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# Dielectric relaxation in a thermotropic side chain liquid crystalline polymer with nematic reentrant phase

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## Abstract

Dielectric spectroscopy of liquid crystalline cyanobiphenyl polyacrylates (CBPA6) with six methylene groups in the side chain has been investigated in the frequency range of 30 Hz–13 MHz and in the temperature interval from 100 to 470 K. From the temperature dependence of  $\epsilon'(T)$ , the anomalies corresponding to sequential phase transitions of liquid crystalline mesophases were revealed. The observed  $\alpha$ - and  $\delta$ -relaxation processes were described by the Vogel–Fulcher–Tammann law. It was found that  $\delta$ -relaxation exhibits a multistage slowing behavior with decreasing temperature. The existence of a reentrant nematic ( $N_{re}$ ) phase upper glassy phase shows us the special conditions for glass transition: the enhancement of the degree of cooperativity in mesogenic subsystems due to corrugation effects results in interaction of the side chain modes with a mixture of segmental and normal modes of the backbone, leading to a step-like anomaly of  $\epsilon'(T)$  at the glass transition.

## 1. Introduction

Polymer liquid crystals are a class of materials which combine the properties of polymers with those of liquid crystals. These hybrid structures possess the same mesophase characteristics as ordinary liquid crystals; in addition they retain many useful and versatile properties of polymers. Moreover, a possibility of chemical variations of the main and side chain compositions of the liquid crystalline polymers (LCP) makes them a promising material for various applications [1, 2]. It is well known that side chain liquid crystalline polymers (SCLCPs) are formed when mesogenic units are attached to the polymer backbone as pendant groups. Over the past few decades, a large number of SCLCPs have been synthesized. On the other hand, the effect of polymer architecture on SCLCP defines the sequence of liquid crystal mesophases and hence, a molecular dynamics evolution of LCP as a function of temperature [3, 4].

Furthermore dielectric spectroscopy has been extensively used in the study of liquid crystals and their phase transitions.

This method is an efficient tool to investigate molecular dynamics and, in a general sense, collective motion processes and subsequent changes in their motions during phase transitions.

Most SCLCPs are based on siloxane, acrylate or methacrylate polymers. Thus, polysiloxane, polyacrylate, polycarbonates, polymethacrylate, and polyvinyl ether based SCLCPs have been extensively investigated in the last two decades using dielectric spectroscopy by several groups [5–18]. Results from these investigations suggest that relaxation processes labeled as  $\gamma$ ,  $\beta$ ,  $\alpha$ ,  $\delta$  with increasing temperature strongly depend on the length of the spacer, the nature of mesogenic groups, and the end groups as well. The temperature dependence of the characteristic peak frequency of  $\gamma$ - and  $\beta$ -relaxations exhibits a linear Arrhenius behavior while  $\delta$ - and  $\alpha$ -relaxations obey the Vogel–Fulcher–Tammann (VFT) relations [4, 8, 14, 15, 17]. Rarely, for  $\delta$ -relaxation of a SCLCP linear Arrhenius evolutions are observed with temperature as reported in [19]. In a study of combined dielectric and viscosimetric measurements [20], Seiberle and co-workers reported the important role of the temperature dependent viscosity in

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the relaxation process. They also established a connection between collective dipole rotational motion and rotational viscosity, described by the Vogel–Fulcher formula for SCLCP. In SCLCP,  $\delta$ - and  $\alpha$ -relaxation processes have a cooperative character [14, 21, 22]. A dipole motive of the relaxation process has been presented in [8, 21, 23]. The  $\delta$ -relaxation indicates rotational fluctuations of the longitudinal component of the mesogenic dipolar group parallel to the long axis of the mesogenic side chain around the local short axis of the mesogen. However, there is some inconsistency in the literature regarding  $\alpha$ -relaxation processes in SCLCP, as discussed in [21, 22]. A group of authors follows the idea that it can be connected with motion of the transverse dipole moment  $\mu_t$  of the mesogenic group, while another group attributes this mode to the segmental relaxation at glass transition ([21] and references cited therein). We believe that the intermolecular interaction during  $\delta$ -relaxation is more complex and may be a reason for a multistage slowing down of motion with temperature. It can be assumed that the similar behavior of the  $\delta$ -relaxation mode influences intramolecular cooperativity and should define a sequence of phase transitions in SCLCP. In [14] it was stated that  $\alpha$ - and  $\delta$ -relaxation modes freeze together at glass transition temperature  $T_g$ . Peculiarities of  $\alpha$ -relaxation in SCLCP, revealed in [21, 22] and the evidence mentioned above [14], require a complementary investigation of dielectric properties at glass transitions. For this purpose a dielectric spectroscopy of unaligned thermotropic side chain liquid crystalline polymer (TSCLCP) poly(6-(4-cyanobiphenyl-4'-oxy)hexyl acrylate) based on biphenylene mesogens spaced with six methylene groups (CBPA6) has been investigated in this work. Additionally, in the past, poly(3-(4-cyanobiphenyl-4'-oxy)propyl acrylate)-CBPA3- having three methylene groups as a flexible spacer has been investigated using the dielectric technique [19]. In that study, four distinct dielectric relaxations for CBPA3 were revealed and information on the order parameter was also obtained from the experimental data. Although, CBPA3 and CBPA6 have similar structures, CBPA6 exhibits a more complicated phase sequence, especially the reentrant nematic phase [24, 25]. With the aim of getting a deeper insight into the existence of this reentrant phase on the dielectric response, we further proceeded in this work with the synthesis and the dielectric study of the CBPA6 polymer. The sequence of phase transitions of CBPA6, reported in [24, 25] is glass  $\xrightarrow{311\text{ K}}$  N<sub>re</sub>  $\xrightarrow{356\text{ K}}$  SmA  $\xrightarrow{388\text{ K}}$  N  $\xrightarrow{396\text{ K}}$  I upon heating. Here, N<sub>re</sub> refers to the reentrant nematic phase.

Theoretical studies have pointed to the effect of reentrant behavior on neighboring phases [26, 27]. On the other hand to the best of the authors' knowledge there has been no dielectric study on the reentrant behavior near the glass transition of liquid crystalline polymers. CBPA6, with reentrant behavior, was chosen for this study, because of its structural similarity to CBPA3 which by itself exhibits no reentrant behavior.

## 2. Experimental details

### 2.1. Materials

6-(4-cyanobiphenyl-4'-oxy)hexyl acrylate (LC6) liquid crystal compound was prepared using the synthetic method described

in detail elsewhere [24]. Monomer LC6 (0.1 g, 0.28 mmol) and initiator AIBN (0.0008 g, 5 mmol) were dissolved in toluene (1 ml) as a solvent in a Pyrex glass tube, thoroughly freeze-thaw degassed and then sealed under vacuum. After reaction for variable time periods at 65 °C, the polymer was precipitated into a large amount of methanol, filtered and purified by reprecipitation into ethanol.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm): 1.2–2.0(m, 8H,  $-(\text{CH}_2)_4$ ), 2.29 (1H,  $-\text{CH}$ ), 3.9–4.0 (t, 2H,  $\text{O}-\text{CH}_2$ ), 4.1–4.2 (t, 2H,  $\text{CH}_2-\text{OAr}$ ), 6.9–7.0 (m, 2H, aromatic), 7.4–7.5 (m, 2H, aromatic), 7.6–7.7 (m, 4H, aromatic).

### 2.2. Characterization

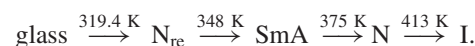
The proposed structures of the monomer and polymer were verified using <sup>1</sup>H-NMR and IR spectroscopy. The <sup>1</sup>H-NMR spectra were measured in CDCl<sub>3</sub> on a Bruker 250 MHz spectrometer. The IR spectra were recorded using a Perkin Elmer spectrum one FT-IR spectrometer. The glass transition temperature determined by DSC measurements is  $T_g = 318\text{ K}$ . The molecular weight of the polymer was measured by gel permeation chromatography using a Waters 996 apparatus equipped with an R410 differential refractometer, 600E pump, and two Waters ultrastyrigel columns (10<sup>4</sup>, 500 Å) and found to be 7291. THF was used as the eluent at a flow rate of 0.3 ml min<sup>-1</sup>. A calibration curve was obtained using polystyrene standards.

### 2.3. Dielectric measurements

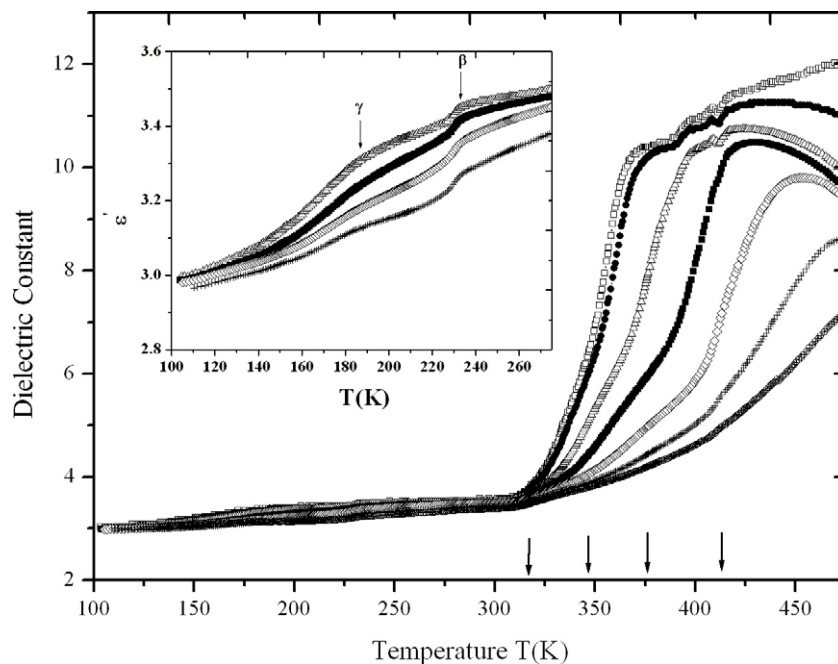
The dielectric measurements were made using an HP-4192A impedance analyzer in the 30 Hz–13 MHz frequency range. The dielectric cell was a parallel plate capacitor with sample thickness of 100  $\mu\text{m}$ . The gold electrodes were used as capacitor plates and uncertainty in the sample thickness was 3%. The impedance analyzer automatically swept 48 frequencies in this interval at approximately every 60 s. Computer control was accomplished via IEEE488. The dielectric measurements were performed in the temperature range 100–470 K at a heating rate of 0.5 K min<sup>-1</sup>. In our setup, temperature was controlled using a 12 bit analog-to-digital converter.

## 3. Results

The dielectric investigations were carried out on unaligned CBPA6 samples. However, the CN terminated side chains near the electrode surface would probably take planar orientation in order to keep the preferred anti-parallel ordering of the side groups [25]. Figure 1 shows the dielectric constant,  $\epsilon'$  versus temperature  $T$  for several frequencies. Anomalies corresponding to the sequence of phase transitions have been observed on the temperature evaluation of  $\epsilon'$ . The phase transition sequence of CBPA6 upon heating is



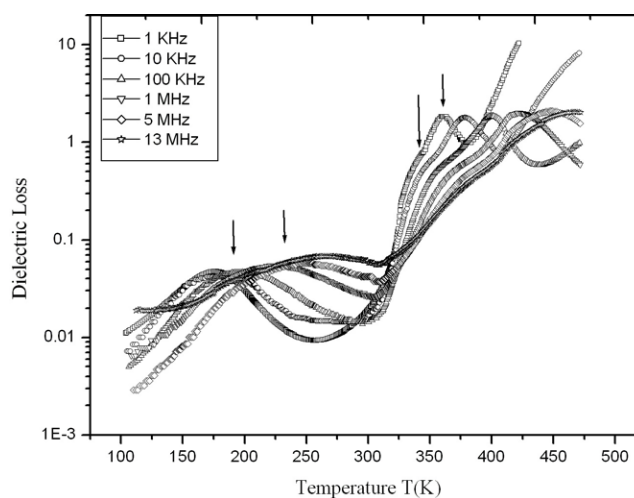
Slight anomalies of  $\epsilon'$  were observed at the isotropization temperature of  $T_I = 413\text{ K}$  together with gradually increasing



**Figure 1.** Temperature dependence of the dielectric constant  $\epsilon'$  of CBPA6 for several frequencies:  $\square$ - 500 Hz,  $\bullet$ - 1 kHz,  $\Delta$ - 10 kHz,  $\blacksquare$ - 100 kHz,  $\diamond$ - 1 MHz,  $+$ - 5 MHz,  $\oplus$ - 13 MHz. The arrows indicate the phase transition temperatures, depicted in the text. Isotropization temperature  $T_i = 413$  K was confirmed by polarization microscopy. In the inset detailed  $\epsilon'$  results at low temperatures at 10 kHz, 100 kHz, 1 MHz, 5 MHz are shown.

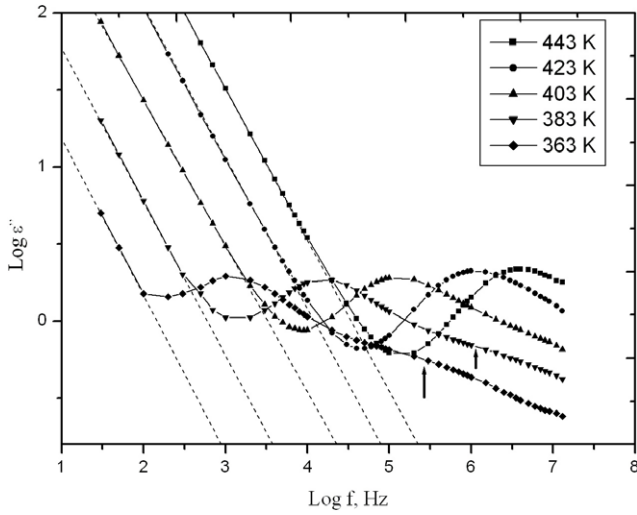
dielectric permittivity in the liquid isotropic phase at 500 Hz. The increase in the low frequency  $\epsilon'(T)$  with temperature is due to the contribution of electrical conductivity of the sample to dielectric response (see figure 3). A broad peak of  $\epsilon'$  and its strong relaxational shifting to high temperature was observed at frequencies higher than 1 kHz. Such behavior of  $\epsilon'$  points to the existence of heterogeneity of isotropic phase at  $T > 413$  K. Evidence of the heterogeneity state was confirmed by polarizing optical microscopy investigations: in the field of vision, droplets of regions with non-zero birefringence have been observed in the isotropic phase (not shown here). At temperatures above, but close to  $T_i$ , spontaneous microphase separation in CBPA6 was observed in the heating and cooling runs. In the isotropic phase the mesogenic side chains are randomly distributed, whereas the regions with non-zero birefringence are polymer-rich regions with favorable layered anti-parallel structure of mesogenic groups [28]. The microphase separation into polymer-rich and mesogen-rich regions in isotropic and liquid crystalline melts was also confirmed by molecular dynamics simulations [29]. Due to the similar structural complexity resulting from phase boundaries between nematic droplets and isotropic phases, the Maxwell-Wagner polarization should take place.

The temperature dependence of dielectric loss,  $\epsilon''$ , is shown at different frequencies in figure 2. Characteristic  $\gamma$ -,  $\beta$ -,  $\alpha$ - and  $\delta$ -relaxation processes have been clearly observed on  $\epsilon''$  versus  $T$  data with increasing temperature. On the  $\epsilon''(T)$  functions,  $\gamma$ - and  $\beta$ -relaxations inherent in the low temperature glassy state are revealed at 186 and 233 K, respectively. It should be noted that no peaks on  $\epsilon''(\omega)$  spectra were found for  $\beta$ -relaxation in the measured spectral window.



**Figure 2.** The evolution of dielectric loss with temperature at different frequencies. The arrows show the characteristic  $\gamma$ ,  $\beta$ ,  $\alpha$ , and  $\delta$  relaxations as temperature increases.

In the investigated compound, CBPA6, there is no bridge in the mesogenic group, thus  $\beta$ -relaxation should correspond to rotational friction of the mesogen around the ether bond. In [17] it was shown that the  $\beta$  process of cyanobiphenyl mesogen units does not provide a contribution to dielectric loss due to coaxiality of its dipole moment to the mesogenic group. But, it would be possible only in the case of ideal packing of anti-parallel side chains in the layered structure when a distance between anti-parallel oriented side chains is acceptable for ordered packing of mesogenic groups. In our



**Figure 3.** Dielectric loss spectrum at different temperatures, including SmA  $\rightarrow$  N  $\rightarrow$  I phase sequence. The dashed lines are almost parallel to each other, with the slope  $s \approx 1$ . The arrows indicate the  $\alpha$ -relaxation anomalies.

case the side chains are linked to each  $[-CH_2-CH_2-]_n$  acrylate segments and a possible distortion of the mutual position of mesogenic units due to geometrical confinement can occur. The occurrence of the violation of coaxiality direction of the dipole moment of the mesogenic unit to its long axis is probably the reason for dielectric anomalies in the region of 233 K.

It is well known that SCLCPs with long spacer groups exhibit a  $\gamma$ -relaxation process [9, 17, 28]. In the TSCLCP with cyanobiphenyl group and three methylene chains  $[-CH_2-]_3$   $\gamma$ -relaxation on  $\epsilon''(T)$  function was observed elsewhere in [19]. The  $\gamma$ -relaxation is a result of  $CH_2-$  groups in the side chains. Due to an even number of groups in  $[-CH_2-]_6$  spacers,  $[C-H]$  bond vectors are compensated in the methylene chains and hence could not yield  $\gamma$ -relaxations. The  $\gamma$ -relaxation in CBPA6 is, therefore, connected with the motion of  $[-CN]$  end groups. Both,  $\beta$ - and  $\gamma$ -relaxations give a contribution to  $\epsilon'(T)$ . In the inset of figure 1, the successive anomalies of dielectric constant at 186 and 233 K have been shown. The  $\gamma$ -relaxation obeys an Arrhenius relation with temperature dependence of the relaxation times varying as  $\tau = \tau_0 \exp(E_\gamma/RT)$ . The temperature dependence of  $\tau_\gamma$  is shown in the inset of figure 5. The calculated activation energy of the  $\gamma$ -process was found to be  $E_\gamma = 37 \pm 2$  kJ mol $^{-1}$ .

Above  $T_g$ , with increasing temperature  $\epsilon''(T)$  increases due to high temperature  $\alpha$ - and  $\delta$ -relaxations. Both processes are shifted to high temperatures as frequency increases. In order to investigate the spectral behavior of the relaxation processes, the conductivity contribution should be subtracted from the dielectric loss. The conductivity contribution was fitted (figure 3) to the well-known formula [2]

$$\epsilon'' = \sigma \epsilon_0^{-1} \omega^{-s}, \quad (1)$$

where  $\sigma$  is the conductivity,  $\epsilon_0$  free space dielectric constant,  $s$  is a fitting parameter, reflecting the physical nature of the

conductivity. It is evident from figure 3 that in a wide temperature range the slope values are close to unity and show that the low frequency part of  $\epsilon''(\omega)$  is affected by free charge migration. As seen in figure 3 the shapes of the absorption maxima belonging to  $\delta$ -relaxation are nearly symmetric at temperatures above the isotropization temperature  $T_1$ . The shape of the  $\epsilon''(\omega)$  peaks broadens with decreasing temperature and an additional anomaly related to  $\alpha$ -relaxation is observed in the high frequency part of the spectra. The attempt at fitting of the dielectric loss spectra shows that the Kohlrausch-Williams-Watts (KWW) relation describes  $\epsilon''(\omega)$  satisfactorily only in the isotropic phase. In a wide temperature range a good fitting of the isothermal  $\epsilon''(\omega)$  was attained using the Havriliak-Negami (HN) relation. For overlapped  $\delta$ - and  $\alpha$ -relaxation the HN relation is used in the view of two functions:

$$\epsilon^*(\omega) - \epsilon_\infty = \sum_k \frac{\Delta \epsilon_k}{(1 + (i\omega_k \tau_{0k})^a)^b} \quad (2)$$

where  $k$  denotes  $\alpha$ - and  $\delta$ -processes,  $a$  and  $b$  are the shape parameters ( $0 \leq a, b \leq 1$ ) representing a degree of the asymmetric broadening of the  $\epsilon''(\omega)$  peak. After having divided the complex relation (2) on the real and imaginary parts, the imaginary dielectric function was fitted by nonlinear least squares to the relation

$$\begin{aligned} \text{Im } F = -\exp \left\{ -\frac{b}{2} \log \left[ 1 + 2(\omega\tau_0)^a \cos\left(\frac{\pi a}{2}\right) \right. \right. \\ \left. \left. + (\omega\tau_0)^{2a} \right] \right\} \sin \varphi, \end{aligned} \quad (3a)$$

where  $\varphi$  is given by

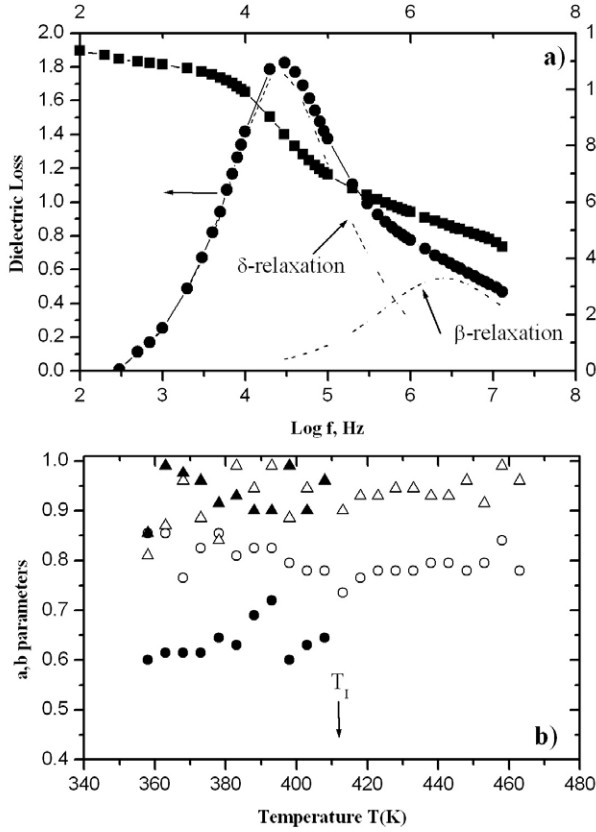
$$\varphi = b \arctan \frac{(\omega\tau_0)^2 \sin\left(\frac{\pi a}{2}\right)}{1 + (\omega\tau_0)^2 \cos\left(\frac{\pi a}{2}\right)}. \quad (3b)$$

Here  $\tau_0$  is the characteristic relaxation times for each  $\alpha$ - and  $\delta$ -processes separately. The examples of the fits to  $\epsilon''(\omega)$  data of CBPA6 are shown in figure 4(a). The evolutions of the HN parameters,  $a$  and  $b$  for both processes are displayed in figure 4(b) as well. As seen in figure 4(a) a broad maximum of dielectric loss is a characteristic feature of the high frequency  $\alpha$ -relaxation. The low frequency  $\delta$ -relaxation peak is relatively narrow and exhibits strong dipole relaxation strength  $\Delta \epsilon'(\omega)$  in a wide temperature range. The  $\delta$ -relaxation is an inherent process for SCLCP and manifests the rotational motion of the longitudinal dipole moment  $\mu_1$  of the mesogenic group around the short axis. Figure 5 shows the relaxation times versus reciprocal temperature for  $\delta$ - and  $\alpha$ -processes of CBPA6. A multistage slowing of the relaxation times of  $\delta$ -process,  $\tau^\delta$ , with decreasing temperature is clearly seen. The idea of a multi-step character of the  $\delta$ -process was suggested in [14]. Here, the experimental confirmation of this complexity was found using the example of CBPA6. The dipole motions of the  $\delta$ -process are essentially cooperative. In each stage of the relaxation times,  $\tau^\delta$  the VFT relation is perfectly fulfilled. With decreasing temperature the  $\tau^\delta$  of side chain motions of CBPA6 can be expressed in view of three of exponentials, as

$$\tau_1^\delta = \tau_{01} \exp\left(\frac{A_1^\delta}{T - T_1}\right) \quad (4a)$$

**Table 1.** VFT fitting parameters for cooperative processes in homopolymer CBPA6.

	$A_1$	$\tau_{01}$ (s)	$T_1$ (K)	$A_2$	$\tau_{02}$ (s)	$T_2$ (K)	$A_g^\delta$	$\tau_{0g}$ (s)	$T_g^\delta$ (K)	$A^\alpha$	$\tau_0^\alpha$ (s)	$T_g^\alpha$ (K)
$\delta$ -process	340	$6.5 \times 10^{-10}$	377	386	$1.5 \times 10^{-8}$	343	305	$4 \times 10^{-7}$	321			
$\alpha$ -process										810	$2 \times 10^{-9}$	318



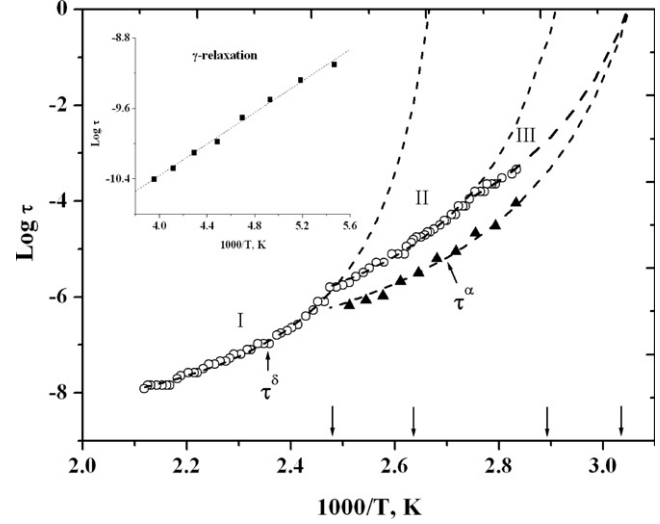
**Figure 4.** (a) Dielectric loss and constant versus frequency for CBPA6 at 388 K. The solid lines are guides to the eye. The dashed lines describe the separation of the  $\delta$ - and  $\alpha$ -relaxations according to the HN relation, (b) the HN parameters are shown for both relaxations.  $\bullet$ — $a^\alpha$ ,  $\blacktriangle$ — $b^\alpha$ ,  $\circ$ — $a^\delta$ ,  $\triangle$ — $b^\delta$ .

$$\tau_2^\delta = \tau_{02} \exp\left(\frac{A_2^\delta}{T - T_2}\right) \quad (4b)$$

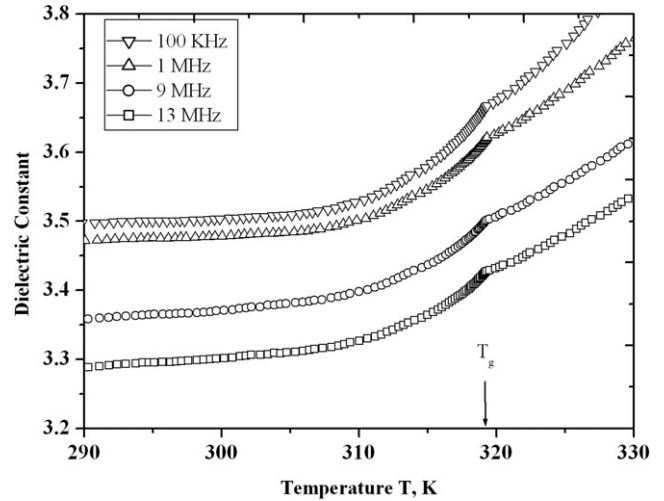
$$\tau_3^\delta = \tau_{0g} \exp\left(\frac{A_g^\delta}{T - T_g}\right) \quad (4c)$$

where  $\tau_0$ ,  $A_1^\delta$ ,  $A_2^\delta$ ,  $A_g^\delta$  and  $T_1$ ,  $T_2$ ,  $T_g$  are VFT fitting parameters of each observed stages. The fitting parameters are tabulated in table 1. Extrapolation of the fitted curves of  $\tau^\delta$  to the long times shows that their crossing with the temperature axis takes place in the regions of the sequential phase transition temperatures of CBPA6.

At the glass transition of CBPA6 a distinguishing peculiarity of dielectric constant  $\epsilon'(T)$  has been found. In figure 6 a step-like anomaly of  $\epsilon'(T)$  at  $T_g$  is clearly seen. To the best of our knowledge, in the literature there has been no similar evidence of an  $\epsilon'(T)$  anomaly in the glass transition



**Figure 5.** Temperature dependence of the  $\delta$ - and  $\alpha$ -relaxation times of CBPA6. The symbols I, II, and III denote the different stages of multistage slowing of  $\tau^\delta$ . The dashed lines describe VFT fitting curves. The arrows indicate the phase transition temperatures.



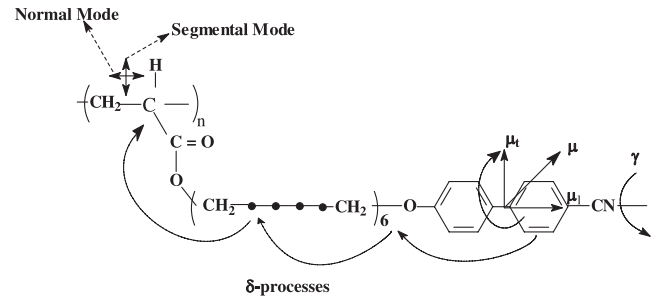
**Figure 6.** The step-like anomaly on the temperature dependence of  $\epsilon'(T)$  at  $T_g$  for several frequencies.

region of any SCLCP. A step-like anomaly of  $\epsilon'(T)$  at  $T_g = 319.4$  K becomes more significant at high frequencies and points out dipole rearrangements at the glass to  $N_{re}$  transition.

#### 4. Discussion

A multistage slowing of  $\tau^\delta$  is possible if during the  $\delta$ -process there is a change of the position of the short rotational axis

along the side chain length as temperature decreases. A similar complexity of the longitudinal motion of the mesogenic dipole moment may be a characteristic feature of the long SCLCP. The slowing of the motions of the side chains in the  $\delta$  process in the isotropic phase turned out to determine the ordering of the mesogenic groups at the transition from nematic to polymeric SmA phase at 375 K. In [20] the connection between rotational mobility of a side chain and microscopic local viscosity in the bulk was established. The rotational mobility  $\nu_r$  of the side chain is related to the side chain length  $L$  and medium viscosity  $\eta_s$  as  $\nu_r \approx 1/\eta_s L^3$ . Due to fluctuation of the local microviscosity in the isotropic phase, polymeric clusters of the SmA phase might appear. With decreasing temperature a moiety of polymer having SmA ordering is increased leading to partial softening of the  $\delta$ -relaxation mode in the isotropic phase. A tendency of the fitting curve of the  $\delta$ -relaxation stage I towards the N-SmA transition at 375 K allows us to conclude that the SmA ordering is formed due to slowing of the rotational motions of mesogenic groups around an ether linkage (O). The VFT constant corresponding to the N-SmA transition,  $A_1 = 340$ , exhibits relatively low values and this indicates that only a partial slowing of side chain dynamics in the  $\delta$ -process occurs in CBPA6 at 375 K. Below  $T_1 = 413$  K both  $\alpha$ - and  $\delta$ -processes are clearly seen in the absorption spectra of CBPA6. The complexity of  $\tau^\delta$  temperature dependence is also observed below  $T_1$ . A slight anomaly of  $\tau^\delta$  in the vicinity of  $1000/T = 2.75 \text{ K}^{-1}$  (figure 5) requires us to apply two additional VFT fits to the  $\delta$ -processes of CBPA6, using the relations (4b) and (4c). The extrapolation of fitting curves of the stages II and III of  $\tau^\delta$  to the long times is satisfactorily coincident with the temperatures of the SmA-N<sub>re</sub> and glass transitions. It is known that the nematic phase possesses a common directional orientation with disordered center of mass of the mesogenic side chains [23], implying that in stage II of the  $\delta$ -relaxation due to the flexibility of the methylene side chain the positions of the short rotational axis can be changed randomly along the next neighbor methylene groups in order to create the conditions for reentrant nematic phase N<sub>re</sub>. We assume that these phenomena should be a general feature of SCLCPs with a long methylene for which the low temperature N<sub>re</sub> phase is realized. Indeed, slowing of the  $\delta$ -process around a randomly arranged short axis in stage II occurs in such a way that molecular corrugation of the mesogenic side chains take places in the N<sub>re</sub> phase. In this case neighboring mesogenic groups within a layer prefer positions of mutual displacement along the long axis of the side chain [26, 27]. Dipole interactions and correlations of cyanobiphenyl mesogens are expected to be strong in the N<sub>re</sub> phase due to a high dipole moment of CN groups (3.95 D) [31], and thus may lead to an increasing of intramolecular cooperativity in the subsystem of LC mesogens within the layered structure. According to the coupling theory [32], Ngai showed that long flexible methylene groups, connected with polymeric backbones, have to mitigate the dynamic constraint and hence decrease the degree of intermolecular cooperativity of local segmental motion of the backbone [4]. Thus, the increase of intramolecular cooperativity in the mesogenic subsystem is not contradictory to the results of [4].



**Figure 7.** A schematic representation of the evolution of the multistage  $\delta$ -process in CBPA6.

In CBPA6 the reentrant nematic phase exists in the temperature interval of 28.6 K, being adjacent to glassy phase ( $T_g = 319.4$  K, see figure 1). A corrugation of the side chains in a random position of methylene groups and relatively strong intramolecular cooperativity in the mesogenic subsystem should cause slowing of the mode which is attributed to the motion of the transverse component of the mesogenic dipole moment,  $\mu_t$ , in the N<sub>re</sub> phase. It is worth remembering here the specific sizes of mesogenic group: the width of a benzene ring is 6.8 Å and the separation of nearest-neighbor mesogens is about 4.8–5.5 Å, which is expected to increase the rotational steric hindrance [26, 30] with decreasing temperature. As pointed out in [26] for the reentrant phase, interpenetrating of the coexistence order and disorder is inherent in the sense of the microscopic mechanism. We suppose that slowing of the transverse rotational motions of the mesogen dipole moment  $\mu_t$  should be squeezed due to corrugation and mutual displacement along side chains, which create a ‘freeze-like’ state of  $\mu_t$  in the N<sub>re</sub> phase. A similar dipole configuration gives an additional contribution to intramolecular cooperativity in the mesogenic subsystem of the layered polymer pattern. The explained complexity of the dipole interaction in the N<sub>re</sub> phase is the reason for the next branch  $\delta$ -relaxation process, denoted as stage III in figure 5. A relatively long  $\tau^\delta$  in stage III indicates a motion of more ‘heavy’ side chain units in the  $\delta$ -process as the temperature approaches  $T_g$ . We assume that the position of the short rotational axis of the  $\delta$ -process in the N<sub>re</sub> phase could be somewhere close to the polymeric backbone. A possible multistage variation of the short rotational axis in the  $\delta$ -processes is depicted in figure 7. Both  $\tau^\delta$  in the N<sub>re</sub> phase and relaxation times  $\tau^\alpha$  associated with segmental motion are well described by the VFT relation. The fitting curves of  $\tau^\delta$  and  $\tau^\alpha$  approach the glass transition temperature with a good accuracy, indicating that both relaxation modes are ‘freezing’ at  $T_g$  (see figure 5). Similar slowing of the relaxation rate of the  $\delta$ - and  $\alpha$ -processes towards to  $T_g$  was observed in different SCLCP compounds in several investigations [14, 16, 17].

The problems of interaction of side chain modes with segmental modes of the backbone were discussed by Mano [21, 22], who suggested the existence of special modes within the mesogens, which would be intimately correlated with segmental  $\alpha$ -relaxation modes [22]. Here, it is worth remembering that backbone motions are governed by segmental and normal modes [33], which in the sense of dipole

motions are perpendicular to each other. Both segmental and normal modes are responsible for long-range diffusive motions of segments at the glass transition. In the layered structure of CBPA6, in the  $N_{re}$  phase, with non-zero resultant dipole moment of the mesogenic subsystem, rotational fluctuations of side chains in the  $\delta$ -process remain active as long as segmental and normal modes are active. An arrangement of the side chain rotational axis nearly to the backbone provides the interaction of the backbone modes with the mesogenic subsystem via the  $\delta$ -relaxation process at the glass transition onset. That might be possible since the relaxation rates of the backbone and  $\delta$ -relaxation are close to each other (figure 5) in the vicinity of the glass transition. The interaction of the modes is the reason for the observation of a step-like anomaly of  $\varepsilon'(T)$  at glass transition (figure 6). The observed  $\varepsilon'(T)$  anomaly at  $T_g$  may not be a general feature for a wide class of SCLCPs, and may be specific for cyanobiphenyl side chains exhibiting the  $N_{re}$  phase.

## 5. Conclusion

In the present study we have investigated the dielectric relaxation in the thermotropic side chain LCPs with a cyanobiphenyl group, containing six methylene chains and have observed the existence of the  $\gamma$ ,  $\alpha$ ,  $\delta$  relaxation processes. The low temperature relaxation rate for the  $\gamma$ -process is found to obey to the Arrhenius relation with activation energy  $E_\gamma = 37 \pm 2 \text{ kJ mol}^{-1}$ . A multistage evolution of the  $\delta$ -process with temperature, reflecting the dipole motion of mesogenic side chains, was observed. Our measurements show that slowing of the  $\delta$ -relaxation rate at every stage corresponds to the sequence of the phase transitions of CBPA6. This evidence allows us to suppose that the short rotational axis of the  $\delta$ -process changes its arrangement along a side chain, which should be a general feature of SCLCPs with long methylene groups in the side chains. At the  $N_{re}$  to glass transition, a step-like anomaly of  $\varepsilon'(T)$  was observed. It was argued that this is specific for the dipole rearrangement in the  $N_{re}$  phase: the corrugation effects of the side chains with random positions of the short rotational axis and the mutual displacements of the mesogenic dipole groups create the conditions for non-zero resultant ( $\vec{\mu}_t, \vec{\mu}_l$ ) dipole moments and hence, a strong cooperativity in the mesogenic subsystem. We think that these peculiarities of the  $N_{re}$  phase support the above-mentioned dynamical constraints in the layered structure via the  $\delta$ -process. The degree of cooperativity of  $\delta$ - and  $\alpha$ -relaxations has been increased with the onset of the glass transition. The glass transition of CBPA6 is accompanied by interactions of non-zero dipole moments of the mesogenic subsystem with a mixture of segmental and normal modes of the backbone through the  $\delta$ -relaxational mode. The observed step-like anomaly of  $\varepsilon'(T)$  is the experimental evidence for these interactions.

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