

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Orientalional properties and dynamics of nematic liquid crystals mixed with dendrimers for electro-optical switches

M. C. W. Van Boxtel Corresponding author^a; M. Wübbenhorst^b; J. Van Turnhout^b; C. W. M. Bastiaansen^{ac}; D. J. Broer^{ad}

^a Department of Polymer Technology, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands ^b Department of Polymer Materials and Engineering, Delft University of Technology, 2628 BL Delft, The Netherlands ^c Dutch Polymer Institute, 5600 AX Eindhoven, The Netherlands ^d Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands

Online publication date: 21 May 2010

To cite this Article Van Boxtel Corresponding author, M. C. W. , Wübbenhorst, M. , Van Turnhout, J. , Bastiaansen, C. W. M. and Broer, D. J.(2004) 'Orientalional properties and dynamics of nematic liquid crystals mixed with dendrimers for electro-optical switches', *Liquid Crystals*, 31: 9, 1207 – 1218

To link to this Article: DOI: 10.1080/02678290410001724737

URL: <http://dx.doi.org/10.1080/02678290410001724737>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Orientational properties and dynamics of nematic liquid crystals mixed with dendrimers for electro-optical switches

M. C. W. VAN BOXTEL^{†*}, M. WÜBBENHORST[‡], J. VAN TURNHOUT[‡],
C. W. M. BASTIAANSEN^{†§} and D. J. BROER^{†¶}

[†]Department of Polymer Technology, Eindhoven University of Technology,
PO Box 513, 5600 MB Eindhoven, The Netherlands

[‡]Department of Polymer Materials and Engineering, Delft University of
Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

[§]Dutch Polymer Institute, PO Box 902, 5600 AX Eindhoven, The Netherlands

[¶]Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven,
The Netherlands

(Received 30 October 2003; in final form 25 March 2004; accepted 7 April 2004)

Novel two-phase materials based on nematic liquid crystals (LC E7) filled with poly(propylene imine) dendrimers of 2–3 nm diameter were investigated for application in light-scattering, electro-optical switches. Polarizing optical microscopy, differential scanning calorimetry and rheological experiments all indicate the presence of a pronounced polydomain structure within these LC mixtures. The molecular ordering and dynamics of the dendrimer-filled nematics were studied in more detail by dielectric relaxation spectroscopy. The director order parameter S_d was derived from the strength of the two principal molecular relaxations, α and δ , in the presence and absence of an electric field. In addition, a three-phase model was applied for determining the size of the different LC populations in the mixture. A substantial decrease in the fraction of randomly oriented LC was found upon application of a d.c. field. Over a broad temperature range the LC molecular dynamics were assessed from the variation in the strength of the dielectric relaxations as a function of the d.c. bias. A fast response was found at room temperature. Electro-optical switching experiments showed that the dendrimer-filled LCs can be switched rapidly from a light-scattering, opaque state to a more transparent state.

1. Introduction

Two-phase mixtures based on a low molar mass LC phase and a polymer or inorganic phase were recently studied for application in light-scattering display devices. Also various light shutter technologies have been proposed based on two-phase mixtures of LC and polymer in which the latter forms the (co-)continuous phase, such as polymer dispersed liquid crystals (PDLCs) [1, 2] or anisotropic chemical gels [3, 4]. Usually, these blends are formed by photopolymerization of reactive monomers that are homogeneously mixed with an LC [5, 6]. Another route in the development of light shutters comprises thermo-reversible, anisotropic physical gels, which are formed via the addition of small amounts of low molecular mass, organic compounds to LC solvents [7, 8]. These functionalized organic additives

are able to associate into 3D finely dispersed, supramolecular structures, primarily through intermolecular hydrogen bonding [9, 10].

In an alternative approach, light-scattering electro-optical switches have been developed that are based on spherical small diameter (<20 nm) silica particles embedded in an LC continuum [11–13]. Recently, LC colloidal dispersions were introduced based on an LC matrix filled with (sub-)micron sized copolymer particles, which associate into a three-dimensional network [14–17]. In the present study the size range of the (spherical-like) dispersed phase is scaled down to 2–3 nm by the use of *dendritic* molecules.

Dendrimers are highly branched macromolecules with a regularly shaped, three-dimensional architecture. Via an appropriate design of the external and internal chemical structures, these single nanometer-sized dendritic molecules can be provided with a well defined number of specific functional groups at specific locations, which endow the dendrimers their versatile

*Author for correspondence; present address Akzo Nobel Car Refinishes BV, Rijksstraatweg 31, P.O. Box 3, 2170 BA, Sassenheim, The Netherlands; e-mail: marysia@wish.nl

nature. Since the introduction of these extraordinary, polyfunctional molecules, numerous appraisals have been made regarding their application as, for example, extractants [18, 19], homogeneous catalysts [20, 21], or host–guest systems [22, 23].

Dendrimers are often represented as perfectly spherically shaped, rigid molecules. In spite of this, the conformation and assembly behaviours of these molecules have been found to be highly dependent on the chemical surroundings [24, 25]. For example, amphiphilic poly(propylene imine) dendrimers functionalized with hydrophobic alkyl chains adopt a completely deformed conformational shape when brought into contact with an air–water interface [26, 27]. Due to preferential interaction of the polar interior with the polar water medium, the dendritic core resembles a floating ‘pancake’ with all the attached alkyl chains directed upwards in the air.

Although the dispersion of dendrimers in isotropic media has been a subject of many studies in the past [20, 28], the immersion of highly branched molecules in an anisotropic LC medium has rarely been studied [29, 30]. In recent reports we have introduced and tested the idea of dispersing poly(propylene imine) dendrimers in a nematic LC for designing (alternative) electro-optical switches with new combinations of relevant properties with respect to, for example, switching kinetics or hysteresis [31–33]. Here, a detailed description will be given of the phase behaviour, morphology, flow properties, molecular ordering and dynamics with respect to the LC phase, and of the electro-optical properties of dendrimer-filled LCs.

2. Experimental

2.1. Materials and sample preparation

The dendrimer-filled nematics were prepared from LC E7 ($n_e = 1.7462$, $n_o = 1.5216$) [34], a four-component liquid crystal mixture of cyanobiphenyls, and a cyanoterphenyl purchased from Merck UK (Poole, England), containing 51% 4-*n*-pentyl-4'-cyanobiphenyl (5CB), 25% 4-*n*-heptyl-4'-cyanobiphenyl (7CB), 16% 4-*n*-octyloxy-4'-cyanobiphenyl (80CB) and 8% 4-*n*-pentyl-4'-cyanoterphenyl (5CT) [35], and fifth generation poly(propylene imine) dendrimers functionalized with apolar alkyl chains. These modified dendrimers, here denoted as DAB-*dendr*-(NHCO-C₁₅H₃₁)₆₄ (DAB, refers to the diaminobutane core), were synthesized via reaction of fifth generation amine-terminated poly(propylene imine) dendrimers (DAB-*dendr*-(NH₂)₆₄) with palmitoyl chloride.†

†The modified dendrimers were kindly supplied by Bas de Waal and Maurice Baars, of the Macromolecular and Organic Chemistry group (SMO) headed by Prof. Dr E.W. Meijer, Eindhoven University of Technology.

A pre-set amount of the dendrimer was homogeneously dispersed in a pre-set amount of the LC E7 together with a small amount of chloroform via ultrasonic mixing, followed by evaporation of the chloroform. Electro-optical cells with (anti-)parallel aligning boundary conditions were filled with the dendrimer-modified LCs (preheated to the isotropic state) by capillary action at $\sim 120^\circ\text{C}$. After filling, the cells were cooled below the clearing point of the LC E7.

2.2. Differential scanning calorimetry (DSC)

The phase transitions of the various dendrimer/LC mixtures were studied with DSC (Perkin Elmer Pyris 1). The samples were measured over a temperature range of -20 to 140°C using heating and cooling rates of 5°C min^{-1} . The reported transition temperatures are the peak values of the corresponding exotherms and endotherms.

2.3. Optical microscopy

The morphology of the dendrimer-filled LCs in electro-optical cells was examined by means of a Zeiss Universal optical microscope in its transmission mode.

2.4. Rheological characterization

Stationary and dynamic rheological experiments were performed with an Ares Rheometric Scientific laboratory instrument, equipped with two circular, serrated parallel plates with diameters of 25 mm. The measuring rig including the sample was contained within an oven, in which the temperature was environmentally controlled. The material was homogenized at an elevated temperature of $\sim 140^\circ\text{C}$, placed between the two plates and subsequently cooled to 26°C . During cooling, the normal force exerted on the upper plate was kept constant by continuously readjusting the distance between the plates. Finally, a rheological analysis was performed on the approximately 0.5 mm thick films after the normal force was observed to remain constant in time. Before each measurement, the samples were heated to the isotropic phase in order to erase their deformation history.

2.5. Electro-optical characterization

The electro-optical characteristics of the electro-optical cells were recorded using a display measuring system DMS 703 obtained from Autronic Melchers (Germany) equipped with a voltage amplifier. Transmittance–voltage characteristics were determined by applying a.c. voltages of 1 kHz square waves, which were increased in steps of 0.5 V at a rate of 5 V s^{-1} . For illumination a halogen light

source of 100 W was used. The cells were held in an aluminium sample holder and positioned on the plate at a height of approximately 10 cm. A detector opening of 0.2 mm was used and the sample–detector distance was set in focus before each measurement. All measurements were referenced against air.

2.6. Dielectric relaxation spectroscopy (DRS)

The dielectric properties of the dendrimer-filled nematics were studied by means of a broadband dielectric spectrometer covering a frequency range from 10^{-2} to 10^6 Hz. This spectrometer utilizes a combination of two measurement systems with overlapping frequency ranges: (1) a frequency response analyser (Schlumberger 1260) equipped with a dielectric interface (developed by TNO) for frequencies between 10^{-2} and 10^4 Hz, and (2) a Hewlett-Packard 4284A precision LCR-meter for frequencies between 10^2 and 10^6 Hz. The sample was placed in a nitrogen cryostat (Novocontrol), whose temperature was controlled to a stability better than ± 0.05 K.

Dielectric experiments were performed on $17.7\ \mu\text{m}$ electro-optical cells with parallel rubbed alignment layers at both sides, and filled with dendrimer dispersions. For reference purposes, a $5.0\ \mu\text{m}$ electro-optical cell filled with pure E7 was used. These glass cells were inserted between gold-plated circular brass electrodes. In order to provide electrical contact between the inner conducting indium tin oxide (ITO) layers of the electro-optical cells and the (outer) sample electrodes, conductive paths around the edges were made by means of silver paint.

The linear dielectric response of the samples was probed with a low a.c. voltage, usually 0.3 V for $17.7\ \mu\text{m}$ cells, in order to prevent changes in the director order due to the probing field. When we were interested in the electric field-induced homeotropic alignment, the small a.c. voltage was superimposed on a d.c. bias of up to 40 V. All dielectric spectra were corrected for the (contact) resistance of the electrodes using an equivalent circuit model.

3. Results and discussion

3.1. Phase behaviour

The phase behaviour of dendrimer-filled LCs based on various fractions of E7 and modified poly(propylene imine) dendrimers was studied by DSC. The pure LC has a nematic to isotropic transition at 60°C , and the dendrimers a crystalline to isotropic transition at 78°C (figure 1). Figure 1 demonstrates that the nematic to isotropic transition temperature, T_{NI} , of E7 shifts to lower values with increasing fraction of dendrimer. The shifts observed are quite large, reaching up to $\sim 8^\circ\text{C}$, which indicates an

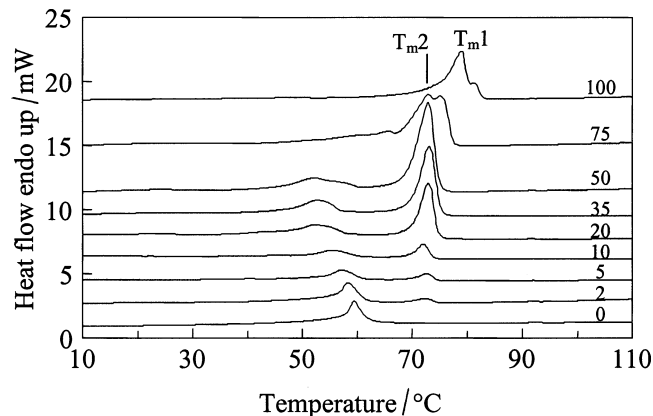


Figure 1. Second DSC heating scans for dendrimer/E7 mixtures with various amounts of dendrimer ranging from 0 (pure LC) to 100 wt% poly(propylene imine) dendrimer.

efficient distortion of the LC order by the presence of the isotropic component, the dendrimer aggregates [36, 37]. This suggests that the dendrimers are highly capable of acting as nucleating agents for the formation of a *polydomain* structure, in which the LC molecules become confined within finite LC domains with a corresponding loss of orientational order.

For the dendrimers, a strong depression in the melting point is observed upon addition of the LC. This melting point depression is indicative of a distortion of the dendrimer alkyl chain ordering by the presence of LC molecules. For a 75/25 w/w dendrimer/E7 mixture two peaks can be distinguished for the dendrimers, indicating the coexistence of a largely undistorted dendrimer phase (T_{m1}) with a perturbed dendrimer phase (T_{m2}).

Furthermore, figure 1 illustrates a significant broadening of the peaks associated with T_{NI} with increasing fraction of dendrimer. It is expected that each LC cluster with its particular domain size undergoes isotropization at a certain characteristic temperature. Therefore, the strong broadening of the T_{NI} peak points to the existence of small LC domains having a broad size distribution [38].

3.2. Morphology

Figure 2 shows optical micrographs of a parallel electro-optical cell with a gap of $5\ \mu\text{m}$, filled with a 20/80 w/w dendrimer/E7 mixture. It appears (a) that the dendrimer molecules have assembled themselves into larger spherical aggregates with a diameter of $\sim 20\ \mu\text{m}$. When viewed under crossed polarisers (b) it becomes evident that the LC molecules are highly disturbed close to the dendrimer aggregates and adopt a *random* orientation. The bulk E7 still has a uniform unidirectional alignment in agreement with the orientation

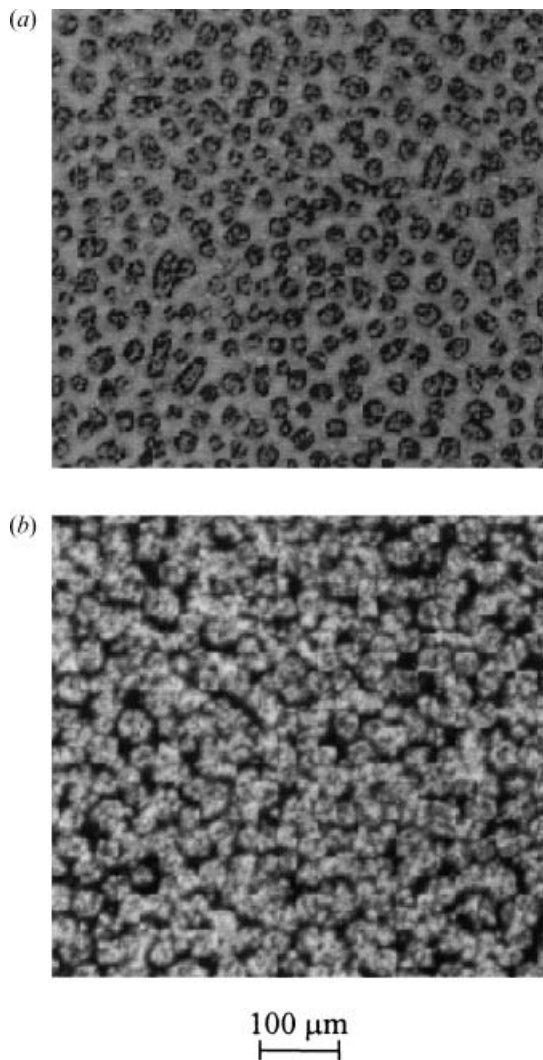


Figure 2. Optical micrographs taken at 22°C of a 5 μm parallel cell filled with a 20/80 w/w dendrimer/E7 mixture (a) viewed without polarizers, and (b) viewed with crossed polarizers.

direction imposed by the rubbed polyimide layers of the cell. Apparently, the presence of the dendritic additive in the LC matrix causes the formation of a polydomain LC structure.

3.3. Rheological properties

The presence of a polydomain LC structure becomes evident not only from the polarized optical micrographs and DSC thermographs of the dendrimer/LC mixtures, but also from, for example, their flow properties which are of importance during the processing and handling of the material. In order to study the impact of the dendrimers on the flow behaviour rheological measurements were conducted on E7 and on dendrimer/E7 mixtures containing various fractions of dendrimers.

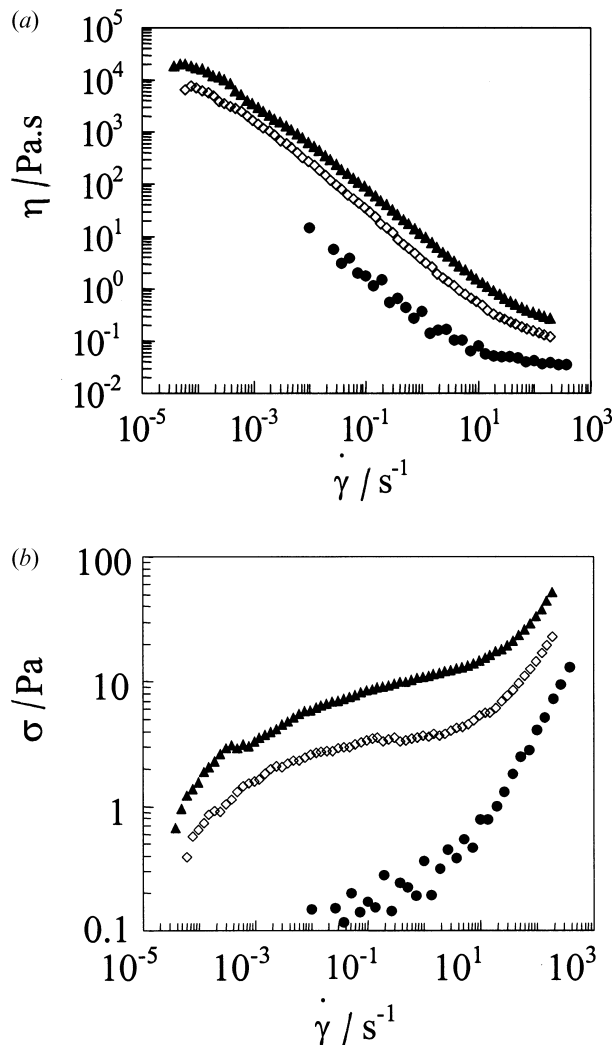


Figure 3. (a) Viscosity η and (b) stress σ as a function of the shear rate $\dot{\gamma}$ for dendrimer/E7 blends with various fractions of the dendrimer: (●) 0/100; (◇) 10/90; (▲) 20/80 w/w dendrimer/LC.

Figure 3 shows the measured viscosity of the samples as a function of the shear rate. For pure LC E7 shear thinning is observed, which is associated with gradual changes in the texture and a decrease in the domain size [39]. After the viscosity has levelled off, another shear thinning region is expected, arising from a further homogenization of the sample. Figure 3(a) nicely illustrates the difference in viscosity level between the dendrimer/LC mixture and the pure LC. The high viscosities appearing at low deformation rates for the dendrimer/LC mixture are attributed to interconnection of the LC domains around the dendrimer aggregates; they comprise LC molecules with a highly distorted orientation, see also figure 2(b). Although a plateau is visible in the viscosity at very low rates, the strong

decrease in viscosity (with a slope closely approaching -1) might be interpreted as an apparent yield stress. The drop in the viscosity is associated with a breakdown of the interconnected LC domains and homogenization of the LC alignment by the flow field. The shift in the (apparent) yield stress with an increasing fraction of dendrimer in the LC is indicative of an increased flow stability of the dendrimer-filled nematics with respect to pure LC at rest. In this respect, figure 3(b) demonstrates that, if one defined an apparent yield stress, its value would be of the order of 1–10 Pa, depending on the filler content. It is also apparent from figure 3(b) that with increasing strain rate the measured stress increases over the whole deformation range. This indicates that for a stress-driven flow of the dendrimer/LC material—which for instance is realized in a coating process used for the incorporation of the modified LC material in a liquid crystal display—the rate will grow gradually in a continuous manner.

3.4. Dielectric behaviour

Dielectric spectroscopy was performed to gain more insight into the orientational and relaxation behaviour of the LC molecules within the dendrimer/LC mixtures. From the spectra obtained for the two-phase mixtures in the unbiased and 40 V biased state, the contribution of the LC matrix (ϵ'_m) was extracted by use of the simple additive mixture rule. This extraction was performed by making use of the fact that in the fully isotropic state the static dielectric constant of the LC matrix of the two-phase mixtures matches the static dielectric constant of pure E7 in the fully isotropic state, $\epsilon'_{s,iso}$, which equals $(2\epsilon'_{s\perp} + \epsilon'_{s\parallel})/3$ [40]. Here, $\epsilon'_{s\perp}$ and $\epsilon'_{s\parallel}$ are the static dielectric constants in the fully planar and homeotropically aligned states, respectively. Using this procedure possible inaccuracies in the sample thickness are also corrected.

For a quantitative analysis of the corrected spectra the measured frequency dependence of $\epsilon'(f)$ and $\epsilon''(f)$ of the samples were fitted by a sum of two Havriliak–Negami (HN) relaxation functions [41], in order to account for the two main relaxation processes α and λ :

$$\epsilon'(\omega, T) = \epsilon_\infty + \sum_{k=1}^2 \Re \left\{ \frac{\Delta\epsilon_k}{[1 + (i\omega\tau_k)^{a_k}]^{b_k}} \right\} \quad (1)$$

$$\epsilon''(\omega, T) = \sum_{k=1}^2 \Im \left\{ \frac{\Delta\epsilon_k}{[1 + (i\omega\tau_k)^{a_k}]^{b_k}} \right\} + \frac{\sigma}{\epsilon_0\omega}. \quad (2)$$

In equations (1) and (2), $\Delta\epsilon_k$, τ_k , a_k and b_k denote the relaxation strengths, the relaxation times and the shape parameters a and b , respectively \Re indicates the real

part and \Im the imaginary part. The second term in equation (2) represents the loss due to the ohmic conduction σ , which is small at low temperatures. Figure 4 shows the Havriliak–Negami fits of the dielectric permittivity (a) and loss (b) of pure E7 and of the E7 matrix of a 10/90 w/w dendrimer/E7 blend, recorded as a function of the frequency at -40°C .

The dielectric loss spectra of figure 4(b) exhibit two peaks. The δ -relaxation peak in the low frequency regime originates from the slow molecular rotation of the LC molecules around their short molecular axis (i.e. with the highest moment of inertia), while the α -relaxation peak in

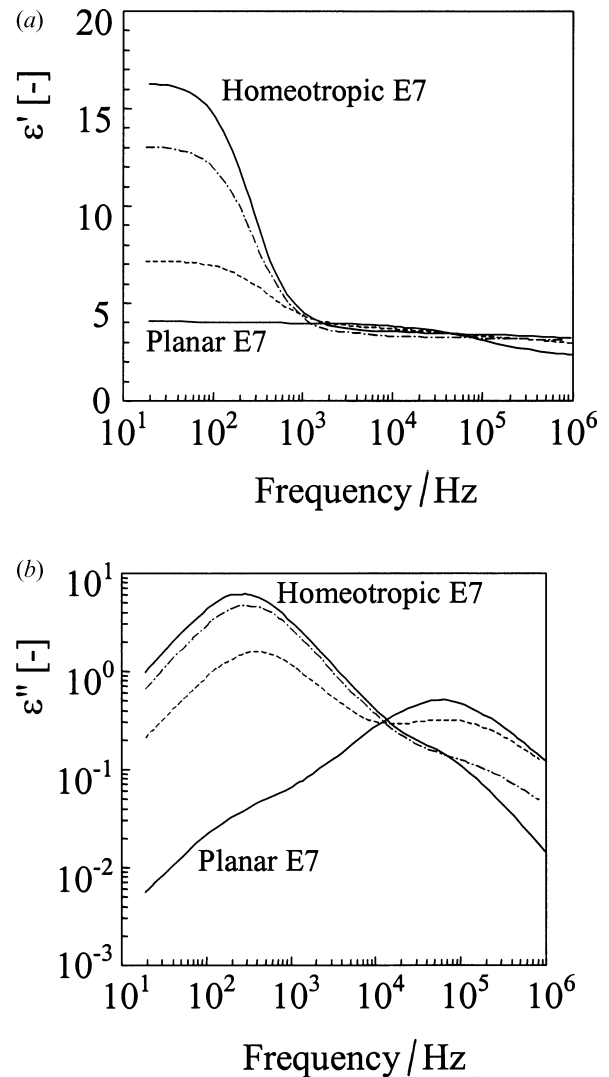


Figure 4. Havriliak–Negami fits of (a) the dielectric permittivity ϵ' and (b) the dielectric loss ϵ'' as a function of frequency ($T = -40^\circ\text{C}$) for pure E7 and for a 10/90 w/w dendrimer/E7 blend: (—) pure E7 in the unaddressed and 40 V addressed state; (--) 10/90 w/w dendrimer/E7 in the unaddressed state; (---) 10/90 w/w dendrimer/E7 in the 40 V addressed state.

Table 1. Director order parameter (S_d) and dielectric strength from fits of the α - and δ -peaks for E7 (in a 5.0 μm parallel cell) and for a 10/90 w/w dendrimer/E7 mixture (in a 17.7 μm parallel cell) in the unaddressed (0 V) and addressed (40 V) state. The S_d applies to the lowest frequency of 20 Hz.

| Dendrimer content/wt % | $\Delta\epsilon_{\perp} (\delta)$ | $\Delta\epsilon_{\perp} (\alpha)$ | $\Delta\epsilon_{\parallel} (\delta)$ | $\Delta\epsilon_{\parallel} (\alpha)$ | $S_d [-]$ | |
|------------------------|-----------------------------------|-----------------------------------|---------------------------------------|---------------------------------------|-----------|-------|
| | $[-]$ 0 V | $[-]$ 0 V | $[-]$ 40 V | $[-]$ 40 V | 0 V | 40 V |
| 0 | 0.0498 | 1.37 | 12.9 | 0.173 | -0.5 | 1 |
| 10 | 3.46 | 0.877 | 9.65 | 0.296 | -0.115 | 0.606 |

the high frequency regime is related to the manifestation of virtually indistinguishable rotations about the long axis and a precessional motion about the director.

The figure clearly shows that, with no d.c. field applied, pure E7 is in a perfectly planarly aligned state within the parallel cell. In the 40 V biased state the pure LC E7 molecules are aligned in a homeotropic manner. The static dielectric constant of the dendrimer/E7 blend in the off-state closely approximates $\epsilon'_{s,iso} = (2\epsilon'_{s\perp} + \epsilon'_{s\parallel})/3$. This suggests a more random, isotropic-like LC orientation, or in other words, an LC *polydomain* structure. This dielectric result clearly indicates that the presence of the dendrimers within E7 highly suppresses the influence of the orientation layers within the parallel electro-optical cell in the unaddressed state. In addition, the dendrimer/E7 blend shows an incomplete reorientation to the homeotropic state, which is an indication that the threshold voltage in the smaller domains exceeds 40 V.

The influence of the dispersed dendrimers on the orientational behaviour of the LC can be quantified by use of the dielectric spectra of figure 4 via the determination of the director order parameter S_d , which is calculated according to [42]:

$$S_d = \frac{3\epsilon'_z - (\epsilon'_{\parallel} + 2\epsilon'_{\perp})}{2(\epsilon'_{\parallel} - \epsilon'_{\perp})} = \frac{3(\epsilon'_z - \epsilon'_{z,iso})}{2(\epsilon'_{\parallel} - \epsilon'_{\perp})} \quad (3)$$

where ϵ'_z denotes the dielectric permittivity measured in the z -direction of the electric field along the surface normal of the parallel plate capacitor used.

From equation (3) it is found that the S_d of the 10/90 w/w dendrimer/E7 sample changes from -0.115 to +0.606 during switching from the off- to the 40 V on-state, while the S_d of the perfectly aligned reference LC sample switches from -0.5 to +1. Figure 4(b) nicely illustrates the differences in LC orientation via the ratio of the dielectric strengths of the two peaks. All fit results obtained from the data of figures 4(a) and 4(b) are summarized in the table.

In the nematic state of the liquid crystal, the dendrimer-filled LC might be considered as a *three-phase* mixture, consisting of (1) the dendrimers as the filler phase, (2) the aligned, 'free' LC as the matrix

phase, and (3) a shell around the dendrimer aggregates consisting of LC molecules with a highly perturbed orientation. This kind of three-phase mixture can be adequately modelled by use of the so-called interlayer model [43, 44]. This model accounts for the presence of a third phase situated at the interface between the matrix and filler phase (figure 5). The interlayer model describes the dielectric behaviour of such a heterogeneous 'core-shell' mixture as follows:

$$\epsilon^* = \frac{\epsilon_f^* \phi_f + \epsilon_1^* \phi_1 X^* + \epsilon_m^* \phi_m Z^*}{\phi_f + \phi_1 X^* + \phi_m Z^*} \quad (4)$$

with:

$$X^* = \frac{[n\epsilon_f^* + (1-n)\epsilon_1^*]}{\epsilon_1^*} \quad (5)$$

$$Z^* = \frac{[n\epsilon_f^* + (1-n)\epsilon_1^*][n\epsilon_m^* + (1-n)\epsilon_m^*] + v n (1-n) (\epsilon_f^* - \epsilon_1^*) (\epsilon_1^* - \epsilon_m^*)}{\epsilon_1^* \epsilon_m^*} \quad (6)$$

$$v = \frac{\phi_f}{\phi_f + \phi_1} \quad (7)$$

where ϵ^* , ϵ_f^* , ϵ_1^* and ϵ_m^* represent the complex dielectric constant of the mixture, the dendrimer filler, the interfacial layer and the continuous matrix (LC E7), respectively. The volume fractions of the dendrimer filler, the interfacial layer, and the matrix material are represented by ϕ_f , ϕ_1 and ϕ_m , and n is the shape or

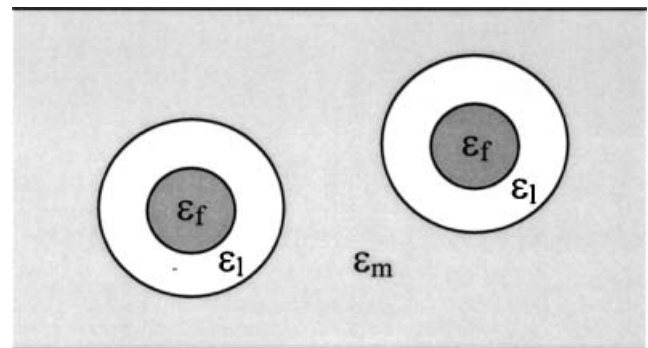


Figure 5. Representation of a nematic LC E7 filled with dendrimer aggregates according to the three-phase interlayer model. The interfacial layer comprises LC molecules with a random orientation, confined within a shell around the spherical aggregates.

depolarization factor of the dispersed phase. The static dielectric constants of figure 4(a) were modelled with equation (4), by using ϕ_1 as the fit variable, and taking $n=1/3$ (this value applies to spherical particles and to randomly orientated ellipsoids). For ϵ'_1 we took the isotropic dielectric constant of E7, ϵ'_{iso} , which has been given earlier: $\epsilon'_{\text{iso}} = (\epsilon'_{\parallel} + 2\epsilon'_{\perp})/3$. The values for ϵ'_{\parallel} and ϵ'_{\perp} were obtained from the fits of the reference experimental curves for homeotropically and planarly aligned E7, while ϵ'_m was taken from the fit of the curve for the matrix E7 in the dendrimer-filled E7.

The fraction of randomly aligned LC around the immersed dendrimers, ϕ_1 , was found with this interlayer model to approximately equal 0.8 for the off-state and 0.2 for the 40 V on-state, based on estimates for ϵ'_f . From these values the thickness D_1 of the layer of randomly oriented LC around the immersed dendrimers can be calculated via $D_1/r_f = [(1 + \phi_1/\phi_1)^{1/3} - 1]$ with r_f the radius of the filler particles. In this calculation, density differences between the LC and dendrimer phase are neglected. If it is assumed that the dendrimers are dispersed as $\sim 20 \mu\text{m}$ spherical aggregates in the E7 (figure 2), the values for ϕ_1 are estimated to correspond to a layer thickness of 10.8 and $4.4 \mu\text{m}$ for the unaddressed and 40 V addressed states, respectively.

The switching between the 0 V unaddressed state and the 40 V addressed state is shown in more detail in figure 6 for pure E7 and for a 10/90 w/w dendrimer/E7 blend. With increasing bias voltage the LC alignment along the electric field lines becomes more perfect. This is expressed by a gradual increase in the ratio between the dielectric strengths of the δ - and α -relaxation peak and by a gradual increase in the static dielectric permittivity. The figure visualizes for both the pure E7 and the dendrimer mixture the existence of an isosbestic point between the δ - and α -relaxation peaks. The presence of an isosbestic frequency, where all curves cross, is indicative of the fact that at this condition the rotational mobility of the LC molecules is unaffected by the presence or absence of an electric field [45]. Additionally, the figure shows no significant effect of the presence of dendrimer in E7 on the relaxation times.

The temperature-dependent orientation of the LC in the 0 and 40 V biased state is shown in figures 7(a) and 7(b). By comparing the orientational behaviour of the LC molecules surrounding the dendrimer phase with the behaviour of pure E7, it becomes clear that the LC molecules acquire less perfectly planarly and homeotropically aligned states in the presence of the dendrimer phase over the entire temperature range. Above T_{NI} and close to T_g (glass transition temperature) of E7, the LC molecules no longer respond to the electric field, due to isotropization and freezing in of the molecular motion, respectively. In the high temperature

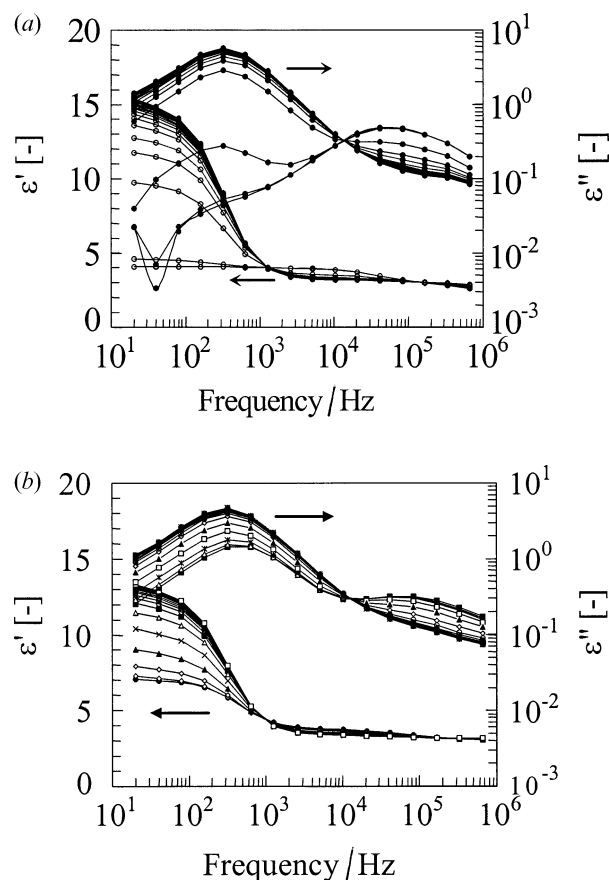


Figure 6. Dielectric spectra for (a) pure E7 and (b) a 10/90 w/w dendrimer/E7 mixture. The spectra were recorded at -40°C during the application of a bias voltage, which was gradually increased from 0 to 40 V in steps of 2 V.

regime, electrode polarization phenomena start to interfere with the measurement due to the accumulation of ions. Figure 8 shows a VFT graph which clearly demonstrates the dependence of relaxation time of the slow δ relaxation for E7 on temperature.

The time and temperature dependence of the reorientation behaviour of the dendrimer-filled nematics was studied by subjecting the dendrimer/E7 mixture to a step-up change ($0 \rightarrow 40 \text{ V}$) and a step-down change ($40 \rightarrow 0 \text{ V}$) of the bias (figure 9). Both the 40 V and 0 V states were continued for 2 min. Figure 9 illustrates the retardation and relaxation response of the pure LC and of the LC molecules within the LC/dendrimer blends directly after application and removal of the bias voltage at time intervals of 2 s.

As far as the time-scales of the experiment allow, the LC molecules immediately respond in both cases to the bias voltage by aligning themselves in the direction of the external field. In contrast, in case of pure E7, the relaxation of the nematic director to the

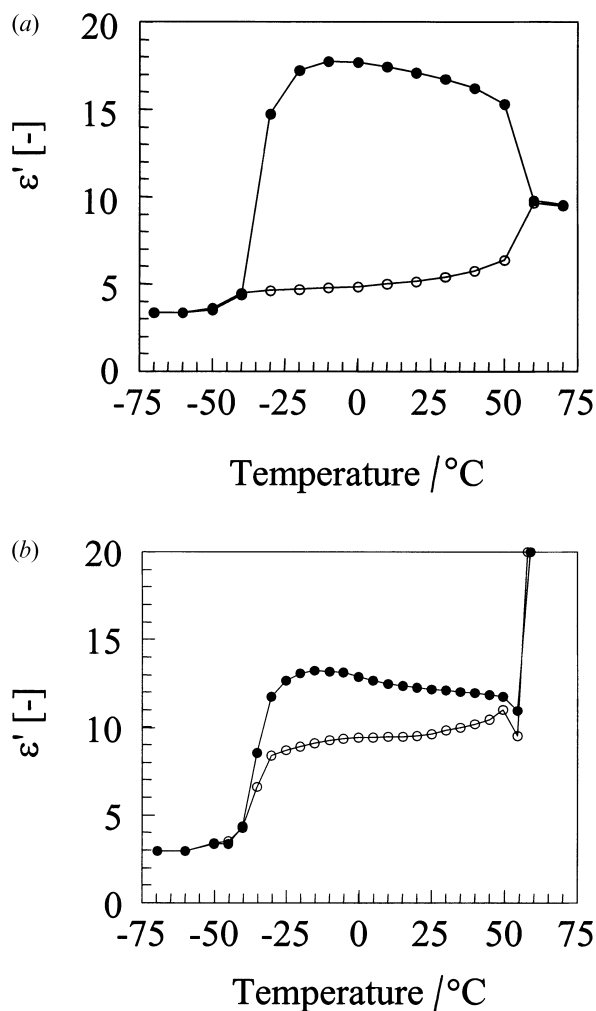


Figure 7. Dielectric permittivity versus temperature for (a) pure E7 and (b) a 10/90 w/w dendrimer/E7 blend scanned at 1 kHz in the 0 V unaddressed state (\circ) and the 40 V addressed state (\bullet).

planar state shows a noticeable slowing at both the highest and lowest temperatures after removal of the bias voltage. The increasing relaxation time for the decay of the nematic order with decreasing temperature is reasonable, since the restoration of the planar order is directly linked to the viscosity of the nematic crystal, which in turn scales with the relaxation times of the two principal molecular relaxations [46]. Hence, only at sufficiently high temperatures do we find an instantaneous decay of the nematic order on the time-scale of our experiment. The delayed relaxation behaviour at the high temperature range is obviously of a different nature. This is most likely associated with the build-up of an internal electric field due to charge accumulation in the vicinity of the electrodes (electrode polarization).

In the case of the dendrimer-filled E7 the charge

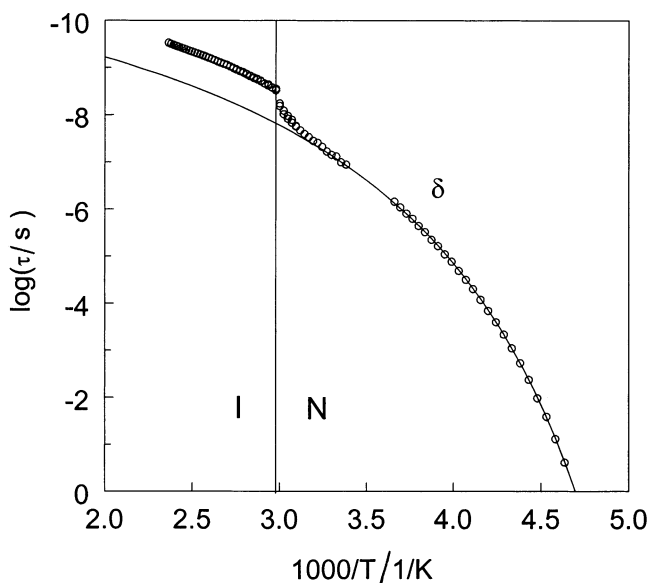


Figure 8. VFT graph showing the relaxation time of the slow δ -relaxation of E7 as a function of temperature.

build up after the application of the step-up voltage, is accompanied by a gradual decrease of ϵ'_s with time. Furthermore, the surface plot demonstrates the occurrence of two different temperature-dependent relaxation phenomena after removal of the d.c. bias, comparable to what is observed for pure E7. In the low temperature regime, again the slow molecular dynamics delays the elasticity-driven relaxation of the orientational order into the 'off' state. At intermediate temperatures ($T \sim -15^\circ\text{C}$), a new delay mechanism appears, the relaxation time of which decreases gradually towards higher temperatures. We attribute this phenomenon to charge-polarization effects on internal surfaces (interfacial relaxation) due to the electrically heterogeneous structure of the E7/dendrimer mixture. Since the relaxation time of such interfacial relaxation (also called the Maxwell-Wagner effect [35, 47]) depends on the local conductivity (being higher than in pure E7) and the characteristic size of the dendrimer-network, interfacial relaxation manifests itself at temperatures far below the occurrence of electrode polarization. At temperatures close to room temperature, switching times are again found comparable to those of pure E7.

3.5. Electro-optical properties

3.5.1. Transmittance-voltage characteristics

For dendrimer-filled LCs it was found that the polydomain structure gives rise to strong light scattering. By the application of an electric field the differences in refractive indices between the LC

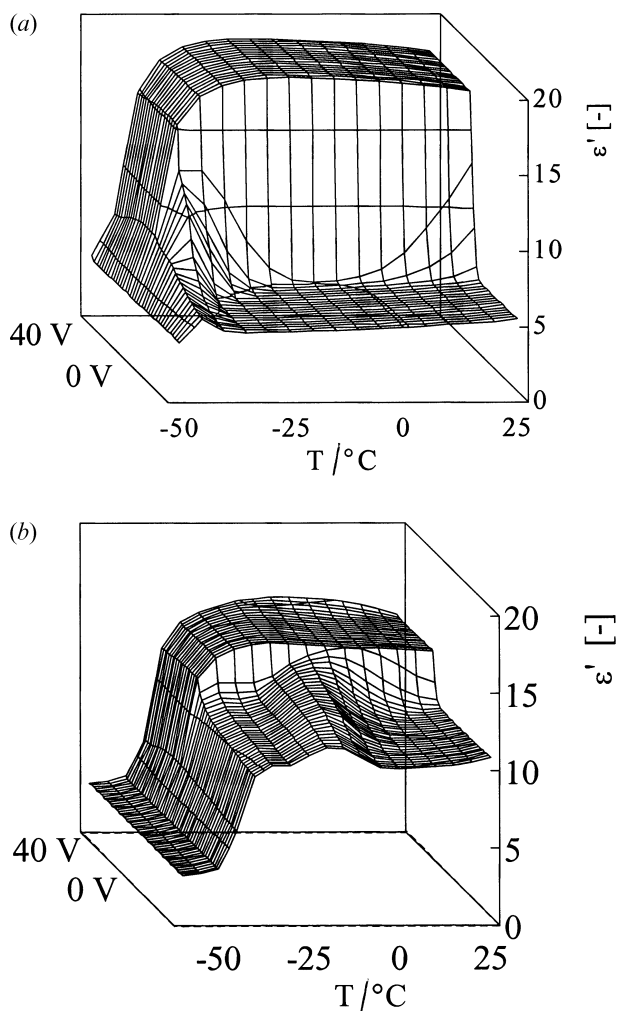


Figure 9. Change in permittivity with time in the temperature range 25 to -60°C for (a) pure E7 and (b) a 10/90 w/w dendrimer/E7 blend, measured at 110 Hz after switching to 40 V (addressed state, curves at the rear) and next to 0 V (unaddressed state, curves at the front). The time interval between the curves is 2 s.

domains are reduced owing to a more homogeneous LC alignment, resulting in a more transparent state. The transmission as a function of the applied voltage during voltage-up and -down scans was measured for dendrimer/E7 mixtures based on various fractions of dendrimer within $17.7\ \mu\text{m}$ parallel electro-optical cells (see figure 10). With increasing fraction of the additive, the transmission in the off-state decreases, while the transmission in the on state at equal voltage also decreases, probably due to the existence of a refractive index mismatch between the dendrimer and the LC phase.

The rather obvious light-scattering capability of the dendrimer mixture can be related to the phase behaviour of the two-phase material. The dendrimer

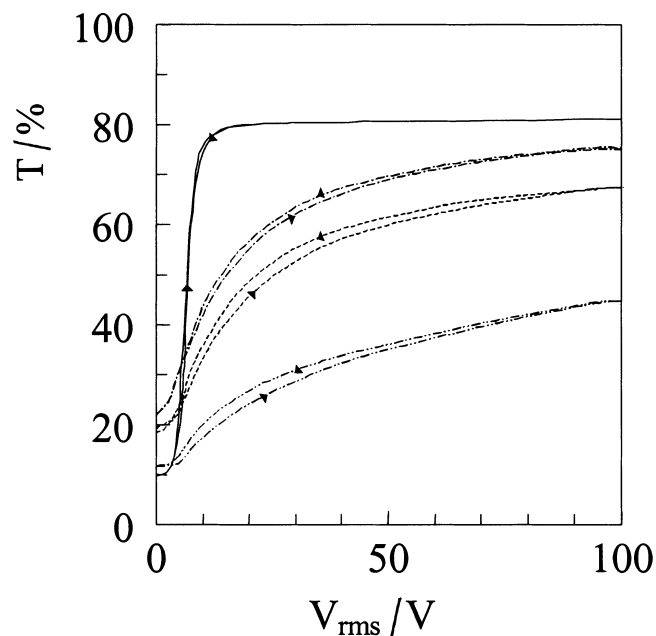


Figure 10. Transmission as a function of the applied a.c. voltage of 1 kHz square wave for $17.7\ \mu\text{m}$ parallel electro-optical cells filled with dendrimer/E7 mixture with various fractions of dendrimer: (---) 5/95; (-·-) 10/90; (-··) 20/80 w/w dendrimer/LC. As a reference, the T - V characteristic of an optimized $7\ \mu\text{m}$ PDLC cell is shown: (—).

has a phase transition from a semicrystalline state to an isotropic state at a temperature above the T_{NI} of the LC E7 (figure 1). During cooling from the isotropic state to room temperature the dendrimer crystallizes before the E7 undergoes its isotropic-nematic transition. This specific order has been demonstrated earlier to enhance the interaction between LC and the dispersed phase [8, 48]. Also, during the voltage step-up scan the transmission increases in a continuous manner with voltage. This confirms the presence of a *broad* distribution of LC domain sizes, as was concluded earlier from the DSC experiments.

A remarkable feature of the dendrimer-filled nematics is that the hysteresis in the electro-optical curves is very small, i.e. the transmittance during the voltage-down scan almost equals that during the voltage-up scan. The absence of hysteresis indicates that the LC molecules follow the same orientational route both upon application and after removal of the voltage [49]. It thus seems likely that the dendrimer additive is able to impose a highly preferential orientational route to the LC, thereby taking over the function of the orientation layers and suppressing the occurrence of hysteresis.

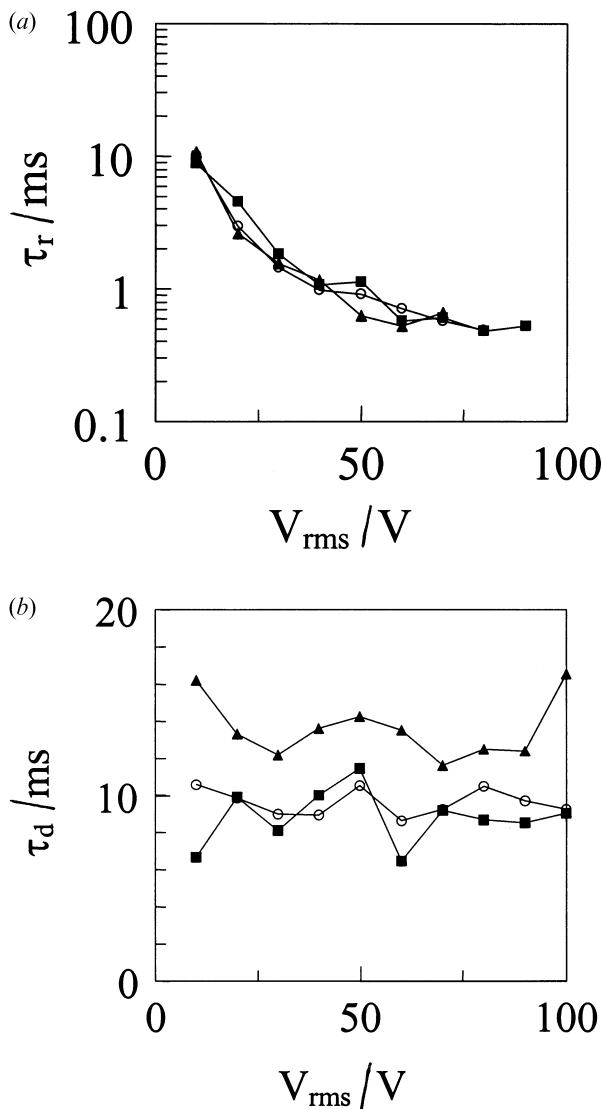


Figure 11. (a) Rise and (b) decay times as a function of the applied voltage for 17.7 μm parallel cells filled with dendrimer/E7 mixtures with various amounts of dendrimer: (\blacktriangle) 5/95; (\circ) 10/90; (\blacksquare) 20/80 w/w dendrimer/LC.

3.5.2. Switching kinetics

The dependence of the rise and decay times, τ_r and τ_d , on the applied voltage is shown in figure 11. As is generally predicted, the response of the LC molecules is strongly accelerated with increasing magnitude of the external field, figure 11(a) [50, 51]. Around the threshold voltage, V_{90} , the rise times are of the order of 0.5 ms. The relation between rise time and applied voltage appears to be unaffected by the concentration of the dendrimer in the two-phase mixtures.

Figure 11(b) shows that the decay times are independent of the applied voltage. This is in agreement with equations derived for τ_d [52, 53]. Higher dendrimer

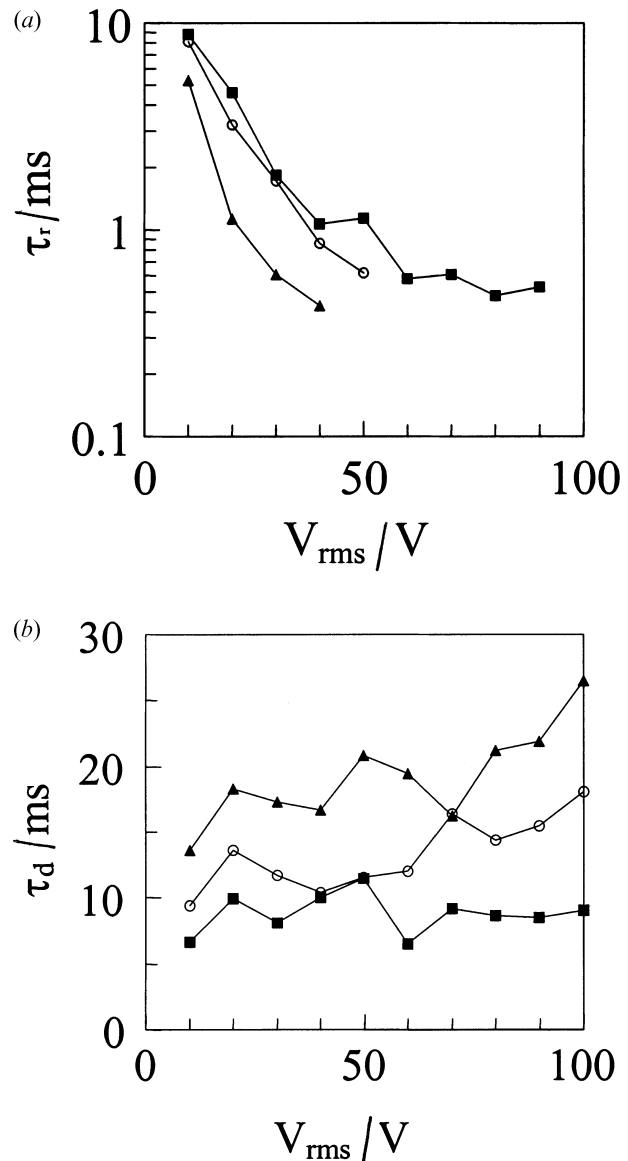


Figure 12. (a) Rise and (b) decay times as a function of the applied voltage for 20/80 w/w dendrimer/E7 mixtures in parallel cells with various cell gaps: (\blacktriangle) 5; (\circ) 8.1; (\blacksquare) 17.7 μm .

concentrations seem to lead to a somewhat faster relaxation of the LC molecules. Although the differences are small, this may indicate that an increased interaction between the LC and the dendrimer phase promotes a faster relaxation of the LC molecules back to their initial orientation state [54].

The influence of the cell gap on the switching times is demonstrated in figure 12. As expected, larger cell gaps give rise to longer rise times [3]. Figure 12(b) suggests a decrease in decay time with increasing cell gap. Thus, as the interaction between the LC and the dendrimer

phase starts to dominate over the interaction between the LC and the orientation layers of the cell, the relaxation of the LC is accelerated upon removal of the electric field. This confirms the idea that the dendrimer phase provides a 'memory' for the orientation of the LC via anchoring forces.

4. Conclusions

A novel light-scattering, easy to make electro-optical switch has been described, based on the addition of poly(propylene imine) dendrimers of 2–3 nm diameter to a nematic LC. Due to the presence of the dendrimer filler the LC molecules become highly distorted in their orientation, resulting in a multidomain structure. These polydomain LCs show a high viscosity and an efficient light scattering ability compared with the pure LC. By the application of mechanical or electric forces the dendrimer-filled LC becomes more uniformly aligned.

Upon application of a step-up d.c. voltage the two-phase materials rapidly switch from a light-scattering, translucent state to a more transparent state via homeotropic LC alignment. Extremely fast rise times are found over a broad range of temperatures. Upon removal of the d.c. bias the LC molecules rapidly reorient back to their initial orientational state at operating temperatures around room temperature. At lower temperatures longer relaxation times were observed, due to the interference of charge-polarization effects, which slow down the molecular dynamics. Hysteresis proves to be virtually absent in the transmittance–voltage scan. This is attributed to the strong interaction between the dendrimer and LC phase.

References

- [1] DOANE, J. W., VAZ, N. A., WU, B. G., and ZUMER, S., 1986, *Appl. Phys. Lett.*, **48**, 269.
- [2] DRZAIĆ, P. S., 1988, *Liq. Cryst.*, **3**, 1543.
- [3] HIKMET, R. A. M., 1990, *J. appl. Phys.*, **68**, 4406.
- [4] YANG, D. K., CHIEN, L. C., and DOANE, J. W., 1992, *Appl. Phys. Lett.*, **60**, 3102.
- [5] AMUNDSON, K., VAN BLAADEREN, A., and WILTZIUS, P., 1997, *Phys. Rev. E*, **55**, 1646.
- [6] GRAND, C., ACHARD, M. F., and HARDOUIN, F., 1997, *Liq. Cryst.*, **22**, 287.
- [7] KATO, T., KUTSUNA, T., and HANABUSA, K., 1999, *Mol. Cryst. liq. Cryst. Sci. Technol., A*, **332**, 2887.
- [8] JANSSEN, R. H. C., STÜMPFLEN, V., VAN BOXTEL, M. C. W., BASTIAANSEN, C. W. M., BROER, D. J., TERVOORT, T. A., and SMITH, P., 2000, *Macromol. Symp.*, **154**, 117.
- [9] MIZOSHITA, N., KUTSUNA, T., HANABUSA, K., and KATO, T., 1999, *Chem. Commun.*, 781.
- [10] KATO, T., KUTSUNA, T., HANABUSA, K., and UKON, M., 1998, *Adv. Mater.*, **10**, 606.
- [11] EIDENSCHINK, R., and DE JEU, W. H., 1991, *Electron. Lett.*, **27**, 1195.
- [12] GLUSHCHENKO, A. V., KRESSE, H., REZNIKOV, Y. A., and YAROSHCHUK, O. V., 1997, *Liq. Cryst.*, **23**, 241.
- [13] KREUZER, M., TSCHUDI, T., DE JEU, W. H., and EIDENSCHINK, R., 1993, *Appl. Phys. Lett.*, **62**, 1712.
- [14] VAN BOXTEL, M. C. W., BROER, D. J., and BASTIAANSEN, C. W. M., 1999, *Abstr. Pap. Am. chem. Soc.*, **218**, 365.
- [15] VAN BOXTEL, M. C. W., JANSSEN, R. H. C., BASTIAANSEN, C. W. M., and BROER, D. J., 2001, *J. appl. Phys.*, **89**, 838.
- [16] ANDERSON, V. J., TERENTJEV, E. M., MEEKER, S. P., CRAIN, J., and POON, W. C. K., 2001, *Eur. Phys. J. E*, **4**, 11.
- [17] MEEKER, S. P., POON, W. C. K., CRAIN, J., and TERENTJEV, E. M., 2000, *Phys. Rev. E*, **61**, R6083.
- [18] BAARS, M. W. P. L., FROEHLING, P. E., and MEIJER, E. W., 1997, *Chem. Commun.*, 1959.
- [19] STEVELMANS, S., VAN HEST, J. C. M., JANSSEN, J. F. G. A., VAN BOXTEL, D. A. F. J., VAN DEN BERG, E. M. M. D., and MEIJER, E. W., 1996, *J. Am. chem. Soc.*, **118**, 7398.
- [20] BOSMAN, A. W., JANSSEN, H. M., and MEIJER, E. W., 1999, *Chem. Rev.*, **99**, 1665.
- [21] KNAPEN, J. W. J., VANDER MADE, A. W., DE WILDE, J. C., VAN LEEUWEN, P. W. N. M., WIJKENS, P., GROVE, D. M., and VAN KOTEN, G., 1994, *Nature*, **372**, 659.
- [22] JANSEN, J., DE BRABANDER-VAN DEN BERG, E. M. M., and MEIJER, E. W., 1994, *Science*, **266**, 1226.
- [23] BOAS, U., KARLSSON, A. J., DE WAAL, B. F. M., and MEIJER, E. W., 2001, *J. org. Chem.*, **66**, 2136.
- [24] BAARS, M. W. P. L., SÖNTJENS, S. H. M., FISCHER, H. M., PEERLINGS, H. W. I., and MEIJER, E. W., 1998, *Chem.-Eur. J.*, **4**, 2456.
- [25] CAMERON, J. H., FACHER, A., LATTERMANN, G., and DIELE, S., 1997, *Adv. Mater.*, **9**, 398.
- [26] SCHENNING, A., PEETERS, E., and MEIJER, E. W., 2000, *J. Am. chem. Soc.*, **122**, 4489.
- [27] WEENER, J. W., and MEIJER, E. W., 2000, *Adv. Mater.*, **12**, 741.
- [28] SCHENNING, A., ELISSEN-ROMAN, C., WEENER, J. W., BAARS, M. W. P. L., VAN DER GAASST, S. J., and MEIJER, E. W., 1998, *J. Am. chem. Soc.*, **120**, 8199.
- [29] LORENZ, K., HOLTER, D., STUHN, B., MULHAUPT, R., and FREY, H., 1996, *Adv. Mater.*, **8**, 414.
- [30] CHEN, F. L., JAMIESON, A. M., KAWASUMI, M., and PERCEC, V., 1995, *J. polym. Sci., B*, **33**, 1213.
- [31] VAN BOXTEL, M. C. W., BROER, D. J., BASTIAANSEN, C. W. M., BAARS, M. W. P. L., and JANSSEN, R. H. C., 2000, *Macromol. Symp.*, **154**, 25.
- [32] BAARS, M. W. P. L., VAN BOXTEL, M. C. W., BASTIAANSEN, C. W. M., BROER, D. J., SÖNTJENS, S. H. M., and MEIJER, E. W., 2000, *Adv. Mater.*, **12**, 715.
- [33] VAN BOXTEL, M. C. W., 2002, PhD thesis, Eindhoven University of Technology, Eindhoven, pp. 1–141.
- [34] KIM, B. K., KIM, S. H., and CHOI, C. H., 1995, *Mol. Cryst. Liq. Cryst. Sci. Technol., A*, **261**, 605.
- [35] ZHONG, Z. Z., SCHUELE, D. E., GORDON, W. L., ADAMIC, K. J., and AKINS, R. B., 1992, *J. Polym. Sci., B*, **30**, 1443.
- [36] MUKHERJEE, P. K., 1997, *Liq. Cryst.*, **22**, 239.
- [37] BELLINI, T., CLARK, N. A., MUZNY, C. D., WU, L., GARLAND, C. W., SCHAEFER, D. W., OLIVIER, B. J., and OLIVER, B. J., 1992, *Phys. Rev. Lett.*, **69**, 788.
- [38] DADMUN, M. D., and MUTHUKUMAR, M., 1993, *J. chem. Phys.*, **98**, 4850.
- [39] LARSON, R. G., 1988, *Constitutive Equations for Polymer Melts and Solutions* (London: Butterworth).

- [40] KRESSE, H., 1998, in *Handbook of Liquid Crystals*, Vol. 2A, edited by D. Demus, J. W. Goodby and G. W. Gray (Chichester: Wiley-VCH), pp.91–112; DUNMUR, D., and TORIYAMA, K., 1998, in *Handbook of Liquid Crystals*, Vol.1, edited by D. Demus, J. W. Goodby and G. W. Gray (Chichester: Wiley-VCH), pp.231–252.
- [41] HAVRILIAK, S., and NEGAMI, S., 1967, *Polymer*, **8**, 161.
- [42] ATTARD, G. S., ARAKI, K., and WILLIAMS, G., 1987, *Br. polym. J.*, **19**, 119.
- [43] STEEMAN, P. A. M., and VAN TURNHOUT, J., 2002, in *Dielectric Broadband Spectroscopy*, edited by F. Kremer and A. Schönhals (Berlin: Springer), pp.495–522.
- [44] STEEMAN, P. A. M., and MAURER, F. H. J., 1990, *Colloid polym. Sci.*, **268**, 315.
- [45] VAN BOXTEL, M. C. W., WÜBBENHORST, M., VAN TURNHOUT, J., BASTIAANSEN, C. W. M., and BROER, D. J., 2003, *Liq. Cryst.*, **30**, 235.
- [46] DE JEU, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (London: Gordon and Breach).
- [47] ROUT, D. K., and JAIN, S. C., 1992, *Jpn. J. appl. Phys.*, **1**, **31**, 1396.
- [48] JANSSEN, R. H. C., STÜMPFLEN, V., BROER, D. J., BASTIAANSEN, C. W. M., TERVOORT, T. A., and SMITH, P., 2000, *J. appl. Phys.*, **88**, 161.
- [49] HIKMET, R. A. M., and BOOTS, H. M. J., 1995, *Phys. Rev. E*, **51**, 5824.
- [50] AMUNDSON, K., 1996, *Phys. Rev. E*, **53**, 2412.
- [51] DOANE, J. W., GOLEMME, A., WEST, J. L., WHITEHEAD, J. B., and WU, B. G., 1988, *Mol. Cryst. liq. Cryst.*, **165**, 511.
- [52] WU, B. G., ERDMANN, J. H., and DOANE, J. W., 1989, *Liq. Cryst.*, **5**, 1453.
- [53] ANDREAU, A., FARHI, R., TARASCON, J. M., and GISSE, P., 2000, *Liq. Cryst.*, **27**, 1.
- [54] MIZOSHITA, N., HANABUSA, K., and KATO, T., 2001, *Displays*, **22**, 33.