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# Nematic and Domain Order Parameters for Partially Oriented Isotropic/Liquid Crystalline Diblock Copolymers: A Dielectric Spectroscopy Study

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**ABSTRACT:** Dielectric relaxation in a liquid crystalline (LC) side chain polymer and in a series of diblock copolymers with polystyrene is investigated using dielectric spectroscopy. The block copolymer morphology is cylindrical with the LC block forming the continuous matrix. Two processes are found in the nematic state with their relative dielectric relaxation strength strongly dependent on block copolymer composition. The spectra are described using the concept of a local order parameter  $S$  and a domain order parameter  $S_D$ . Application of electric or mechanical fields induce a homeotropic orientation of the nematic domains in the homopolymer without significantly influencing the local order parameter. The block copolymers display a spontaneous orientation even in thick films ( $d < 300$  nm).

## 1. Introduction

Liquid crystalline microphase separated block copolymers composed of incompatible liquid crystalline (LC) and isotropic blocks (I) are a relatively new class of compounds. With respect to the formation of structure on a mesoscopic length scale they offer two distinct mechanisms. One is the microdomain ordering caused by the strong repulsive interaction between both blocks. As a second factor, the orientational order of the mesogens in the LC block is to be considered. In these systems, one or both blocks may form the microdomains with well-defined dimensions typically ranging from a few nanometers to 100 nm.<sup>1</sup> Common types of microdomain forms are spheres, cylinders, and lamellae which may be tuned at the level of chemical synthesis. This combination of a liquid crystalline phase with its own characteristic inter-mesogen distance (typically less than 1 nm) and the formation of domains in different morphologies has stimulated a growing academic as well as industrial interest.<sup>1,2</sup>

In previous publications, we have reported on the investigation of a series of di- and triblock copolymers with the liquid crystalline block either confined within spherical, cylindrical or lamellar domains or forming the continuous matrix.<sup>3,4</sup> Small- and wide-angle X-ray scattering has been applied to study structure on a wide range of length scales. The dependence of domain order on the orientational order is studied by variation of temperature and crossing the transition temperature of the liquid crystalline to the isotropic phase. The LC phase in our case is a nematic phase. The nematic order of the LC clearly favors the cylindrical over the spherical domain form and may thus cause a variation of structure with temperature at the LC phase transition. For one example we find the order-to-order transition in the domain structure triggered by the nematic–isotropic phase transition of the liquid crystalline matrix.<sup>4</sup>

For the same set of diblocks the molecular dynamics was studied using dielectric spectroscopy in a wide frequency range.<sup>5,6</sup> The dielectric absorption displays regimes of coopera-

tive  $\alpha$ - and  $\delta$ -relaxation as well as the so-called local  $\beta$ - and  $\gamma$ -processes. They are related to the reorientational dynamics in the LC block. Both cooperative processes display a weak variation with the microdomain dimensions (confinement effect). The relaxation times are clearly shorter (by a factor of 10) in domains than in the matrix.<sup>5</sup> A similar but smaller effect is observed for the  $\beta$ -process reflecting mesogen rotation around long axis. The  $\gamma$ -process (spacer motion) due to its local nature remains the same in the matrix as in domains. All these data indicate that the molecular dynamics of the LC block has a rather weak dependence on microdomain size and only slightly deviates from that of the corresponding LC homopolymer representing a continuous undisturbed LC matrix. The smallest accessible LC microdomain dimension was about 10 nm in the copolymers investigated.

It is well-known that the macroscopic alignment of LC side-chain polymers can be varied systematically by applying an external electric, magnetic or mechanical field.<sup>7,8</sup> For example, homeotropic (H-) and planar (P-) alignment can be achieved by slowly cooling the sample from the isotropic to the nematic phase in the presence of a strong ac electric field. The type of the resulting orientation for a given polymer is controlled by the frequency of the aligning electric field. It has been shown that the dielectric data for unaligned and aligned materials can provide information about the order parameter  $S$  which describes the orientation of mesogen fragments with respect to the local director of a nematic domain.  $S$  is defined as

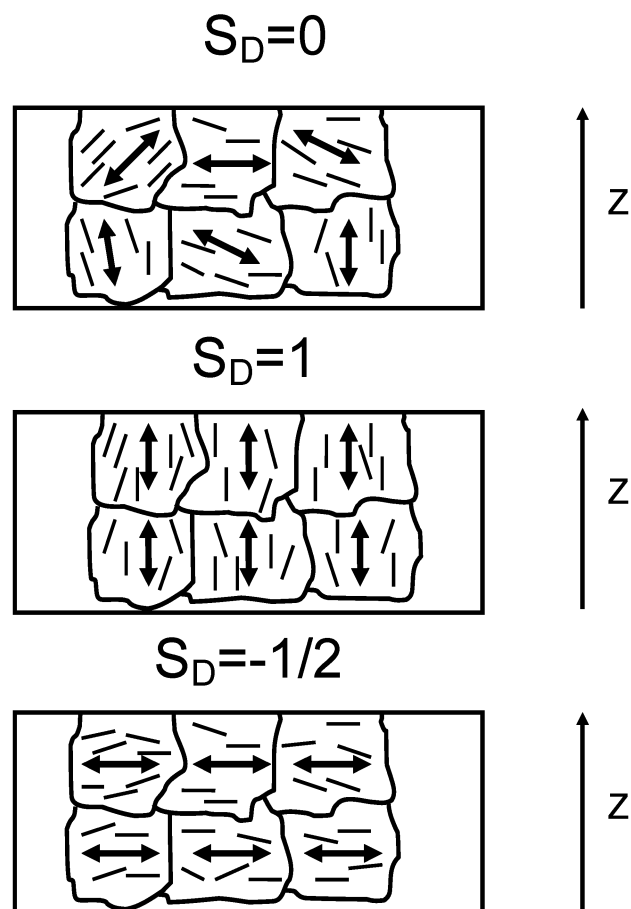
$$S = \frac{\langle 3 \cos^2 \theta - 1 \rangle}{2} \quad (1)$$

$\theta$  is the angle between the mesogen and the locally defined domain director  $\mathbf{n}$ . Here we call this parameter the nematic order parameter  $S_N$ . At the same time, the orientation of the nematic domains with respect to a laboratory axis  $Z$  can be expressed by a domain order parameter  $S_D$ .<sup>7</sup> In principle these two order parameters are independent. In the absence of spontaneous macroscopic orientation we have  $S_D = 0$ . For fully H-aligned domains we will have  $S_D = 1$  and  $S_D = -1/2$  for P-alignment. Figure 1 schematically shows these limiting cases.

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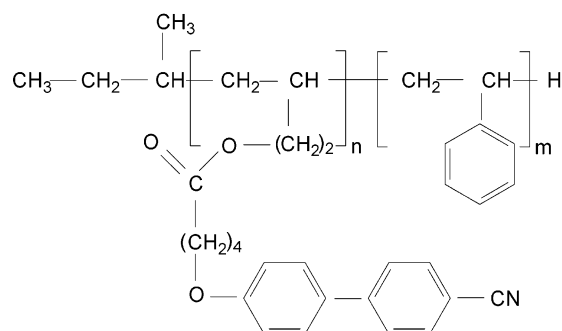
**Figure 1.** Schematic representation of possible orientations of nematic domains with respect to a laboratory  $z$  axis in LC polymers. The small lines represent the mesogen fragments, whereas the double arrows indicate the preferred orientation of domain director  $\mathbf{n}$ .

For the case of the block copolymers this now raises the interesting question how the induced order will interfere with the domain microstructure of LC/I diblock copolymers. Guided by this idea we have undertaken an investigation of the dielectric relaxation in three LC/I copolymers and the corresponding LC homopolymer aligned by external ac electric or mechanic field. The block copolymer domain structure of the three copolymers investigated is a continuous LC matrix with embedded, hexagonally packed PS cylinders.<sup>3</sup> Analysis of the dielectric spectra allows us to estimate  $S_N$  and  $S_D$  and relate them to the order developing in the systems. Reheating of the aligned copolymer to its isotropic state removed completely the induced orientation.

## 2. Experimental Section

**Synthesis and Characterization of the LC/PS Block Copolymers.** The details of the synthesis of PS/LC copolymers and their characterization are described in ref 4. The LC block consists of cyanobiphenyl mesogens coupled to poly(1,2-butadiene) through valeric acid spacers (Figure 2).

The polymers are denoted as PSLC  $x/y$  where  $x$  is the fraction of PS block in volume percent and  $y$  is the content of the LC block. All PS/LC diblock copolymers have a narrow molecular weight distribution with polydispersity index less than 1.1. DSC and polarized microscopy data reveal that the mesomorphic behavior of LC blocks is only slightly influenced by the copolymer composition and is basically characterized by the sequence  $g/\sim 35$  °C/ $n/\sim 120$  °C/ $i$ . As a result of the strong incompatibility between the PS block and the LC block the polymers were found to be microphase separated in the full temperature range from 25 up to 170 °C. Table 1 summarizes the results obtained for the domain



**Figure 2.** Chemical structure of copolymers investigated.

structure on the basis of the SAXS patterns. In all cases the two-dimensional hexagonal microstructure characterized by a lattice constant  $a$  and cylindrical PS domains of radius  $R$  was observed. The LC block forms a continuous LC matrix. For all copolymers only one type of mesophase structure was obtained independent of temperature.

**Dielectric Spectroscopy (DS) and Sample Alignment.** Dielectric experiments were carried out in a wide frequency range. From  $10^{-2}$  to  $10^6$  Hz, the complex impedance of a sample capacitor was measured using a Solartron-Schlumberger frequency response analyzer SI 1260 equipped with a Chelsea Dielectric Interface. In the frequency range  $10^6$ – $10^8$  Hz, a rf impedance analyzer (HP 4191A) was employed. The sample capacitor consisted of two gold-coated stainless steel electrodes. It was filled with the polymer at +150 °C. The sample thickness was varied between 27 and 300  $\mu\text{m}$ . Sample temperature in the range +20 to +160 °C was controlled in a nitrogen gas jet (Quattro, Novocontrol GmbH) with a stability better than 0.05 °C.

The samples were aligned in situ in the dielectric cell by the following procedure. The sample was heated above  $T_{NI}$  in order to melt the LC matrix into its isotropic state. At this temperature the sample was annealed for 1 h with an ac voltage switched on. After that the cell with the ac voltage kept on was cooled to +20 °C at a rate of 0.2 °C/min. The alignment electric field was switched off and the dielectric data were collected at fixed temperatures in heating runs with temperature steps of 5–10 deg allowing for sample equilibration after each temperature change. The frequency of the alignment electric field was 20 Hz. By variation of the electric field strength  $E$  between 0 and 30 kV/cm, different degrees of homeotropic alignment were achieved.

The same capacitor was used for the preparation of mechanically oriented samples. The frequency and amplitude of shearing field were 0.1 Hz and 4 mm, respectively. Two parallel electrodes were sheared at +115 °C in the nematic phase for 3 min. Then sample was rapidly removed from the hot stage. Such mechanical treatment induces H-alignment.

## 3. Experimental Results and Discussion

**3.1. Dielectric Relaxation of Unaligned Samples.** The unaligned LC copolymers and the related LC homopolymer were studied in our earlier papers.<sup>5,6</sup> We therefore only briefly comment on their dielectric properties. Since in the investigated compositions each block of the copolymer forms separate domains it is helpful to consider the individual dielectric behavior of the LC and PS homopolymers. A strong dipole moment of the cyanobiphenyl mesogen fragment is the main source of dielectric relaxation in the LC homopolymer as well as in LC copolymers. Two main relaxation processes denoted as  $\delta$  and  $\alpha$  are observed in the LC state. In the isotropic state they overlap to form one broad intensive absorption band. Such behavior is typical for side chain LC polymers.<sup>7–9</sup> The other block, the polystyrene, displays a typical  $\alpha$  relaxation with weak relaxation strength at temperatures above 100 °C. Its absorption band has an intensity less than 0.01. Thus, it is impossible to

**Table 1. Molecular Weight and Hexagonal Lattice Parameters (Lattice Constant  $a$  and Cylinder Radius  $R$ ) for the Copolymers Investigated**

LC/I block copolymer	MW g/mol	microstructure	morphology	$t$ [°C]	$a$ [nm]	$R$ [nm]
PSLC 7/93	77 000	hexagonal	PS cylinders in LC matrix	25	$33.6 \pm 0.1$	$4.5 \pm 0.2$
PSLC 14/86	53 700	hexagonal	PS cylinders in LC matrix	30	$27.4 \pm 0.1$	$5.5 \pm 0.1$
PSLC 19/81	104 300	hexagonal	PS cylinders in LC matrix	25	$46.6 \pm 0.2$	$1.0 \pm 0.1$

resolve the PS block contribution from dielectric spectra in the compounds studied. Taking this fact into account, our further analysis will only focus on the dielectric behavior of LC phase.

**3.2. Dielectric Relaxation of Aligned Samples.** As an example, Figure 3 shows the dielectric spectra recorded for the LC homopolymer aligned by electric fields  $E$  of 1.7 and 9.6 kV/cm, respectively. As expected, both relaxation processes denoted as  $\delta$  and  $\alpha$  were observed in the LC state for both cases.

The effect of orientation on the dielectric relaxation is obviously strong. The  $\delta$ -process is enhanced and the  $\alpha$ -process is diminished remarkably on going from unaligned to aligned material. This is even more clearly demonstrated in Figure 4, which compares dielectric spectra at +90 °C for different alignment field strengths. Relaxation strength is continuously shifted from the  $\alpha$ - to the  $\delta$ -process with increasing the alignment field. The qualitative observation shows that we are inducing a homeotropic alignment in our sample by the application of the electric field.<sup>8</sup> We point out that in our experiments the direction of measuring and the alignment field coincide.

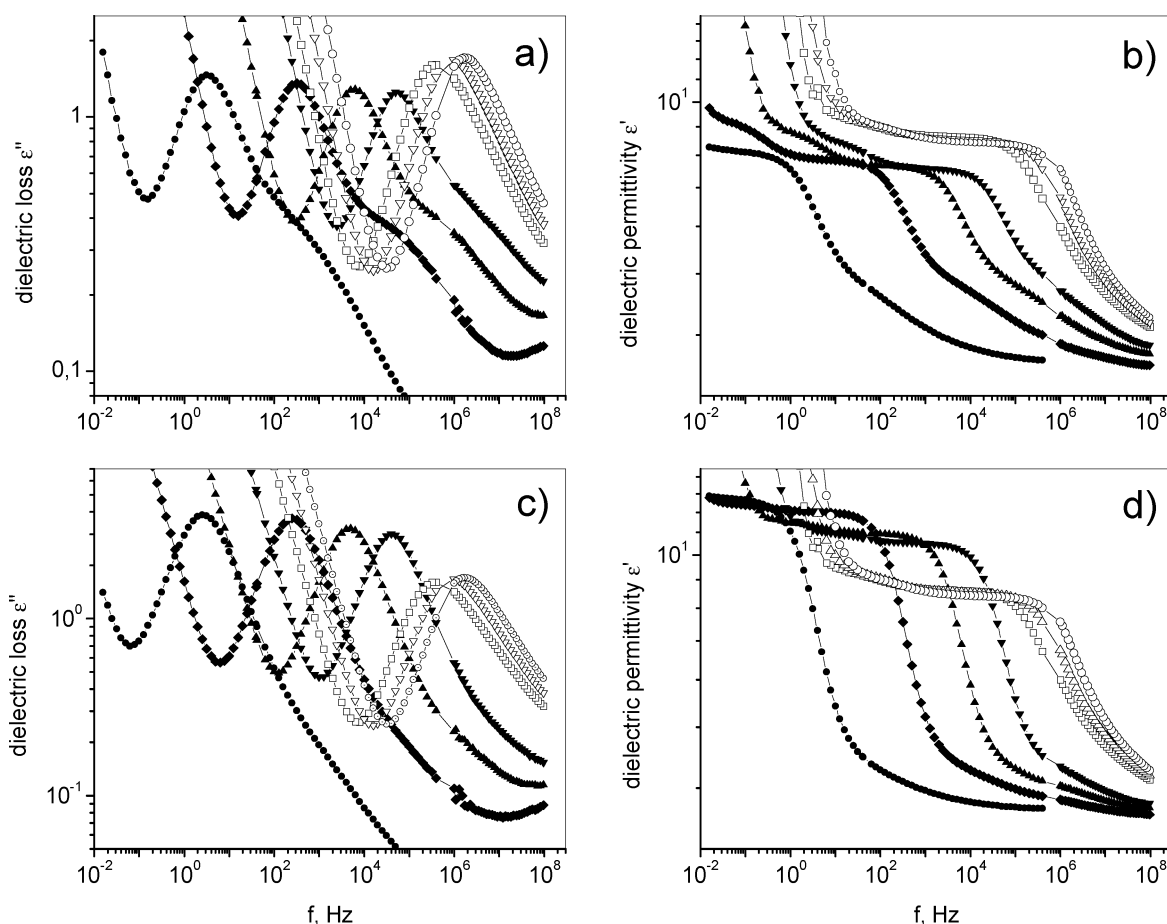
To describe quantitatively the experimental spectra recorded in the LC state, the isothermal data of the dielectric loss curves  $\epsilon''(\omega)$  were fitted to a superposition of two Havriliak–Negami

(HN) functions<sup>10</sup> and a conductivity contribution:

$$\epsilon^*(\omega) - \epsilon_\infty = \sum_k \frac{\Delta\epsilon_k}{(1 + (i\omega\tau_k)^{\alpha_k})^{\gamma_k}} - \frac{i\sigma}{\epsilon_0\omega^s} \quad (2)$$

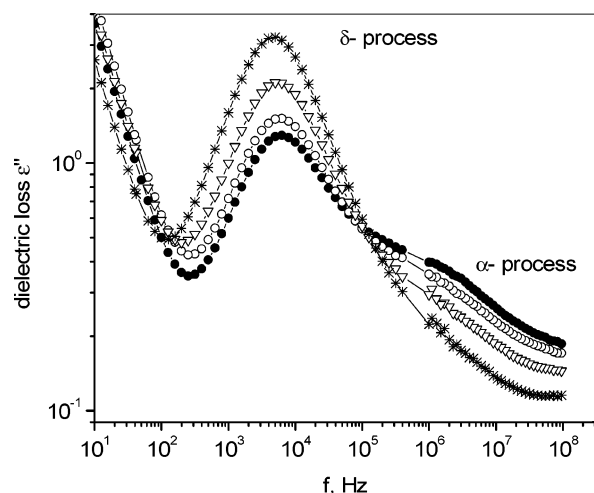
$\epsilon_0$  is the vacuum permittivity,  $\omega$  is angular frequency ( $\omega = 2\pi f$ ),  $\Delta\epsilon_k$  is the relaxation strength, and  $\tau_k$  is the relaxation time of the  $k$ th process. The shape parameters  $\alpha_k$  and  $\gamma_k$  describe the symmetric and asymmetric broadening of the relaxation peak, respectively. For purely ohmic behavior  $\sigma$  denotes the dc conductivity and the exponent  $s$  equals one. Values of  $s$  different from 1 are only used for a qualitative description of  $\epsilon(\omega)$ . In the case of  $\alpha = \gamma = 1$  the HN function reduces to that of a Debye relaxation process. Special cases are the symmetric Cole–Cole function ( $\alpha < 1$ ,  $\gamma = 1$ ) or the asymmetric Cole–Davidson function ( $\alpha = 1$ ,  $\gamma < 1$ ).

Equation 2 was fitted to the experimental data using a nonlinear least squares algorithm. One assumption was taken to stabilize the results of the fit. We fix the shape parameter  $\gamma$  for  $\delta$  mode to be equal 1, because the  $\delta$  mode of the side chain LC polymers is found to be well described by a symmetric distribution of the relaxation times.<sup>7</sup> Within this model the fit

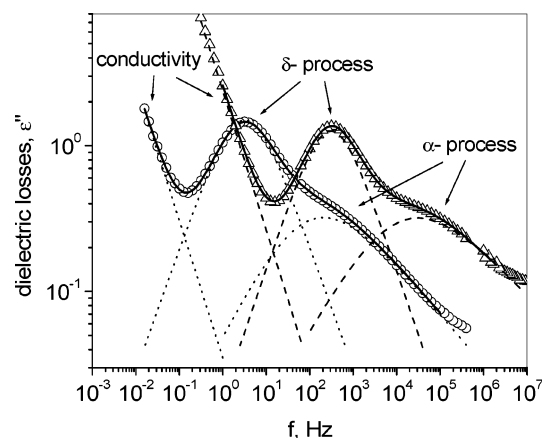


**Figure 3.** Dielectric spectra for LC homopolymer (PSLC 0/100) aligned by  $E = 1.7$  kV/cm (a,b) and  $E = 9.6$  kV/cm (b,c) at different temperatures: (●) +50 °C; (◆) +70 °C; (▲) +90 °C; (▼) +110 °C; (□) +120 °C; (▽) +130 °C; (○) +140 °C. Filled and open symbols are for LC and isotropic states, respectively. The thickness of the LC film is 100  $\mu\text{m}$ . The errors are smaller than the size of the symbols.





**Figure 4.** Dielectric loss  $\epsilon''$  for LC homopolymer (PSLC 0/100) at +90 °C aligned by external ac field of frequency 20 Hz and different amplitude  $E$  (kV/cm, rms): (●) 0; (○) 2.4; (▽) 3.8; (\*) 9.6. The errors are smaller than the size of the symbols.



**Figure 5.** Example of the fitting results for the LC homopolymer at +50 (○) and +70 °C (△) aligned by  $E = 1.7$  kV/cm. The errors are smaller than the size of the symbols. The solid line is the sum of the three curves shown by the dashed lines: at +50 °C,  $\alpha$  relaxation ( $\Delta\epsilon = 1.58 \pm 0.05$ ;  $\alpha = 0.59 \pm 0.04$ ;  $\gamma = 0.59 \pm 0.06$ ;  $\tau = (1.75 \pm 0.16) \times 10^{-3}$  s),  $\delta$  relaxation ( $\Delta\epsilon = 3.48 \pm 0.06$ ;  $\alpha = 0.84 \pm 0.01$ ;  $\gamma = 1.00$ ;  $\tau = (5.05 \pm 0.04) \times 10^{-2}$  s), and conductivity contribution ( $\sigma/\epsilon_0 = 0.20 \pm 0.01$ ;  $s = 0.94 \pm 0.01$ ); at +70 °C,  $\alpha$  relaxation ( $\Delta\epsilon = 1.74 \pm 0.03$ ;  $\alpha = 0.55 \pm 0.03$ ;  $\gamma = 0.60 \pm 0.06$ ;  $\tau = (1.32 \pm 0.19) \times 10^{-5}$  s),  $\delta$  relaxation ( $\Delta\epsilon = 3.04 \pm 0.04$ ;  $\alpha = 0.88 \pm 0.01$ ;  $\gamma = 1.00$ ;  $\tau = (5.14 \pm 0.02) \times 10^{-4}$  s), and conductivity contribution ( $\sigma/\epsilon_0 = 14.8 \pm 0.07$ ;  $s = 0.95 \pm 0.01$ ).

routine provides stable results for the relaxation times of  $\delta$  and  $\alpha$  processes for all copolymers studied. The accuracy in the determination of HN parameters was generally better than 10%. Figure 5 shows an example of the fit results at +50 and +70 °C for the LC homopolymer aligned by  $E = 1.7$  kV/cm. It is seen that both relaxations are nicely separated using this procedure.

Heating the aligned copolymer to its isotropic state leads to complete removal of the induced orientation. We also find that the transition temperature  $T_{NI}$  is practically independent of the degree of alignment developed in the sample.

In the isotropic state we observe one absorption band which is well described by a single HN-function. This is seen in the curves for  $T > T_{NI}$  of Figure 3 (open symbols).

The results of the HN-fits at +90 °C for LC homopolymer oriented at different alignment field  $E$  are summarized in Figure 6. The mean relaxation time for the  $\delta$  mode becomes slightly longer for well aligned samples, whereas the  $\alpha$  processes is

virtually independent of the degree of induced alignment (see Figure 6a). The quantities which change markedly with variation of  $E$  are  $\Delta\epsilon_\delta$ ,  $\Delta\epsilon_\alpha$ , and consequently  $S_D$ . On increasing  $E$ , we can discriminate three regimes of induced order (see Figure 6b,c). For clarity these regimes are separated by vertical dotted lines on Figure 6. Within regime I, up to 2 kV/cm, there is no observable induced orientation. Apparently a minimal energy is required to activate the ordering of the nematic domains. In the second regime,  $2 < E < 6$  kV/cm, the extent of alignment is rapidly increased with  $E$ . The cooling rate during the orientation process plays an important role in this regime. The effect of this kinetic factor was demonstrated in earlier work.<sup>8</sup> When the cooling rate is increased the extent of alignment decreases. Samples cooled with a rate of 20 °C/min did not align even in the presence of a very strong ac field. In the present work the cooling rate was set to be 0.2 °C/min. At that condition for  $E \sim 6$  kV/cm most nematic domains are aligned as is seen in the saturation observed for the relaxation strengths in Figure 6b and c. Therefore, in regime III with further increase of  $E$  only weak changes of the dielectric relaxation are observed. For several LC polymers, it has been shown that extent of alignment was essentially complete for  $E > 12.5$  kV/cm.<sup>7,8</sup>

Let us now turn to the method of evaluating  $S_N$  and  $S_D$  from the dielectric spectra. We recall that the nematic order parameter  $S_N$  describes the orientation of mesogens inside nematic domains with respect to a local director  $\mathbf{n}$ , whereas the director order parameter  $S_D$  gives an estimate of the average alignment of the local directors with respect to the laboratory axis  $Z$ . In the present work the directions of the  $Z$  axis, the measuring and the alignment electric fields all coincide as depicted in Figure 1.

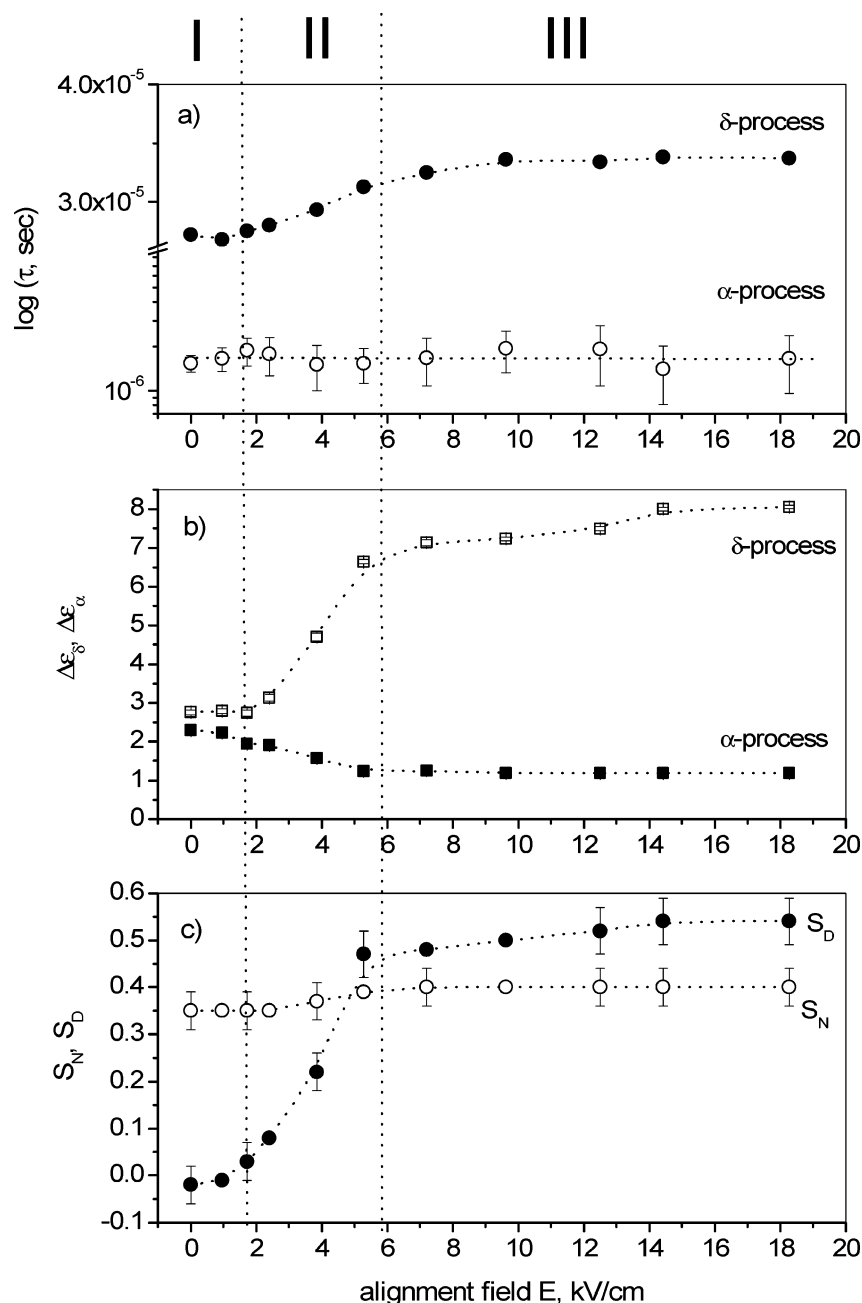
**Nematic Order Parameter  $S_N$ .** To calculate  $S_N$  we have used the Meier and Saupe concept of the retardation factor for the longitudinal component of the dielectric spectra, i.e., the  $\delta$  mode.<sup>11</sup> Various models have been proposed for the microscopic dynamics underlying the  $\delta$  process in side chain LC polymers.<sup>7-9,12-15</sup> The most extensively discussed model for the  $\delta$  relaxation assumes a cooperative rotation of the mesogen group around its short axis. The large relaxation strength and its dependence on the longitudinal component of the side group dipole moment confirm this model. Figure 7 displays the activation diagram for  $\delta$  mode in LC and isotropic states for LC homopolymer. It is clearly seen from Figure 7 that the relaxation time is distinctly retarded on passing through the isotropic–nematic phase transition. The retardation factor  $g_{||}$  is defined as

$$g_{||} = \frac{\tau_\delta}{\tau^*} \quad (3)$$

where  $\tau^*$  corresponds to a hypothetical state for which the nematic potential is “switched off”. At the desired temperature in the LC state  $\tau^*$  is obtained as an extrapolated value from the isotropic region assuming an Arrhenius-like temperature dependence of relaxation rates. To apply this concept we fit our data in the isotropic state to the Arrhenius equation:

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right) \quad (4)$$

$\tau_0$  is the preexponential factor and  $E_a$  the activation energy. We then extrapolate this  $\tau(T)$  into the LC phase as is shown in Figure 7. This method can only be applied for temperatures close to  $T_{NI}$  (see Figure 7).<sup>12</sup> Therefore, we restrict our further analysis to one reference temperature  $T = +90$  °C.



**Figure 6.** Relaxation time  $\tau$ (a), relaxation strength  $\Delta\epsilon$ (b) and order parameters  $S_N$  and  $S_D$ (c) for LC homopolymer at +90 °C vs strength of external alignment ac field  $E$ . The thickness of the LC film is 100  $\mu\text{m}$ . The dotted vertical lines separate schematically the three regimes of order established at elevating  $E$ .

The effect of the nematic potential  $\sigma$  on the relaxation time of the  $\delta$ -process was shown to be a retardation as described by eq 3 in the work of Meier and Saupe.<sup>11</sup> They give the retardation factor as

$$g_{\parallel}^{\text{MS}} = \frac{\tau_{\delta}}{\tau^*} = \frac{e^{\sigma} - 1}{\sigma} \quad (5)$$

An improved theory<sup>16</sup> has recently extended this expression to

$$g_{\parallel} = \frac{\tau_{\delta}}{\tau^*} = \frac{e^{\sigma} - 1}{\sigma} \left( \frac{2}{1 + 1/\sigma} \sqrt{\frac{\sigma}{\pi}} + 2^{-\sigma} \right)^{-1} \quad (6)$$

This expression may be used to derive the nematic potential from the experimentally determined retardation factor.

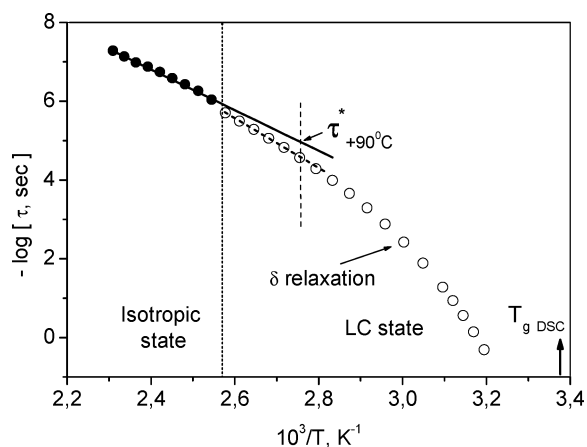
In the mean-field theory of the nematic state Meier and Saupe have calculated order parameter  $S_N$  using a simplified form of

the orientational distribution function,  $f(\Theta)$ , which is related to  $\sigma$ . Recently Kalmikov and Coffey have derived the relation between  $S_N$  and  $\sigma$  as follows:<sup>17</sup>

$$\sigma \approx \frac{3S(5 - \pi S)}{2(1 - S^2)} \quad (7)$$

Combining the experimental  $\sigma$  values as deduced from eq 5 with eq 7 it is possible to calculate the nematic order parameter  $S_N$ . Recently this approach has been successfully applied for  $S_N$  calculation for several classes of low molecular weight nematogenes.<sup>18</sup> The  $S_N$  values determined from dielectric data and other relevant methods (NMR, infrared absorption and optical birefringence) are found to agree well.

We have calculated  $S_N$  at +90 °C for all polymers studied in their unaligned and aligned states using the route described



**Figure 7.** Activation diagram for the  $\delta$  relaxation in LC ( $\circ$ ) and isotropic ( $\bullet$ ) phase for LC homopolymer. The solid line is the fit of eq 4 to the data in isotropic phase. The arrow indicates  $T_g$  determined by DSC and vertical dotted line defines  $T_{NI}$  for LC block, respectively. The errors are smaller than the size of the symbols.

above. Figure 6c shows the dependence of  $S_N$  on the alignment field  $E$  for the LC homopolymer. Only a weak variation of  $S_N$  with increasing  $E$  is observed. That experimental finding implies that an aligning field does practically not affect the mesogen arrangement inside a nematic domain. However, the whole domain may be effectively oriented by the external field. The parameter  $S_D$  should immediately reflect such an alignment. Let us now turn to the  $S_D$  evaluation from dielectric data.

**Domain Order Parameter  $S_D$ .** According to the theory of Attard four relaxation modes contribute to the overall dielectric loss spectrum for a partially aligned sample:<sup>8</sup>

$$A_{00} = (\mu_l^2/9)(1 + 2S_D)(1 + 2S_N) \quad (8)$$

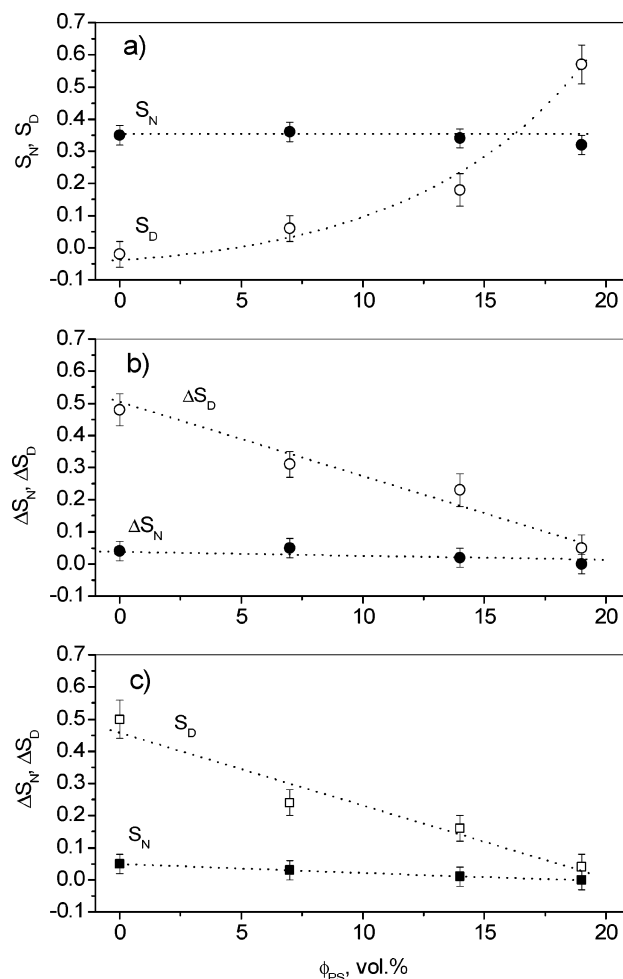
$$A_{10} = (\mu_t^2/9)(1 + 2S_D)(1 - S_N) \quad (9)$$

$$A_{01} = (2\mu_l^2/9)(1 - S_D)(1 - S_N) \quad (10)$$

$$A_{11} = (2\mu_t^2/9)(1 - S_D)(1 + S_N/2) \quad (11)$$

the  $A_{ij}$  values correspond to the relaxation strengths of mode  $ij$ .  $\mu_l$  and  $\mu_t$  are the longitudinal and transverse components of the molecular dipole moment, respectively. The application of Attard's equations to the dielectric data analysis is described in detail in refs 8 and 9 and in Moscicki's review.<sup>19</sup> Taking into account that  $\mu_l \gg \mu_t$  for cyanobiphenyl moiety<sup>20</sup> we can expect only two major absorption bands in the dielectric spectra— $A_{00}$  and  $A_{01}$ —which are indeed observed as  $\delta$  and  $\alpha$  modes, respectively.

There is a broad discussion in the literature concerning the nature of the  $\alpha$ -process in LC side chain polymers. The number of contributing modes as well as their molecular origin are questioned. Experimentally the  $\alpha$  process is usually found to be broad in frequency. There have been attempts to fit the  $\alpha$  process to a superposition of two<sup>15</sup> or even three<sup>14</sup> modes. These results are not in contradiction to our consideration because in these studies the mesogen fragment of the compounds investigated in general possesses a prominent transverse component of dipolar moment. It has also been supposed that the segmental mode of LC block (dynamic glass transition) may contribute to the dielectric loss in the considered frequency window.<sup>13–15</sup> In the copolymers under study the main chain of LC block does not contain any polar groups. Moreover, the motion of the main chain and the polar mesogen fragment is decoupled due to its



**Figure 8.** Order parameters  $S_N$  and  $S_D$  for unaligned (a),  $\Delta S_N$  and  $\Delta S_D$  for mechanically (b) or electrically with  $E = 9.6$  kV/cm (c) aligned copolymers vs PS volume fraction. The thickness of the samples is 100  $\mu\text{m}$ . All values have been calculated at +90  $^\circ\text{C}$ . The dotted lines are guide lines for the eye.

long spacer. The polar COO group in the spacer gives rise to its own local motion ( $\gamma$ -relaxation).<sup>6</sup> Therefore, the LC block segmental mode itself cannot strongly contribute to the overall dielectric polarization.

Thus, neglecting the contribution from the transverse component of cyanobiphenyl mesogen fragment for system tested in the present work, we can calculate  $S_D$  from eqs 8 and 10. The quantities  $S_N$ ,  $A_{00} = \Delta\epsilon_\delta$  and  $A_{01} = \Delta\epsilon_\alpha$  are determined from the experimental data as described. Figure 6c displays the variation of  $S_D$  vs alignment field  $E$  for the LC homopolymer at +90  $^\circ\text{C}$ . As expected the unaligned sample results in  $S_D = 0$  and thus a random orientation of nematic domains. This also justifies the assumptions made above. The whole  $S_D(E)$  dependence fits well to the three stage mechanism of order established for increasing  $E$  (see above). The maximal value for  $S_D = 0.55$  was reached at  $E \sim 18$  kV/cm. Because of electrical breakdown we cannot further increase strength of alignment field.

**Nematic and Domain Order Parameters for LC/I Block Copolymers.** We have employed the same approach to determine the order parameters  $S_N$  and  $S_D$  for three LC/I block copolymers with variation of the polystyrene volume fraction: PSLC 7/93, PSLC 14/86, and PSLC 19/81. Prior to discussing the effect of an alignment field we now have to consider the unaligned samples. Figure 8a shows  $S_N$  and  $S_D$  obtained at +90  $^\circ\text{C}$  for the unaligned copolymers. The  $S_N$  is invariant on going

from one sample to another. This means that the embedded PS hexagonal lattice does not affect the orientational order inside the nematic domain. At the same time  $S_D$  grows with increasing PS volume fraction. This observation suggests a spontaneous H-alignment of nematic domains developing in the block copolymers. We note that the unaligned PSLC 19/81 and the aligned ( $E = 18$  kV/cm) LC homopolymer have practically the same  $S_N \sim 0.35$  (see Figure 6c).

The efficiency of an alignment field on the block copolymers can be expressed by two parameters  $\Delta S_N$  and  $\Delta S_D$  defined as the difference between corresponding values for aligned and unaligned samples. Parts a and b of Figure 8 display  $\Delta S_N$  and  $\Delta S_D$  for copolymers investigated aligned by mechanical (shear) and electrical ( $E = 9.6$  kV/cm) fields, respectively. Apparently the preparation of aligned samples by both methods results in the H-alignment with comparable  $\Delta S_D$  values. This shows that mechanical and electrical alignment fields with strength of  $E = 9.6$  kV/cm provided approximately the same degree of nematic domain alignment. The LC homopolymer can be aligned easily by mechanical as well as electrical fields. The corresponding  $\Delta S_D$  parameters have nearly the same values of about 0.5. However, the block copolymer PSLC 19/81 shows only a small range of additional alignment by an external field using the same procedures ( $\Delta S_D \sim 0.05$ ). The degree of spontaneous H-alignment for PSLC 19/81 is rather high (see Figure 8a) and the applied external field therefore has only a weak effect. Parts b and c of Figure 8 demonstrate that the efficiency of the aligning field decreases with the degree of spontaneous orientation.

The  $\Delta S_N$  parameter on the other hand only displays a weak dependence on the aligning field. For all samples studied it has a value in the range 0–0.05.

All parameters discussed above were obtained on samples with a thickness of 100  $\mu\text{m}$ . To check for a possible influence of sample thickness on developing orientation we have compared the order parameters for thicknesses 27, 50, 100, and 300  $\mu\text{m}$ . We find that the experimentally determined order parameters do not depend on thickness for unaligned as well as for aligned polymers. This allows us to conclude that sample thickness does not influence the parameters studied.

**3.3. Influence of the Hexagonal Lattice on the Nematic LC Mesophase.** The results presented so far have been used to determine properties describing the state of order in the LC homopolymer and the LC matrix of the block copolymers. The morphology of the three LCPS copolymers investigated in the present study is characterized as a continuous LC matrix with embedded cylindrical PS domains. These domains are ordered on a hexagonal lattice.

For the block copolymers the intermesogen distance  $d_N$  was found to be 0.43 nm and was only weakly dependent on PS volume content.<sup>3</sup> The  $T_{NI}$  for the block copolymers was a few degrees higher than in related LC homopolymer. This may be an indication of a weak stabilization of LC phase due to hexagonal lattice embedded. A similar but stronger effect was observed for a smectic lamellar block copolymer microstructure.<sup>21,22</sup> On the basis of our DSC results one can conclude that the thermotropic behavior of the nematic phase is only slightly influenced by hexagonal PS lattice.

In addition to that we find that the order parameter  $S_N$  does neither depend on the presence of the hexagonal lattice nor on the alignment. Orientational order inside nematic domains is not influenced by the polystyrene domains. In view of the observation that the  $S_N$  parameters do not depend on the supporting hexagonal lattice one can suppose that the LC

homopolymer and LC/I copolymers are built up essentially from the same nematic domains. Therefore, their thermotropic behaviors are also identical.

It was now shown above that the PS hexagonal lattice in the diblock copolymer induces a spontaneous alignment of the nematic domains. The extent of the spontaneous alignment varies strongly with the PS volume fraction (see Figure 8a). The unaligned PSLC 19/81 has a nematic order parameter of  $S_D = 0.61$  reflecting a homeotropic orientation of nematic domains. For comparison, the LC homopolymer has  $S_D$  equal to  $-0.02$  and  $+0.55$  for unaligned and maximally aligned samples, respectively. The high degree of spontaneous H-alignment in PSLC 19/81 is the reason we were able to induce only a weak additional orientation by electrical or mechanical fields applied (see Figure 8b,c). The parameter  $\Delta S_D$  for this polymer is only  $\sim 0.05$  for mechanically and electrically aligned samples. The copolymers containing lower fraction of PS block (PSLC 7/93 and PSLC 14/86) can be additionally oriented by external field. The corresponding  $\Delta S_D$  parameters have values of  $\sim 0.3$  and  $\sim 0.2$ , respectively.

#### 4. Conclusions

The present dielectric study of unaligned and aligned samples composed of hybrid LC/I block copolymers exhibiting cylindrical morphology has demonstrated that an embedded hexagonal lattice of PS domains has no strong impact on structure within nematic domains. As a result the cooperative reorientational dynamics of mesogen fragments<sup>6</sup> as well as the nematic order parameter  $S_N$ , which reflects mesogen orientation inside nematic domain, do not significantly differ between the LC homopolymer and the LC/I block copolymers. This fact can also explain the similarities in their thermotropic behavior. However, the PS hexagonal lattice induces a spontaneous H-alignment of nematic domains with respect to external surfaces. The extent of the spontaneous alignment strongly depends on the PS volume fraction. We find that the unaligned copolymer with the highest PS content (PSLC 19/81) has a domain order parameter  $S_D$  comparable to a fully oriented LC homopolymer. Our attempts to induce an additional order in this copolymer were unsuccessful. At the same conditions the copolymers containing lower fraction of PS block (PSLC 7/93 and PSLC 14/86) can be effectively oriented by mechanical and electrical fields.

In analogy to the triblock copolymer (I/LC/I) composed from the same isotropic and LC blocks, for which the orientation of cylinders of the hexagonal lattice was found to be following the nematic director,<sup>23</sup> we can also expect the parallel alignment of the PS cylinders and nematic director in diblock copolymers studied. Such an alignment causes the smallest distortion of the nematic field by the embedded hexagonal lattice and vice versa. Experiments that determine the orientation of the polystyrene domains in the block copolymers are currently in progress.

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