clearing temperature were observed somewhere below $\epsilon'_{\max}(T)$ for

CBPAn, $n = 8, 9, 11$. It is reasonable to expect this difference since the beginning of the isotropization process is entropically driven due to the extremely flexible polymeric backbone and spacers, whilst $\epsilon'_{\max}(T)$ can be connected with the final disordering of dielectrically active CN terminated dipole mesogens at T_i .

Before considering the details of the evolution of the relaxation processes in these CBPAn compounds it might be useful to look at the general landscape of temperature dependence of the relaxation times, as an example in Fig. 2 is presented for CBPA9 polymer. At temperatures below T_i , the relaxation times of rotational motion of the mesogenic side chains and the segmental motion are well described by the VFT formula and they converge to glass transition temperature, signaling the cooperativity of α - and δ -processes. Since in CBPA9 compound only the SmA phase exists below T_i one can notice that δ -relaxation times in the SmA phase smoothly obey VFT fitting curve as well. On the other hand there are some peculiarities in the temperature dependence of the α -relaxation mode, and only the average trends of the relaxation times exhibit a slowing down towards T_g . A step in the α -relaxation time is observed in the vicinity of 365 K. We have pointed out that in the temperature region of $T > 365$ K the ionic conductivity becomes dominating in CBPAn compounds with long methylene groups. The evolution of the relaxation times of the conducting ions, τ_{ion} , obtained from the imaginary part of $M''(\omega)$, are also displayed in Fig. 2. At low temperatures, within our experimental window, the γ -relaxation mode, which is attributed with local motions of methylene groups, was measured for CBPAn, $n = 6, 8, 9, 11$ samples.

Worthwhile recalling is the fact that for CBPAn compounds, there is no bridge between mesogenic phenyl groups in the side chain. Hence CN terminated phenyl groups possess axial symmetry about the long axis of the side chain. In this case, the contribution of the rotational motion of the transverse component, μ_{\perp} , of the mesogenic dipole moment to dielectric loss labeled as β -relaxation mode is not anticipated in CBPAn.

Moreover, the γ -relaxation process exhibits essentially Arrhenius behavior with temperature. The activation energies decrease with increasing length of methylene groups. The general landscapes of the evolution of the relaxation times are found to be similar for all investigated CBPAn compounds. The fitting parameters of the relaxation processes for each polymer are tabulated in Table 1. The

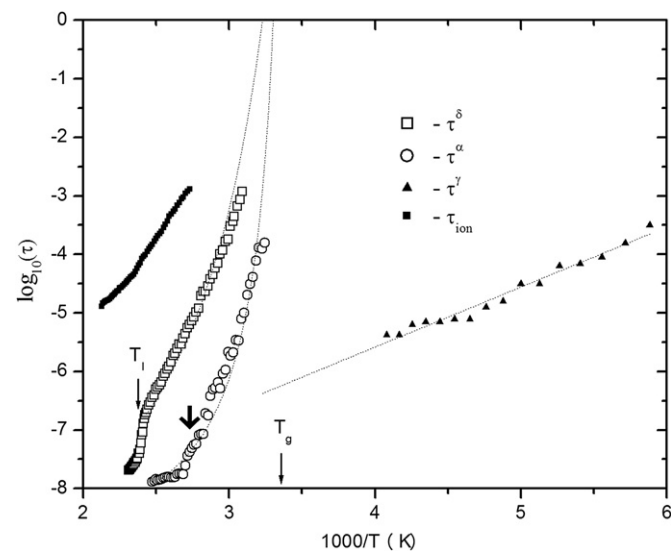


Fig. 2. Temperature dependence of δ -, α - and γ -relaxation times for CBPA9 sample: □ – τ^{δ} , ○ – τ^{α} , ▲ – τ^{γ} . Relaxation time of conducting ions τ_{ion} is denoted by ■. Dashed lines are the fitting curves.

Table 1The Vogel–Fulcher–Tammann (VFT) parameters of α -, δ - and γ -processes. T_{VFT} was determined at $\tau = 100$ s.

Process and parameters									
Polymer	T_g	δ -process			α -process			γ -process	
		A_{VFT}	τ_0 (s)	T_{VFT} (K)	A_{VFT}	τ	T_{VFT} (K)	E (kJ/mol)	τ_0 (s)
CBPA6	319	772	3×10^{-10}	309	810	4×10^{-11}	282	11.8	3×10^{-9}
CBPA8	299	872	4.5×10^{-10}	275	400	4×10^{-10}	285	10.7	7.5×10^{-7}
CBPA9	299	1150	9×10^{-11}	260	310	8×10^{-10}	288	8.6	4.4×10^{-7}
CBPA11	298	60	5.5×10^{-10}	263	200	2×10^{-9}	293	4.9	1.3×10^{-6}

details of relaxation processes discussed below, give a direct experimental evidence on how the mesophase transformations influence the molecular cooperative motions in CBPA n compounds.

3.1. The δ -relaxation process

The obtained dielectric loss spectra of unaligned CBPA n polymers is dominated by the weight of absorption rotational motion of the mesogenic groups around the short axis. Fig. 3 presents 3D plots of temperature dependence of the δ -relaxation times of various CBPA n compounds. Due to the high dipole moment of terminal CN group [24] dipole interactions and correlations of cyanobiphenyl mesogens are expected to be strong. They define a decisive evolution of the δ -relaxation time with temperature in the SmA phase. At temperatures below T_i , the steepness of $\tau^\delta(T)$ decreases with increasing the number of methylene groups in the side chain, due to the mitigation of interactions between the mesogenic dipoles and the backbone. Similar effects have been observed in another SCLCP as well in the vicinity of T_g [7]. While no remarkable anomalies in the trend of $\tau^\delta(T)$ in smectic phases of CBPA9 and CBPA11 with decreasing temperature were seen, a declination in the behavior of $\tau^\delta(T)$ at $1000/T = 2.78 \text{ K}^{-1}$ and also at $1000/T = 2.73 \text{ K}^{-1}$ was found in CBPA6 and CBPA8. At these temperatures, the SmA–N_{re} transition occurs in those polymers. The probability of multistep δ -process in SCLCP has been pointed out by Schönhals and coworkers [13]. Recently we have found that temperature dependence of $\tau^\delta(T)$ in CBPA6 polymer can be represented as overlapped non-Arrhenius evolutions [20]. The question is, what is the peculiarity of the motions of mesogenic side chains in the N_{re} phase? As is well known that in the nematic phase the center of mass of the mesogenic units is disordered with common directional orientations of dipole

moments [1,17]. Due to the flexibility of methylene spacer, the rotational motion of the mesogens might occur not only around the ether linkage (O) but also around the short axis, the positions of which can be changed randomly along the next neighbor methylene groups [20]. As temperature decreases, the slowing of the motion of δ -process around a randomly arranged short axis occurs in such a way that the molecular corrugation of the mesogenic side chains takes place in the N_{re} phase. In the case of corrugation effect, neighboring mesogenic groups within a layer prefer positions of mutual displacement along the long axis of the side chain. It should be noted that the width of a benzene ring is 6.8 Å and the separation of nearest-neighbor is about 4.8–5.5 Å [25–27]. A mutual displacement of mesogens with similar specific sizes is expected to increase the rotational steric hindrance in the N_{re} phase. The motion of the mesogens in δ -branch is affected by randomization of transverse dipole component, μ_t , of mesogenic groups due to the corrugation of long side chains. Obviously a local intramolecular constraint in the N_{re} phase with similar dipole motives should be different from those in the SmA ordering in the adjacent phase. Thus, the relaxation rate of mesogenic side chain motions around randomly distributed rotational short axes with the onset of the N_{re} phase “stumbles” and these result in the observed anomaly of τ^δ at the SmA–N_{re} transition in CBPA6 and CBPA8 compounds. The randomness of rotational short axes strongly influences the width parameters of dielectric absorption peak for δ -relaxation. As seen from Fig. 4, a_{HN}^δ exhibits a fluctuation with decreasing temperature in the N_{re} phase. Uncertainty of a_{HN}^δ value in the N_{re} phase implies that the redistributive dynamics of δ -relaxators is a temperature activated process.

A crucial influence of the methylene spacers length on δ -process is found in the isotropic phase of CBPA n polymers. As seen from

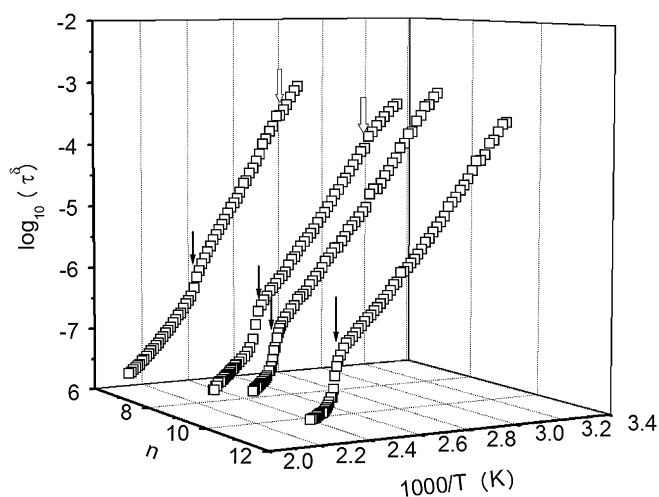


Fig. 3. Temperature dependence of δ -relaxation times of CBPA n , $n = 6, 8, 9, 11$. The data of CBPA6 was taken from [20] for comparison. The (\square) indicate the temperature of N_{re} transitions.

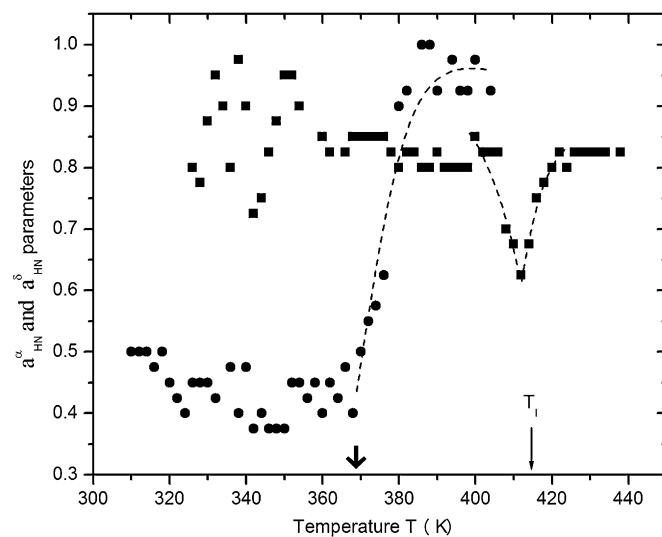


Fig. 4. Evolution of HN shape parameters a_{HN}^α (\bullet) and a_{HN}^δ (\blacksquare) on the example of CBPA8. The HN b parameters for both α and δ processes (not shown for clarity) lie between 0.9 and 1.

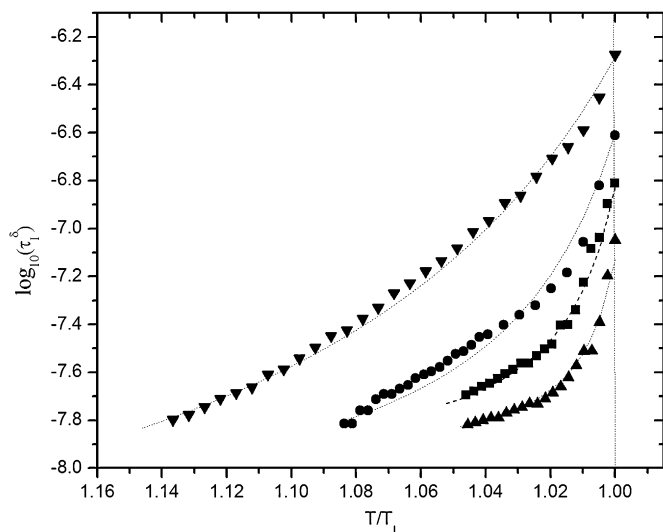


Fig. 5. Evolution of δ -relaxation times in the isotropic phase of CBPA n versus normalized temperature T/T_i : ∇ – CBPA6, \bullet – CBPA8, \blacksquare – CBPA9, \blacktriangle – CBPA11.

Fig. 5, δ -relaxation times slow down with decreasing of number of methylene groups in the whole temperature range of the I phase. Rotational motions of mesogenic dipoles are hindered by the conformational mobility of methylene chains as the spacer length becomes shorter. The evolution of δ -relaxation times in the I phase is well described by the VFT relation for all CBPA polymers under investigation. In the isotropic phase, where the mesogenic dipoles are in the fully disordered state the rotational relaxation times of the side chains, τ_i^δ , should be proportional to the rotational friction coefficient, as $\tau_i^\delta = \xi_i/2\pi$ [28]. This implies that the rotational viscosity of the medium due to the motion of the side chains in the I phase is well portrayed by the VFT relation.

The increasing in rotational micro-viscosity establishes the conditions for short-range intermolecular interactions in the subsystem of mesogenic dipoles, which lead to co-organization of dipole aggregations [27,29]. The increase in τ_i^δ with temperature implies that the correlation length of elementary mesogenic aggregations increases so that a crossover time of δ -processes within cooperatively rearranging dipolar aggregations (CRDA) can be considered as the time required to build up long range interactions of the mesogenic dipoles at the I–LC ordering phase transition. The CRDA of different sizes are responsible for strong relaxation shifts of the dielectric constant in the isotropic phase with increasing frequency of the measurement field. As seen from Fig. 5 the crossover time decreases approximately by one order of magnitude when the number of methylene groups increases from 6 to 11. Thus, the weakening of the constraints on the motion of the backbone promotes organization of long range order of LC mesophase at faster motions of the side chains in the δ -processes within CRDA.

For all CBPA n polymer with long side chains, the width parameters of δ -processes, a_{HN}^δ , exhibit a minimum at T_i . As an example, as depicted in Fig. 4 for CBPA8, a_{HN}^δ changes from 0.83 to 0.62, whereas in CBPA11 it varies in the 0.9–0.45 interval in the region of isotropization transition. Here, it can be concluded that the length of methylene chains strongly influences the distribution of elementary relaxators of δ -processes in the vicinity of T_i , implying a progress of inhomogeneities for fast moving mesogenic side chains.

3.2. The α -relaxation processes

Recently, extensive investigations about the influence of the LC backbone length and the backbone conformations on the LC

ordering in polyacrylate SCLCP with fixed spacer length were carried out by Shibaev et al. [30]. The authors found that the increasing of backbone length is the reason of frustrated behavior of mesogenic side chains at the SmA–N_{re} transitions, and this phenomenon is found only for polyacrylates. In this study while the backbone length was kept constant, the length of methylene spacers was varied. The details of the temperature dependence of the α -relaxation time, $\tau^\alpha(T)$, displayed in Fig. 6, show an “adventurous” evolution in CBPA n with various long methylene spacers. For all CBPA n samples with long spacer lengths, a nearly temperature independent part of $\tau^\alpha(T)$ at high temperatures in the LC mesophase was observed. The temperature position of the τ^α step, denoted as (\downarrow) , below which τ^α becomes temperature dependent, decreases with increasing spacer length. No remarkable anomalies were observed in τ^δ -relaxation times in the region of the τ^α step either in the dielectric constant or in the DSC thermograms. The temperature independent behavior of τ^α is caused by strong mitigation of the dynamical constraints of the backbone due to long spacers. The symmetry of the dielectric loss peak, indicated by $a_{HN}^\delta = 0.9$ –1, shown in Fig. 3, confirms that the segmental motions of CBPA n in this temperature range occur in the medium with minimal local constraints of the backbone. One can suppose that near constancy of α -relaxation time is a sign of the onset plasticization of the backbone by long methylene spacers [15,16]. The absence of the anomalies in τ^δ implies that CN terminated mesogenic side chains preserve their own packing in the mesophase due to their pronounced dipole interaction. The peak of $\epsilon'(T)$ at T_i in CBPA n with long side chains is defined only by frustration of long range ordering in the subsystem of cyanobiphenyl mesogens.

Indeed, the effect of backbone plasticization of CBPA n with long spacers is the main cause of the remarkable conductivity of these polymers although they are “good” dielectrics, as shown in Fig. 7a. Approximately at $T \geq 365$ K in the conductivity spectra a frequency independent behavior in $\sigma(\omega)$ became dominant for CBPA8, 9, 11 polymers at low frequencies. The source of d.c. conductivity might be the impurity ions, which gain the mobility with the plasticization of the backbone. Temperature dependence of the relaxation times of conducting ions, τ_{ion} , obtained from the imaginary part of the electrical modulus, $M^* = 1/\epsilon^*$, is in accord with $\sigma_{ion}(T)$ in all investigated CBPA n samples. The low relaxation rate of the conducting ions correspond to low value of the conductivity, indicating

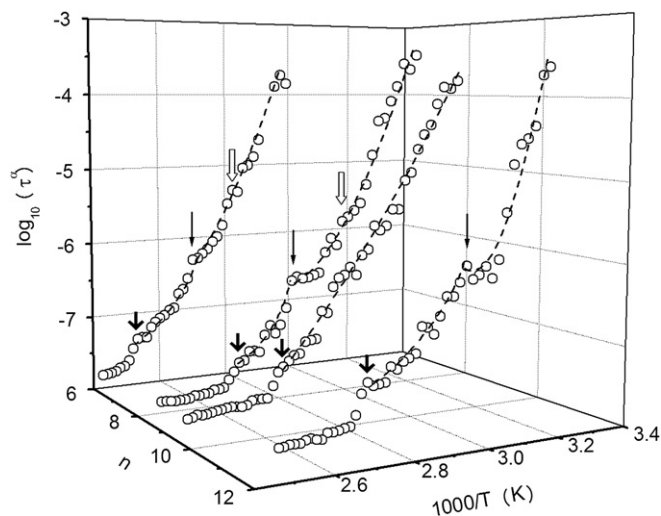


Fig. 6. Temperature dependence of α -relaxation times of CBPA n , $n = 6, 8, 9$ and 11 in LC mesophases. The (\square) denote the temperature of N_{re} transitions in CBPA6 and CBPA8. Dashed lines are guide to the eye.

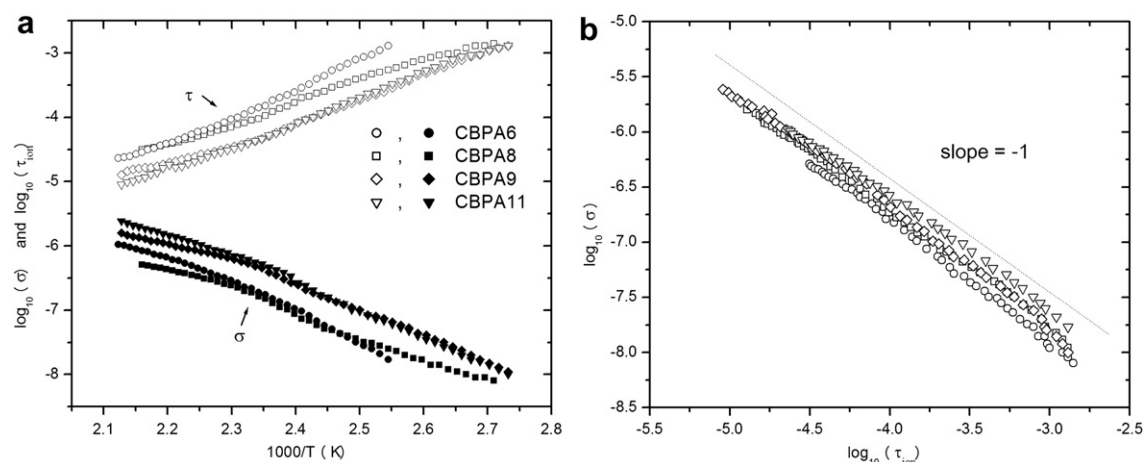


Fig. 7. a) Temperature dependence of ionic conductivity, σ_{ion} , measured at 30 Hz and relaxation times of conducting ions. b) Conductivity of each LC polymer is plotted against its relaxation time. The dash line has a slope of -1 .

that carriers are located at the energy minima at low temperature for long times [31]. According to the Debye–Stokes–Einstein law, σ_{ion} varies linearly with $1/\tau_{ion}$, so that the slope of $(d \log \sigma_{ion})/(d \log \tau_{ion})$ is equal to unity [32,33], as shown in Fig. 7b. The coupling of the backbone with mesogens is strongly mitigated by long methylene spacers and this promotes a decrease in the viscosity of lamellar structures of the polymeric backbone at $T > 360$ K. The direct current of impurity ions along polymeric backbones is probably supported by the process of hopping nearly equipotential wells, which is favourable in the low viscosity state of LC mesophase of CBPA n . As seen from Fig. 7b the same slope ~ 1 is also observed in both isotropic and polymeric LC mesophases, confirming that the conductivity mechanism is identical in a wide temperature range. Thus, the specific, nearly temperature independent α -relaxation processes in CBPA n compounds can be attributed to the plasticization of polymeric state within the smectic mesophase.

Furthermore, a complex structure of non-Arrhenius evolution of α -relaxation times was observed in CBPA6, CBPA8 and CBPA11 polymers with decreasing temperature. In CBPA9 compound the α -relaxation process slows down without any remarkable anomalies since only the SmA mesophase exists in this polymer [2]. Due to the low dipole moment of the backbone, the coupling process with mesogenic side chains play a decisive role in the contribution of segmental motions to dielectric spectra. The anomalies of α -relaxation times, labeled with (\downarrow) in Fig. 6, are located at temperatures higher than the N_{re} transition in the interior of the SmA mesophase in CBPA6 and CBPA8, whereas in CBPA11 polymer the similar anomaly is observed close to the SmA–SmC transition. This phenomenon, probably, is a reflection of different phase transition sequences caused by the odd-even number of $[-CH_2-]$ groups in the side chain, on the segmental dynamics of the polymer. Moreover, it has been discussed that in the smectic phase, the backbone chains constitute an oblate arrangement and are confined between sublayers of the interdigitated mesogenic structure [30]. Dynamical constraints on the segmental motions increase with decreasing temperature in such a way that the packing density of $[-CH_2-]$ groups increases in the intralayer volume of the oblate structure. In this case, the intramolecular interaction of mesogenic dipoles with the backbone is expected to increase. A rearrangement of the mesogens from the orthogonal ordering of the SmA mesophase to the tilted ordering of the SmC phase results in an anomaly of the α -process in CBPA11, as depicted in Fig. 6.

In CBPA6 and CBPA8 polymers the phase sequences are N–SmA– N_{re} and SmA– N_{re} , respectively. At a first glance, the idea that the

SmA layers melt on cooling to the N_{re} phase can be used to explain the observed anomalies of α - processes in CBPA6 and CBPA8, denoted as (\downarrow). A neutron scattering investigation has recently demonstrated that in CBPA n polymers with the N_{re} phase the backbone conformation is transformed from an oblate to a prolate structure in the N_{re} phase [34]. It is difficult to understand which kind of backbone conformation change takes place from dielectric measurements. However it is clear that changes in segmental motion dynamics upon cooling are precursors of the δ -relaxation anomaly corresponding to the N_{re} transition. We suppose that, in the case of CN terminated side chains, the influence of conformational changes of the oblate structure of backbones has a diffusive nature due to the strong interaction between the mesogenic dipoles. Although dynamical constraints on the motions in α - and δ -processes increase with decreasing temperature, the effect of the flexibility of methylene chains in mitigation of the coupling of the backbone and dipolar mesogens remains considerable. Thus, for dipolar frustration of the smectic layers to be realized with the onset of the N_{re} phase, corrugation of mesogenic side chains should be accomplished [26,35,36]. Molecular corrugation of side chains randomizes the positions of center of mass of mesogens and helps to realize the disordered distribution of the dipoles in the nematic phase. For the reentrant phases, the interpenetrating coexistence of the common order and disorder is inherent in the sense of the microscopic mechanism [26]. Remarkably, it should be noted that the shape parameters of the dielectric loss, a_{HN}^2 , of α -processes turned out to be very sensitive to the backbone transformation from the state of low viscosity to the oblate arrangement of the smectic phase (see Fig. 3). The a_{HN}^2 parameter abruptly decreases in the region of 370 K below which α -relaxation times become temperature dependent. Pictures of the shape parameters which are similar for the investigated CBPA n with long side chains, indicate that the time scale distribution of the segmental relaxators widen with constraints of oblate structure of the backbone.

3.3. Local processes

At low temperatures, below the glass transition, local motions of the side chains in the γ -relaxation branch were also observed in the dielectric spectra. Temperature dependence of the γ -relaxation times for CBPA n with $n = 8, 9, 11$ together with the re-examined CBPA6 data were found to exhibit Arrhenius behavior and is depicted in Fig. 8. The slopes of the fitting lines decrease with increasing the number of methylene groups in the side chain. The obtained activation energy values are given in Table 1. For the short

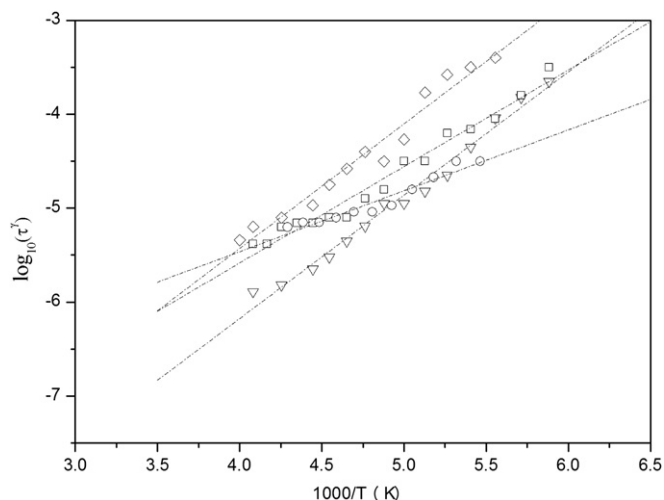


Fig. 8. Temperature dependence γ -relaxation for CBPA6(\diamond), CBPA8(∇), CBPA9(\square) and CBPA11(\circ). The lines are fitting according to Arrhenius relation of relaxation times.

methylene spacer, the activation energy of γ -process was found to be 32 kJ/mol [11]. Comparing this with the obtained data for long methylene side chains, one can notice the regular decrease in the activation energies of γ -motions with number of $[-CH_2-]$ groups. Although the backbone and the mesogens are squeezed at low temperatures, the mobility of methylene group is affected by the length, probably due to the environmental local free volume of the long spacers. Local free volume increases with increasing spacer length and hence less energies are required to activate the mobility of a longer side chain in the γ -process.

4. Conclusion

In short we have examined of the temperature evolution of segmental and side chain relaxational modes in liquid crystalline polymers with different phase transition sequence.

For cyanobiphenyl polyacrylates with a long side chains we have found that δ -relaxation processes in the isotropic phase are strongly affected by the length of methylene spacer. In δ -processes, the characteristic crossover time of mesogenic motions for co-organization of long range LC order decreases with decreasing methylene spacer length which implies that a formation of interdigitated layer structure of mesophase is sterically hindered by the degree of backbone and mesogens coupling in the vicinity of T_i .

More importantly, the α -processes of CBPA n with long side chains were found to be nearly temperature independent. This behavior results from the effects of plasticization of the backbone and probably is inherent for CBPA n with long side chains. In addition the temperature interval of the low viscosity state expands with the increasing number of methylene groups in side chains. Furthermore the transformation to the low viscosity state takes place without any LC mesophases transition. The entire process of α -relaxation time from VFT description to the state of diminished dynamical constraints of backbone motions occurs as a crossover in the high temperature part of the SmA phase. The appearance of the backbone plasticization trigger the ionic conductivity. The Debye–Stokes–

Einstein relation gives a linear slope of unity which confirms the d. c. transport of ions that is inherent for low viscosity state of polymers.

In both CBPA6 and CBPA8, δ -relaxation times undergo anomalies at the reentrant transition to the nematic phase due to molecular corrugation effects of the side chains. We have also noted that the observed anomaly of α -process is a precursor of the N_{re} transition upon cooling, suggesting that the transformation of constraints of oblate structure of backbone layer possesses a diffusive character with decreasing temperature. An extended conformation of oblate structure of polymeric layers with temperature is required for realization of molecular corrugations of methylene spacers of the side chains.

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