How to align a nematic glassy phase – different conditions – different results

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Abstract

Influence of different factors on nematic alignment and relaxation dynamics in supercooled mixture of liquid crystals E7 was investigated by means of dielectric and rheo-dielectric spectroscopy. Results show that elevated pressure or application of strong oscillatory shear aligned the nematic director parallel to the electrodes. On the other hand, if after the shear treatment a static electric field is applied an alignment of the nematic director perpendicular to the electrodes is even better than in the sample quenched and aligned by bias field without the shear treatment.

Introduction

Liquid crystals (LC) belong to the category of materials in between liquid and solid states. In thermotropic liquid crystals the nematic phase is a state with the lowest order. In this state molecules have no long range positional order but their long axes are preferentially aligned with respect to a common unit vector called the nematic director. Although ordering in the nematic phase occurs spontaneously below clearing temperature, T_{I-N}, the degree of order can be changed by different factors. Most common way to increase the order is application of strong electric or magnetic field, however, that method can be affected by some drawbacks, such as turbulent flows driven by strong dc electric currents. Thus, for fundamental and applicational purposes it is important to find alternative ways to change and/or increase order of the mesophase.

One of important and well studied LC materials is blend of four nematic cyano substituted polyphenyls called E7[1]. This mixture is widely used in polymer dispersed liquid crystal materials working in normal conditions because it offers a wide range of operating temperatures for application in displays, privacy windows, optical shutters etc.[2]. E7 exhibits a single clearing temperature, TI-N=334K and no other calorimetric transitions down to the glass transition at Tg=211K. The switching behavior of this system, able to orient the director order parameter under external electric field, has been studied by dielectric spectroscopy and other techniques in pure state [1], confined in a colloidal network [3], as well as in polymer composites [4]. Thanks to the natural anisotropy in motion of individual molecules with respect to the director, these studies [1, 3-4] could analyze the dielectric permittivity of E7 in perfect alignment conditions (perpendicular or parallel to the electrodes), obtained in electro-optical cell with orientation induced by treated surface of electrodes. Considering Z the axis perpendicular to the plane of electrodes and an uniform electric field throughout gap filled by the sample, the effective permittivity measured for E7 in different alignment conditions was shown to be the sum of two contributions:

$$\langle \varepsilon_Z \rangle = \varepsilon_{||}\,(1 - S_d)/3 + \varepsilon_{\perp} 2\,(1 + S_d)/3 \qquad (1)$$

where $S_d=(3<\cos^2\theta>-1)/2$ is called order parameter, θ is the average angle between Z and the nematic director. $\varepsilon_{//}$ and $\varepsilon_{\perp}$ are the permittivity of aligned mesophase when the director is parallel (S_d=1) and perpendicular (S_d=-0.5) to the electric field.

The present paper report, beyond the usual alignment method based on electric field, two alternative methods to align the mesophase parallel to the electrode, namely to squeeze the sample at very high pressure or to apply very strong shear flow. For the first time, an almost perfect alignment of this kind is obtained also for very large electrode gaps. Moreover, the effect of shear alignment is explored over a broad large temperature range, from above nematic transition to the glassy state, whereas in literature this effect has been explored in nematic liquid crystals only within a limited interval. Finally, thanks to the analysis of the relaxation map, we provided an estimate about the number of correlated molecules participating to the structural α-process.

Material and Methods

The nematic liquid crystal E7 was purchased from Merk (Darmstadt, Germany) and used without further purification. The sample is a mixture of four components. It contains 51 wt. % of 4-cyano-4'-pentyl-1,1'-biphenyl (5CB), 25 wt. % of 4-n-heptyl-4'-cyanobiphenyl (7CB), 16 wt. % of 4,4'-n-octyloxycyanobiphenyl (8OCB) and 8 wt. % of 4'-n-pentyl-4-cyanoterphenyl (5CT).

Dielectric spectra of E7 in the frequency range from 10^{-2} Hz up to 10^{7} Hz have been recorded for samples subjected to oscillatory shear flow at temperatures ranging from 353 K to 225 K, by means of the rheo-dielectric technique. The plate-plate geometry was used, with the two shearing plates serving as electrodes of a capacitor. Solartron 1260 was used as dielectric response analyzer together with Novocontrol BDC as broadband dielectric converter. The peak-peak voltage oscillator was reduced to 0.1 V in order to produce negligible alignment during the dielectric measurements. The ARES Rheometrics was employed as torsional mechanical spectrometer. The quiescent state was obtained by slowly cooling the sample from above the clearing point up to the target temperature. Shear oscillatory deformation was applied under conditions of controlled deformation amplitude, choosing different shear rates and amplitudes, including the range of the non-linear viscoelastic response. Moreover, spectra under a d.c. bias voltage of 10 V were acquired. In order to obtain a reference measurement for the state of complete alignment (perpendicular or parallel to the electrodes) of the nematic director, dielectric measurements of E7 in cells with treated surfaces and under strong magnetic field were also performed. The high pressure measurements were performed using parallel plate capacitor placed in a Teflon bellows mounted in the high-pressure chamber. This setup allows the measurements in temperature range from -20 to 100°C under pressure up to 1.8GPa. Pressure was measured by a Nova Swiss tensometric meter, which had an accuracy of 10 MPa. Temperature was controlled to within 0.5 K by means of liquid flow from a thermostatic bath.

Results and discussion

Broadband dielectric spectroscopy operating in frequency range from GHz down to mHz was applied for studying properties of glass-forming E7[5]. In the isotropic phase this material exhibits single non-Debye relaxation loss peak. As shown in the inset of Fig.1, belowT_{I-N} =334K three new relaxation processes are observed. The dominating Debye-like process with the highest amplitude is called primary (also λ or δ) relaxation and has origin in rotation of the molecules (5CB, 7CB, 8OCB) around their molecular short axes. It has to be noted, that below 240K amplitude of the peak decreases, what could be interpreted as a transition to the new phase. However, neither differential calorimetry studies or structural measurements provide evidence for any transition in the vicinity of this temperature. As there is no explanation of this phenomenon yet [5,6] we will try to shed new light on it later. Also a slower process, visible on low frequency wing of the primary process and called S-relaxation is still under debate because its origin is unknown [6]. Third, fastest process is called tumbling mode. Bras et al. reported that the specific heat spectroscopy gives one relaxation process which have exactly the same temperature dependence as the tumbling mode. On the basis of this its relation with glass transition has been reported [1].

Also temperature dependences of relaxation times τ are different in isotropic and nematic phases, respectively. As depicted in Fig.1, in the isotropic phase single relaxation process is quite well reproduced by the Arrhenius law whereas in the nematic phase temperature behavior of τ has clearly non-Arrhenius character for all three processes, described by the Vogel-Fulcher-Tamman relation[7]. Although the temperature dependences for all processes in nematic phase are different, however their timescales seem to coincide close to the T_g.

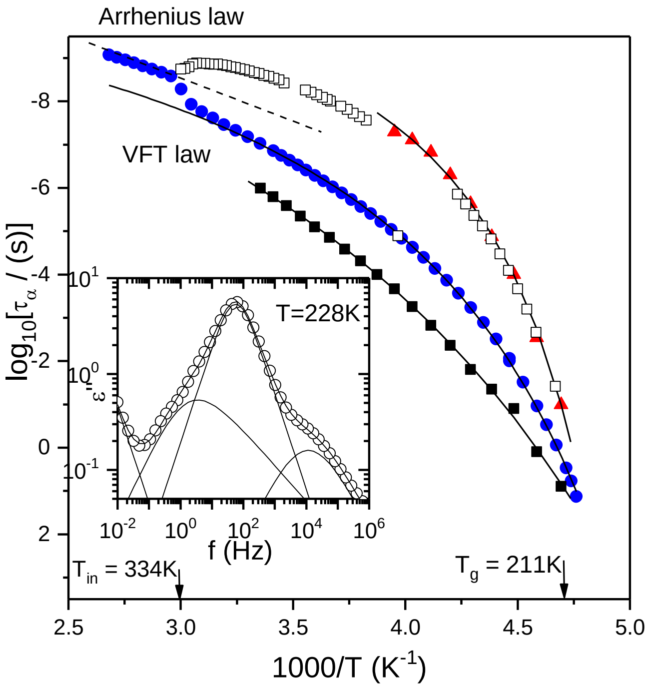

Figure 1 (Color online) Activation plot for the data from measurements at ambient pressure. Relaxation times for E7 system are represented by black squares are for S-process, blue circles for δ-process, red triangles are for the tumbling mode. The open squares are the data from[1]. The solid lines are VFT fits. Inset: spectrum taken at T=228K with Havriliak-Negami fits for the three visible processes separately. The main relaxation process is described by Debye function (i.e. α=γ=1).

The amplitudes of different processes are governed by macroscopic orientation of the sample. Changes of the amplitudes reflect the change in the degree of either parallel or perpendicular alignment of the sample in the nematic phase which can be controlled by different factors. Mierzwa et al.[5] showed that after application of bias field of 300V/mm to the E7 sample at ambient pressure the intensity of the tumbling mode becomes weaker whereas the intensity of the primary relaxation measured close to T_g is higher in bias oriented sample. It has to be emphasized that this difference becomes more pronounced below 230K. In other words, increased amplitude of the primary process and decreased of the α-relaxation are the manifestations of the increased nematic alignment perpendicular to the electrodes whereas opposite behavior indicates on the parallel alignment. It has to be emphasized that higher order of the mesophase in the E7 under bias voltage doesn't change peak position i.e. relaxation dynamics remains invariant[5].

Different picture comes into view after application of high pressure for the E7 samples. High pressure setup used in our investigations was described in ref.[8]. Fig.2a presents the comparison of high pressure loss spectra with and without bias voltage of 10V, and spectra measured at ambient pressure for self oriented sample for two different λ-peak positions, close and far from T_g, respectively. It is clear that intensity of the λ-process markedly decrease at elevated pressure even after application of the bias voltage. Moreover, without bias field amplitude of the primary and α-relaxation of the pressurized E7 decreases and increases, respectively, achieving similar levels. Possible explanation of this pronounced difference between the degrees of order of nematic phase under low and high pressure conditions is that during pressurization molecules are aligned parallel to the electrodes. As it will be evident later, such orientation could be related to the flow, parallel to the electrodes, coupled to the density changes in the cell. In consequence also static dielectric permittivity in mesophase is lower than in isotropic phase of pressurized sample what is typical for alignment perpendicular to measuring field.

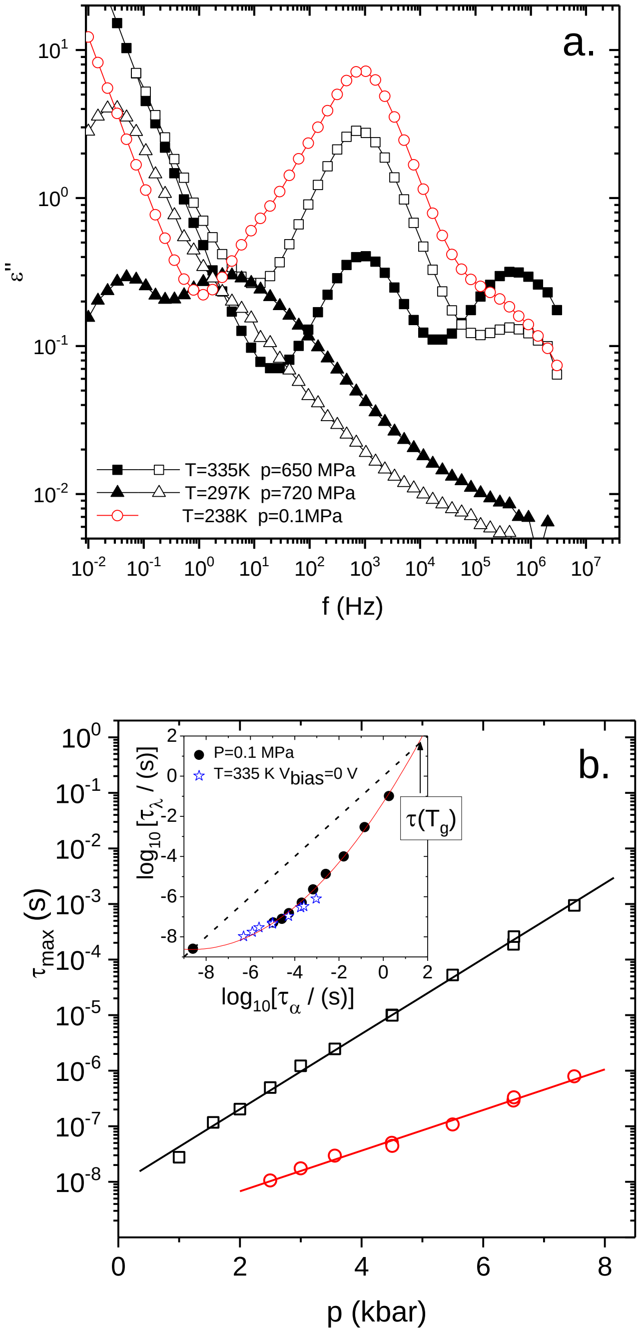

Figure 2 (Color online) (a) Selected spectra measured at p=650MPa during isothermal run (T=335K) and at T=297K during isobaric run (p=720MPa). Empty squares and triangles represent spectra measured under bias field U=10V (E=200V/mm). Empty (red) circles represent spectra measured at ambient pressure without bias voltage (b) Pressure dependent activation plot of the data measured without bias voltage at T=335K. In the inset the $\log(\tau_\lambda)$ vs. $\log(\tau_\alpha)$ dependency is shown.

The pressure evolution of relaxation times measured without bias voltage is presented in Fig.2b. Analyzing pressure dependence of the primary and α-relaxations we found almost linear behavior well portrayed by a simple volume activation law:

$$\tau = \tau_0 \exp\left(\frac{P\Delta V}{RT}\right) \qquad (2)$$

where R is a gas constant, τ_0 is the value of τ at atmospheric pressure and ΔV denotes activation volume determined as 43.48 cm^3/mol and 23.49 cm^3/mol for λ- and α-processes, respectively. Contrary to the results from ambient pressure measurements that keep the system in amorphous state, during isothermal densification at T=335K the E7 crystallizes at p=750MPa. However, crystallization can be avoided by fast isobaric cooling to the glassy state. A plot of $\log(\tau_\lambda)$ vs. $\log(\tau_\alpha)$ obtained from the data at isothermal and isobaric condition gives a second order polynomial dependence with the two timescales separate at the T_{I-N} and approaching each other around T=210K (see inset Fig.2.b). It is worth noticing that the differences between the pressure dependences of relaxation times τ determined from data obtained with and without DC-bias were not significant.

Third way to change alignment of the nematic phase of the E7 is application of mechanical stress on the sample and was studied by rheo-dielectric method described in [6]. Dielectric spectra of the E7 in the frequency range from 10^{-2}Hz up to 10^7Hz have been recorded for sample subjected to oscillatory shear flow at temperatures ranging from 353K to 225K. The quiescent state was obtained by slow cooling the sample from above the clearing point up to the target temperature. Shear oscillatory deformation was applied under conditions of controlled deformation amplitude, choosing different shear rates and amplitudes, including the range of the non-linear viscoelastic response. For large amplitude oscillatory shear, as in our case, a model [9] has been proposed: effective shear strain rate should be equal to the product of the strain amplitude γ_0 and angular frequency ω. Moreover, spectra under a bias voltage of 10V were acquired with and without oscillatory shear. In order to obtain a reference measurement for the state of complete alignment (perpendicular or parallel to the electrodes) of the nematic director, dielectric measurements of E7 in cells with treated surfaces and under strong magnetic field were also performed [6]. The overall effect is shown in Fig.3, where loss spectra are shown for different alignment conditions and shear amplitudes at the temperature of *T*=252K. Different shear conditions lead to different degrees of orientation of the mesophase: the higher the shear frequency ω, or shear amplitude γ_0, the higher was the intensity of the α-process and the lower of the slower λ-processes. The effect of the shear flow on the dielectric response can be explained by taking into account the director distribution in the nematic texture (the mesophase is mainly aligned parallel to the electrodes under shear) and the anisotropy in motion of the individual molecules with respect to the director. At high shear rate a limit value is attained, coinciding to the case of order parameter S_d=-0.5, i.e. perfect parallel alignment to electrode plane (see eq.1). The main effect is to vary the relative intensity of the different components of the loss spectra, whereas the relaxation rates are negligibly affected. In other words, the effect of shear is to change the relative distribution of orientation and not to affect dynamics.

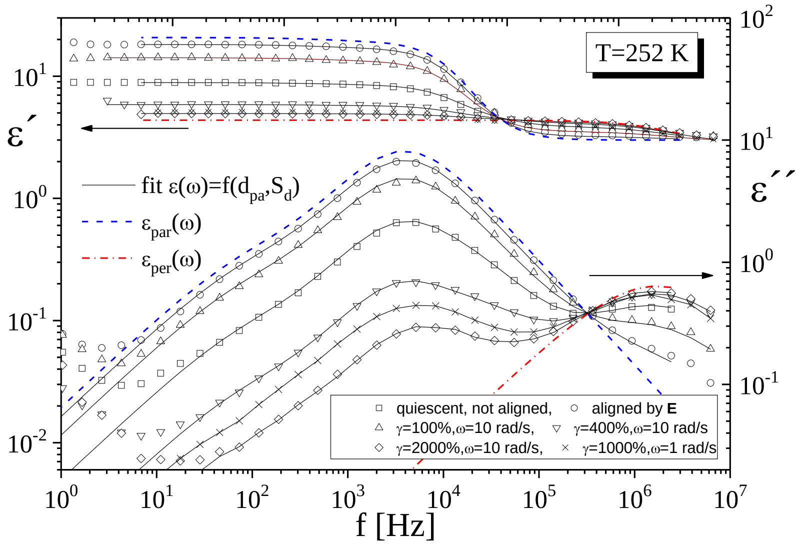

Figure 3 (Color online) Bilogarithmic plot of real (left axis) and imaginary (right axis) permittivity vs. frequency measured at P=0.1 MPa and T=252 K under different oscillatory shear conditions and also with applied electric bias. Lines are fit according to the eq.1 that combines the two limiting permittivities (parallel and perpendicular to the local nematic director) with a parameter that is related to the order parameter of the system (Sd=1 and -0.5, for bue and red line respectively).

Fig.4 shows the overall effect of different alignment procedures on the value of static permittivity, εs, at various temperatures or pressures. The depicted data correspond to the isotropic phase, not dependent of the alignment conditions, as well as nematic phase where the permittivity tensor has two different values depending of the sample alignment.

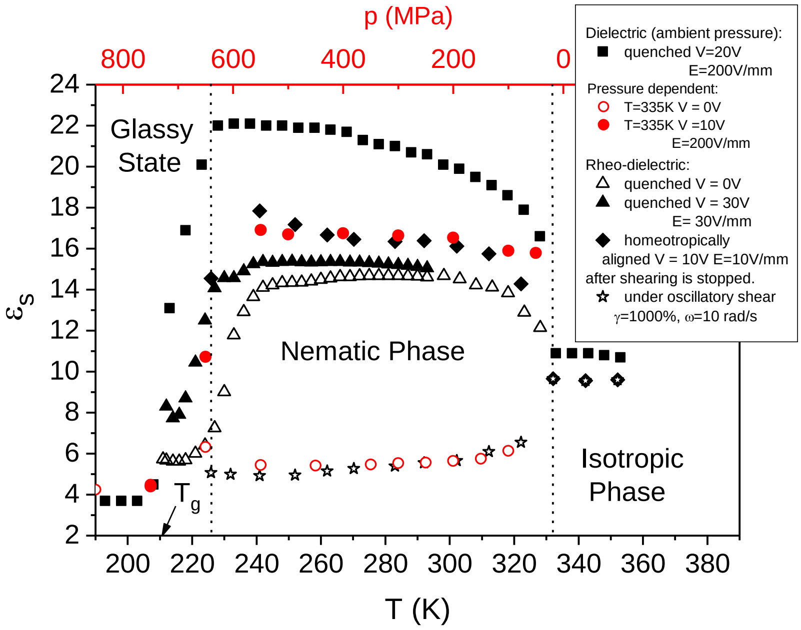

Figure 4 (color online) Comparison of the static dielectric permittivity obtained during rheo-dielectric and pressure (red) measurements without (open symbols) and with (closed symbols) bias electric field

The alignment effect of bias voltage becomes visible in the nematic phase. For the sample quenched at ambient pressure under bias field the value of ε_S is markedly higher than for the same sample self oriented. As was mentioned above, this increase of the ε_S is one of the evidences of increasing alignment of the mesophase parallel to the ordering field. Under strong oscillatory shear the nematic director is mainly parallel to the electrodes and the ε_S

attains very low values, much lower even than for sample in isotropic phase. On the other hand, if after the shear treatment a bias voltage is applied then an ordered domain with the nematic director parallel to the bias field is obtained. In that case larger value of the ε_s can be obtained than when a homeotropic alignment was induced just by cooling from the isotropic phase to the target temperature with bias field of 30V/mm. In fact, most of the defects and polydomains are destroyed under shear and then the large domains are formed and can easily be aligned by the bias field subsequently applied leading to the larger order parameter.

Presented in Fig.4 (upper axis) effect of pressurization on the nematic phase is similar to that of strong oscillatory shear: nematic director is mainly parallel to the electrodes. In consequence value of the ε_s during densification is comparable to the value under oscillatory shear. Also in that case application of aligning bias field of 200V/mm changes the position of the nematic director what is pointed out by increase of the ε_s. However, this increase of order is much lower than degree of order of the field aligned sample at ambient pressure. Actually, the highest value for static permittivity (corresponding to perpendicular alignment to the electrodes) is obtained for high bias electric field at ambient pressure, while the lowest one is obtained for high pressure or oscillatory shear stress and no bias field. The lowest limit values coincide for these two cases as if the parallel alignment to the electrode would be maximized (order parameter S_d=-0.5).

Another interesting result to note that the value of ε_s, or the dielectric strength of the λ-relaxation, for samples oriented perpendicular to the electrodes, decreases markedly below some temperature (located at ~225-230K). This phenomenon can be explained taking into account the dynamics. First of all, as shown in the inset of Fig.2b or in Fig.1, in the region below 250K τ_λ and τ_α approach each others. In other words, close to T_g, the temperature dependence of the (α-) tumbling mode is much steeper than that of the λ-relaxation and eventually the two timescales merge around T=208.5K, where $\log_{10}(\tau/s)=1.52$. It is clear that the two kinds of motion involved in α- and λ-processes are characterized (at least in the high temperature region) by two different activation volumes, smaller and larger, respectively, associated probably by the different associated molecular size. A similar phenomenon was observed for the α- relaxation and the chain dynamics of linear polymers. A recent paper [10] tried to explain the increasing steepness of α-relaxation time of a linear polymer in terms of increasing number of dynamically correlated chain segments. In particular the merging was interpreted as corresponding to conditions under which the length scale of the two processes become equivalent. The number of "correlated units" for α-relaxation can be estimated by the function introduced by Berthier at al.[11]:

$$N_c = \frac{k_B}{\Delta c_P}\left(\frac{\beta_K}{e}\right)^2\left(\frac{d\ln\tau_\alpha}{d\ln T}\right)^2 \qquad (3)$$

where e is Euler's number, β_K is the Kohlrausch exponent of the α-process, Δc_P is the isobaric heat capacity change at T_g and k_B is the Boltzmann constant. A calculation for N_c related to α-relaxation of E7 shows that N_c increases from almost 1 at the temperature of isotropic-nematic transition (T=335K) up to about 200 in the vicinity of the glass transition.

The molecular volume associated to λ-process, i.e. to the rotation of cyanobiphenyls around the short axis, can be estimated to be $V_\lambda = L^3$ where L is the average length of the cyanobiphenyl 5CB or 7CB (around 1.26-1.3 nm[12]) or of the longer 8OCB and 5CT (around 1.6-1.7 nm). Averaging in composition number of the nematic compounds, the length for the main axis can be estimated around 1.37 nm. The ratio between the volume correlated to this motion and that involved with α-process, i.e., with the rotation around the long axis $V_\alpha = 4/3\pi r_w^3$ (r_w is the van der Waals radius of benzene, r_w =1.77Å) can be an estimate of the number of correlated molecules at the merging point $N_c \sim V_\lambda/V_\alpha = 3/(4\pi)(L/r_w)^3 \approx 110$.

Such comparison could be questioned to some extent because of the fact that there is still no strict relationship between the correlation length and correlation volumes. However, the results obtained herein are rather consistent. In any case it is clear that below T=230K the size of fluctuations related to α-relaxation becomes comparable or even bigger than the size of cyanobiphenyl long axis, hindering so a good alignment of the mesophase, at least in a reasonable time. This result can illustrate the possible problems that can prevent the formation of an arrested (or "glassy") ordered nematic phase: the alignment of the mesophase is made more and more difficult by existence of a growing dynamic correlation volume that become bigger and bigger on approaching T_g.

Conclusion

As a conclusion, presented results of dielectric and rheo-dielectric investigations of the E7 mixture of nematic liquid crystalline materials demonstrate influence of different conditions on nematic order of the mesophase. At ambient pressure the nematic phase is self oriented perpendicularly to electrodes of the capacitor. In that case application of the bias field only increases ordering of the mesophase. However, it was possible to attain better ordering if after the shear treatment a static electric field perpendicular to the electrodes was applied. Another situation takes place in the case of measurements under high pressure or strong oscillatory shear: the nematic director is parallel to the electrodes. It means that densification or oscillatory shear can be crucial for changing an ordering of the mesophase. These results can be useful in further development of theoretical models of the nematic phase and in new technological applications of ordering the mesophase not only for the E7 but for all liquid crystalline materials.

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References

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[1] A. R. Bras, M. Dionisio, H. Huth, Ch. Schick and A. Schönhals, PRE **75**, 061708 (2007) and references therein

[2] L. Bedjaoui, N. Gogibus, B. Ewen, T. Pakula, X. Coqueret, M. Benmouna and U. Maschke, Polymer **45** (2004) 6555-6560

[3] M.C.W.Van Boxtel, M.Wubbenhorst, J. Van Turnhout, C.W.M.Bastiaansen, D.J.Broer, Liquid Crystals, **30**, 2 , 235–249 (2003)

[4] A. R. E. Bras, O. Garcia, M. T. Viciosa, S. Martins, R. Sastre, C. J. Dias, J. L. Figueirinhas and M. Dionisio, Liquid Crystals, **35**, 4, 429–441(2008)

[5] M. Mierzwa, M.Paluch, S.J.Rzoska, J.Ziolo and U.Maschke p. 201 in ‘Soft Matter under Exogenic Impacts’ ed. S. J. Rzoska, V. A. Mazur, NATO Science Series 2007

[6] S. Capaccioli, D. Prevosto, A. Best, A. Hanewald and T. Pakula, J. Non-Cryst. Solids **353**, 4267 (2007)

[7] H. Vogel, J. Phys. Z. **22**, 645 (1921); G. S. Fulcher, *J. Am. Ceram. Soc*. **8**, 339 (1925); G. Tamman and W. Hesse, *Z. Anorg. Allg. Chem*. **156**, 245 (1926)

[8] M. Paluch, M. Sekula, S. Pawlus, S. J. Rzoska, J. Ziolo, and C. M. Roland, *Phys. Rev. Lett.* **90** 175702 (2003)

[9] D. Doraiswamy, AM Mujumdar, I Tsao, AN Beris, SC Danforth, AB Metzner, J. Rheol. **35**, 647 (1991)

[10] D. Fragiadakis, R. Casalini, R. B. Bogoslovov, C. G. Robertson, and C. M. Roland, Macromolecules, **44**, 1149–1155 (2011)

[11] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L’Hote, F. Ladieu, M. Pierno, Science 2005, **310**, 1797

[12] O. Urakawa, E. Ohta, H. Hori, K. Adachi, Journal of Polymer Science: Part B: Polymer Physics, Vol. **44**, 967–974 (2006)