Macromol. Symp. ***154,*** *24–35 (2000)*

Electro-Optical Switches Based on Polymer and Dendrimer Filled Nematics

Marysia van Boxtel[1], Dick Broer[1, 2], Cees Bastiaansen*[1], Maurice Baars[1], Rob Janssen[1]

[1]Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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

SUMMARY: Two-phase systems which can be switched electrically between a light scattering and a transparent state can be prepared based on either a dispersion of well-defined sub-micron sized crosslinked polymeric particles in a liquid crystal (LC) matrix (Polymer Filled Nematics, PFN's) or on a dispersion of palmitoyl-functionalised poly(propylene imine) dendrimers in an LC (Dendrimer Filled Nematics). The present paper describes the preparation of both systems and their properties. The PFN's can be electrically switched between a scattering and a transparent state by an appropriate choice of materials and refractive indices. The preparation of the disperse polymeric phase is separated from the preparation of the polymer/LC blend, which enables control over the morphology of the system. Rather surprisingly, it is found that, due to the rheological properties of the PFN blends, stable films of the blends can be simply produced by conventional coating processes. The dendrimer-stabilised nematics require extremely low switching voltages to switch from a scattering to a highly transparent state. Moreover, the switching process is totally reversible and hysteresis effects appear to be absent.

Introduction

During the past three decades, a variety of liquid crystal display (LCD) configurations have been proposed(1). In the early 1970s an electro-optical cell, based on a twisted nematic (TN) liquid crystal mode, was introduced, which became widely used in small area applications(2, 3). This TN cell electrically switches the polarisation direction of the light. Linearly polarised light is generated by a first polariser and, in case of transmissive displays, visual perception of the switching is generated by an analyser(4, 5). In this way TN cells can be electrically switched between a transparent and a dark state. However, the required presence of the polarisers often imposes rather severe limitations on the brightness and energy efficiency of

CCC 1022-1360/00/$ 17.50+.50/0

these devices. Moreover, the TN cell construction is rather complex, what makes the production of these devices laborious.

These drawbacks of the TN displays have stimulated extensive research activities into other electro-optical switches$^{1)}$. For instance, in the mid 1980s a light shutter device was developed consisting of nematic LC droplets dispersed in a solid continuous polymeric matrix (Polymer Dispersed Liquid Crystals, PDLC's) $^{6,\ 7)}$. By matching the refractive index of the polymeric phase to one of the two refractive indices (n_o) of the LC, these PDLC's can be electrically switched between a scattering and a transparent state. Usually, these PDLC blends are prepared via polymerisation of a reactive monomer that is dissolved in a LC material$^{8)}$. During polymerisation, phase separation takes place, resulting in droplets of LC embedded in a polymer matrix. However, this phase separation is never complete and, therefore, an accurate control over the morphology of the PDLC blends is lacking.

More recently, electro-optical switches consisting of a continuous LC phase and a dispersed, spherical inorganic phase with small diameter (< 20 nm) were investigated$^{9,\ 10)}$. These LCD's can be switched from a scattering to a transparent state due to polydomain formation of the LC in the off-state and homeotropic alignment of the LC in the on-state. Due to the small size of the dispersed particles, refractive index matching between the two phases is unnecessary.

A new approach in the field of scattering systems is the formation of polydomain structures via addition of low molecular weight functionalised compounds to LC solvents. These so-called gelling agents are able to form supramolecular assemblies via intermolecular interactions, and therefor cause physical (thermo-reversible) gelation of the LC phase$^{11,\ 12)}$.

Dendritic macromolecules, which have a highly and regularly branched architecture, are also known to show characteristic and interesting (self-)assembly behaviour in bulk or in contact with another medium, dependent on their modification. Recently, modification of dendritic structures with mesogenic endgroups$^{13\text{-}17)}$ and their interaction with LC's$^{18)}$ have been topics of high interest. However, experimental studies concerning the application of modified dendrimers in electro-optical switches have received less attention$^{19)}$.

In the first part of this paper, a new display principle is reported, based on a dispersion of well-controlled sub-micron sized crosslinked polymeric spheres in a continuous LC matrix, which we refer to as the so-called "Polymer Filled Nematics (PFN's)". These blends were designed with the objective to improve the morphology of the blends and thus to improve the optical and electro-optical properties of polymer/LC mixtures. Here, some initial experimental results are presented concerning the synthesis of polymer particles and the characterisation of the polymer/LC blends with respect to phase behaviour, rheological and electro-optical characteristics.

In the second part of this paper, the use of dendrimers as nucleating agents for introduction of director disorder in a nematic LC matrix is explored. Compared to the PFN's, the size of the primary particles in the disperse phase is strongly reduced. Moreover, the chemical nature of the dendritic disperse phase is considerably different from the polymeric disperse phase.

Experimental Section

Methyl methacrylate (MMA; 99%, Aldrich) and divinylbenzene (DVB, a 55 % mixture of para and meta isomers; p.a., Aldrich) were each purified with an inhibitor adsorption column (Aldrich). N-heptane (extra pure) was obtained from Merck and was used as received. A steric stabiliser, a polystyrene-b-poly(ethylene-co-propylene) diblock copolymer containing 38.5-42 % wt/wt of styrene units (Kraton G-1701x, M_w = 1.1.105 g/mole, $M_w/M_n \approx 1$) was purchased from Shell. A dibenzoyl peroxide was used, containing 25 % wt/wt water (DBP; p.a., BPM Breda). The LC material E7 (n_o = 1.5216, n_e = 1.7462), a eutectic mixture of cyanobiphenyls and a cyanoterphenyl, was purchased from Merck Ltd. A fifth generation palmitoyl-functionalised poly(propylene imine) dendrimer was synthesised at the Eindhoven Polymer Laboratories.

The components and the amounts of components that are used in a typical polymerisation experiment are shown in Table 1.

Table 1. Recipe for the preparation of 800 nm sized highly crosslinked, refractive index matched P(MMA/DVB) copolymer particles using an initial monomer concentration of 20 % wt/wt and stabiliser concentration of 4 g/l.

Component	Amount (g)
n-heptane	138.9
MMA	25.81
DVB	8.91
DBP (75 % pure)	0.221
Kraton G-1701x	0.817

The dispersion polymerisation was performed under nitrogen in a sealed, mechanically stirred, thermostated glass reactor at a temperature of 70 °C. Before use the organic solvent n-heptane was flushed with nitrogen for about 20-30 minutes to remove oxygen. The solvent was added to the reactor together with the steric stabiliser Kraton G-1701x. The nitrogen flushing was continued in the reactor and the reactor was heated to reaction temperature under continuous stirring in order to dissolve the stabiliser. Next, the monomers MMA and DVB, containing the dissolved initiator DBP, were added to the clear solution. After flushing for another five minutes the reactor was sealed off. The polymerisation process was carried out for 47 hours.

The conversions of the separate monomers after dispersion polymerisation were determined by analysing the concentrations of unreacted monomer in the dispersion with a gas chromatograph Hewlett Packard 5890 series II, equipped with a Hewlett Packard capillary column (5 % phenyl methyl silicone crosslinked, length = 25 m, i.d. = 310 μm film = 0.52 μm). Cyclohexanol was used as an internal standard.

The thermographs of the polymer/LC blends and the pure LC were recorded by a differential scanning calorimeter Perkin-Elmer DSC 7 with heating and cooling rates of 20 $K.min^{-1}$. The change in enthalpy (per unit mass) at the nematic-isotropic transition temperature (T_{N-I}) was calculated out of the area under the peak at T_{N-I}.

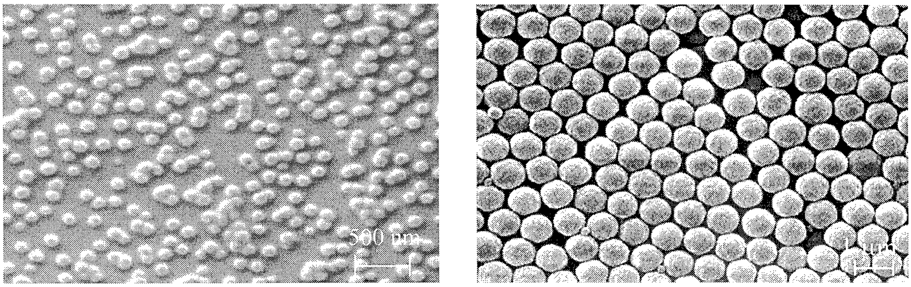
Stationary rheological experiments were performed with an Ares Rheometric Scientific Laboratory instrument, equipped with parallel plate geometry.

The morphology of the dendrimer/LC blends was studied with a Zeiss Universal Microscope, with crossed polarisers.

Electro-optical measurements were performed by use of a combination of a Black Star Jupiter 500 0.1 Hz - 500 kHz function generator and an AC high voltage amplifier. The AC voltage applied across the samples was a square wave with a frequency of 1 kHz.

Results and Discussion

First, the experimental results concerning the preparation of the PFN blends consisting of a polymeric disperse phase and a continuous LC phase are discussed. The polymer particles were prepared via radical dispersion polymerisation in an organic medium20-22). The motivation for choosing this polymerisation method was that the LC, the matrix material of the final blend, is soluble in the organic polymerisation medium. The dispersion polymerisation was started using the monomers methyl methacrylate (MMA) and



a) b)

Fig. 1. a) Environmental Scanning Electron Micrograph of 85 nm sized polymer particles and b) Scanning Electron Micrograph of 800 nm sized polymer particles, after removal of the polymerisation solvent.

divinylbenzene (DVB), a crosslinking agent. The monomers were added to the polymerisation medium in a specific ratio in order to match the refractive index of the polymer particles to the ordinary refractive index n_o of the LC. The proper ratio of the monomers was calculated from the Lorentz-Lorenz equation[23)]. In case of the poly(methyl methacrylate-co-divinylbenzene) polymer, index matching is obtained by starting from a MMA/DVB ratio of 74.33/25.67 % wt/wt.

In the dispersion polymerisation process, particle size and particle size distribution are influenced by several factors, e.g. initial monomer concentration, stabiliser concentration, temperature[21, 22, 24, 25)]. In order to produce polymer particles in a broad range of particle sizes, several dispersion polymerisations were performed under varying conditions. This resulted in the production of virtually monodisperse polymer particles with particle diameters between 27 and 900 nm. Figure 1 shows an Environmental Scanning Electron Micrograph of small 85 nm sized particles and a Scanning Electron Micrograph of 800 nm sized particles, which were obtained in a yield of 96 and 100 % wt/wt, respectively. In some cases the chemical composition of the polymer particles was determined by analysing the amounts of unconverted monomer in the reaction medium. In all cases it was found that the conversions of the two monomers were similar to each other, indicating that the monomer ratio in the copolymer was equal to the initial composition and that the refractive index of the copolymer was indeed equal to the ordinary refractive index of the LC.

After the synthesis of the dispersed polymeric phase, polymer/LC blends were prepared by adding a pre-set amount of the nematic LC E7 (g –61.5 N 59.9 I)[26)], to a pre-set amount of the dispersion of the polymer particles in n-heptane. Subsequently, the organic solvent was

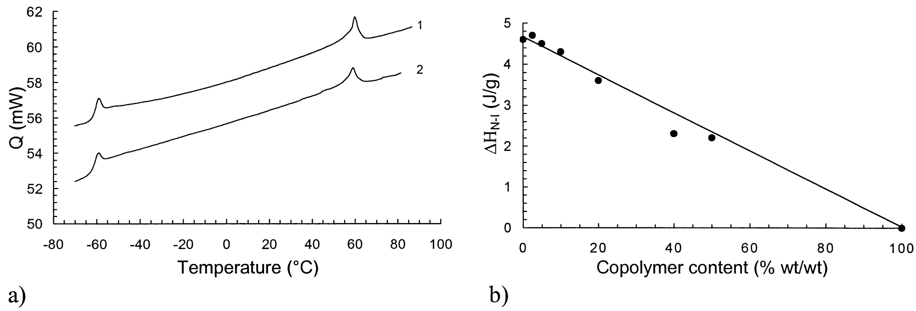


Fig.2. Differential Scanning Calorimetry measurements which show a) thermographs of (1) LC E7, (2) a 10/90 % wt/wt polymer/LC blend. The under curve (2) was shifted vertically for clarity; b) change of enthalpy per unit mass at the nematic-isotropic transition temperature as a function of the blend composition.

evaporated under vacuum at room temperature for 24 hours. The resulting dispersions of the polymer particles in the LC showed a milky-white appearance.

The phase behaviour of the blends was examined by Differential Scanning Calorimetry (DSC) measurements. Figure 2 shows the DSC thermographs of the pure LC E7 and of a 10/90 % wt/wt polymer/LC blend. It is obvious that no shift takes place of the onset temperature of the nematic to isotropic transition (T_{N-I}) of the LC, which confirms that virtually no traces of polymeric material are present in the liquid crystalline phase. The possible presence of the LC material in the polymeric phase was investigated by examining the change in enthalpy per unit mass at the nematic-isotropic transition as a function of the blend composition. The observed linear relation between the two parameters indicates that virtually no LC material is present in the polymeric phase.

A rather remarkable property of the blends is that they exhibit a paste-like rheology and

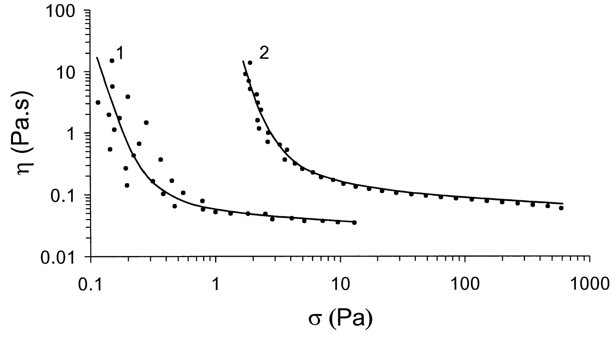


Fig. 3. The viscosity as a function of the calculated shear stress for (1) the pure LC E7 and (2) a 5/95 % wt/wt polymer/LC blend containing 85 nm sized copolymer particles.

that coating of the blends on a substrate with conventional coating techniques is rather straightforward. The rheological properties of a 5/95 % wt/wt polymer/LC blend were investigated in some more detail and it was found that this mixture exhibited thixotropic rheological behaviour$^{27)}$. Thus, in order to perform reproducible measurements, the blend was pre-sheared before measurement in order to break up any network, that was formed in the blend due to connection of polymer particles. Even after pre-shearing the (now liquid-like) blend still possesses a yield stress of approximately 2-3 Pa (Figure 3). Probably, the presence of a yield stress in combination with the absence of a large density difference between the polymeric and the LC phase enhances the stability of the blends.

Some initial experiments were also performed concerning the electro-optical behaviour of the PFN blends. An electro-optical cell was produced from a 10/90 % wt/wt polymer/LC mixture containing 85 nm sized polymer particles by sandwiching a droplet of the blend between glass substrates equipped with conducting indium tinoxide (ITO) layers. Glass spacers of 14 μm were used to define the cell thickness. Figure 4 shows the optical properties of this particular cell. The figure illustrates that the initially white (opaque) PFN blend indeed becomes transparent by the application of an electrical field (7 $V.\mu m^{-1}$), due to a close matching of the refractive index of the polymer particles with the ordinary refractive index of the LC material. If desired, the transparent state can be turned black by simply adhering a black background film to the cell.

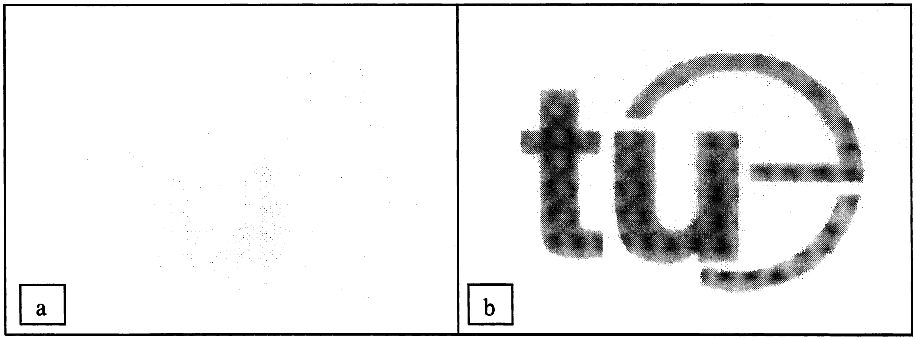


Fig. 4. a) Scattering off-state and b) transparent on-state for a PFN cell with a cell thickness of 14 μm, filled with a 10/90 % wt/wt polymer/liquid crystal blend containing 85 nm sized particles. Logo-cell distance is equal to 3 mm.

In the second part of this study, mixtures were investigated based on the commercially available LC mixture E7 and a fifth generation palmitoyl-functionalised poly(propylene

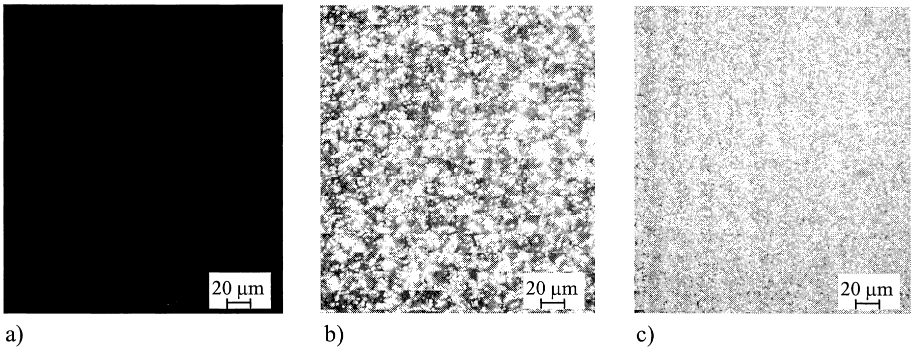


Fig. 5. Optical micrographs of a) the pure LC E7, b) a 3.5/96.5 % wt/wt dendrimer/LC blend, and c) a 10/90 % wt/wt dendrimer/LC blend.

imine) dendrimer, namely a poly(propylene imine) dendrimer with a 1,4-diaminobutane core molecule, functionalised with 64 palmitoyl endgroups, with NHCO as the type of linkage (c 72 I)[28]. Mixtures of the LC and the palmitoyl-dendrimer were prepared containing 0-50 % wt/wt dendrimer. The mixtures were homogenised by heating above the melting temperature of the semi-crystalline dendrimer. Upon cooling of the mixtures, highly viscous pastes were formed. Electro-optical cells with a thickness of 6 μm were prepared. Planar alignment was provided by rubbed polyimide layers. The sample cells were capillary filled with the dendrimer/LC mixtures at elevated temperatures.

Figure 5 shows optical microscopy photographs of the sample cells filled with,

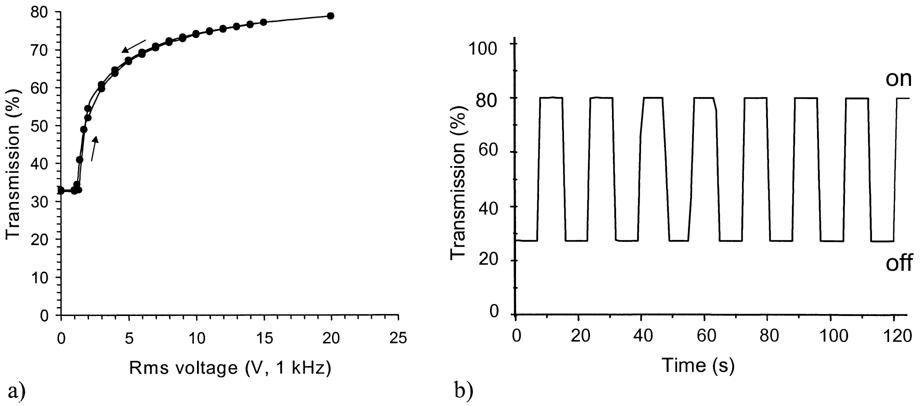


Fig. 6. a) Transmission-voltage characteristic and b) transmission as a function of time during repeatedly applied step-voltages, for a 6 μm thick cell with planar alignment filled with a 10/90 % wt/wt dendrimer/LC blend.

respectively, the pure LC E7, a 3.5/96.5 % wt/wt dendrimer/LC blend and a 10/90 % wt/wt dendrimer/LC blend, between crossed polarisers. As expected, the planary aligned pure LC appears black between crossed polarisers when the nematic director is parallel to one of the two polarisers. Upon addition of only 3.5 wt% of palmitoyl-dendrimer to the LC material, the LC matrix already becomes distorted and a polydomain structure with random orientation is observed. By the addition of 10 wt% of palmitoyl-dendrimer, this distortion of the orientational order becomes even more obvious, and the domain size is further reduced. Also, the cells filled with the palmitoyl-dendrimer/LC blends exhibit light scattering in the off-state, which becomes stronger with increasing dendrimer content.

Electro-optical experiments were performed with the cells filled with the dendrimer/LC blends. Figure 6 shows the transmittance-voltage curve for an electro-optical cell filled with a 10/90 % wt/wt palmitoyl-dendrimer/LC blend. The figure shows that the scattering polydomain state can indeed be switched to a transparent monodomain on-state. Rather surprisingly, extremely low switching voltages are observed in combination with excellent switching kinetics. Moreover, reversible switching is observed (Fig. 6b) between the scattering off-state and the transparent on-state without the occurrence of significant hysteresis effects.

Next, the electro-optical characteristics were recorded for several dendrimer/LC blends, with dendrimer content ranging from 0 to 50 % wt/wt. In Figure 7 the contrast ratio between the off- and on-state as a function of the blend composition is shown. Apparently, optimal contrast ratios are obtained for blends, of which the content of the dendritic disperse phase is approximately 10 to 20 % wt/wt.

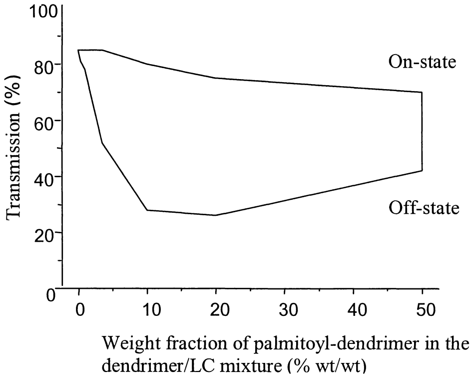


Fig. 7. Transmission-window for 6 μm thick cells with planar alignment filled with palmitoyl-dendrimer/LC mixtures.

Conclusions

Via radical dispersion polymerisation in organic medium, well-defined, crosslinked polymer particles were produced in a broad range of particle sizes. Rheologically stable, paste-like blends were prepared based on polymer particles with diameters ranging from about 80 to 800 nm and liquid crystalline materials. The polymer/LC blends appear to be completely phase separated and can be electrically switched from a scattering to a transparent state by the application of relatively high voltages.

Electro-optical switches were also produced based on mixtures of a dendrimer and a liquid crystalline material. The best switching characteristics were obtained with 10/90 and 20/90 % wt/wt dendrimer/LC mixtures. These blends can be reversibly switched between a scattering and a transparent state by the application of extremely low voltages. Moreover, hysteresis effects during repeated switching of the blends were hardly observed.

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