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Thermo-Reversible Gelation of Liquid Crystals using Di-Benzylidene-D-Sorbitol

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Abstract

Mechanically stable thermo-reversible gels of the liquid-crystal LC-E7 with 1,3:2,4-Di-O-benzylidene-D-sorbitol (DBS) form white light-scattering films that are reversibly switchable to a clear state by AC electric fields. It is established that the light-scattering nature of DBS/LC-E7 gels is an intrinsic material property that originates from the occurence of a monotectic-type point (``mesotectic´´) at very low DBS-concentration in the phase diagram of the DBS/LC-E7 system.

Introduction

In the current contribution we report on the phase behaviour of a thermo-reversible electro-responsive gel consisting of the commercially available ingredients 1,3:2,4-Di-O-benzylidene-D-sorbitol (DBS)[1] and the liquid-crystal LC-E7. From the (quasi-binary) phase diagram of

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DBS/LC-E7, based on differential scanning calorimetry (DSC) thermograms, it is concluded that the DBS/LC-E7 system displays a monotectic-type[2] 3-phase equilibrium $\{L\} = \{N+C_2\}$, in which isotropic liquid $\{L\}$ coexists with a birefringent liquid $\{N\}$ and a solid-like $\{C_2\}$ phase. Previously, the term ‘‘mesotectic´´ was introduced for this equilibrium-type to denote that it is an intermediate of true monotectic, for which $\{L_1\} = \{L_2+C_2\}$, and a eutectic $\{L_1\} = \{C_1+C_2\}$.[3] Of specific importance to the current work is the location of the ``mesotectic´´ in the phase diagram of DBS/LC-E7, resulting in the formation of white light scattering films at all practically relevant materials compositions. Since the gelled films are demonstrated to be reversibly switchable to a clear state upon application of an AC-electric field, DBS/LC-E7 may be used in scattering-based display applications. In this respect, the system forms an alternative to Polymer Dispersed Liquid Crystals (PDLCs),[4,5] anisotropic gels based on LC-diacrylate networks,[6] and LC-phases stabilised with fumed silica particle networks.[7]

Experimental

1,3:2,4-Di-O-benzylidene-D-sorbitol (T_m = 225 °C, ρ = 1.04 g/cm^3, purity > 96%), with the trade name Millad 3905, was used as received from Milliken Chemical. LC-E7, a multicomponent cyanobiphenyl and terphenyl mixture (see Ref. 8 for its composition; $T_{N/I}$ = 60 °C, ρ=1.06 g/cm^3, $\varepsilon_{//}$ = 19 and $\varepsilon_{\perp}$ = 5.2, and Δn = 0.225), was used as obtained from Merck.

Samples were prepared by dissolving mg-amounts of DBS in droplets of LC-material at elevated temperatures (up to 190 °C for the samples containing the highest amounts of DBS). Since LC-E7 shows a somewhat increased evaporation at these temperatures, sample compositions were determined by re-weighting after cooling to room temperature.

Calorimetric analysis was performed using a Perkin Elmer DSC 7 differential scanning calorimeter (DSC). Experiments were run at 10 °C/min in O-ring sealed pans (Perkin Elmer, type nmbr. 0319-0218), suppressing vaporisation heat effects. Before sealing the filled capsules, their contents was homogenised at elevated temperatures and the composition was determined by re-weighting.

Electro-optical cells were prepared by mounting two glass plates coated with transparent ITOelectrodes (Type 327 735 PO from Merck) on top of each other with a UV sensitive sealant (UVS 91 by Norland Products Inc.) applied to the edges, and subsequent curing. No orientation layers were used. Mono-disperse silica spheres, applied to one of the plates by spin coating from a volatile alcohol dispersion (10 s at 1000 rpm), assured a 18 μm spacing between the plates. Finally, cells were rapidly filled by capillary action at temperatures well above the sol-gel transition of the particular sample.

Results and Discussion

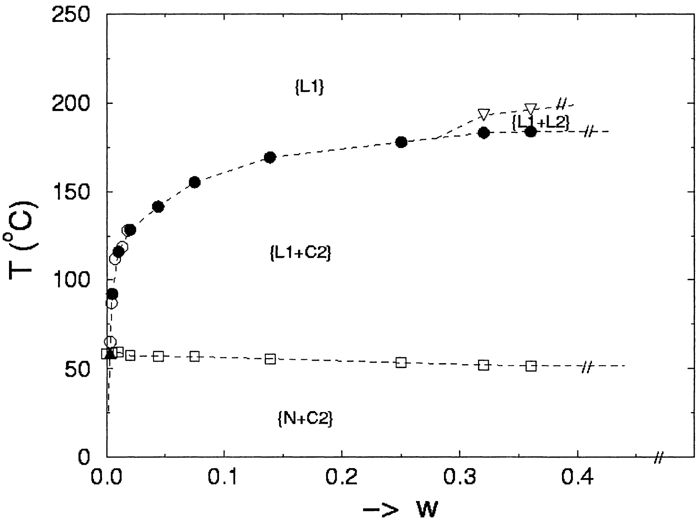

Figure 1: Phase diagram of the DBS/LC-E7 system. Transition temperatures (□), (●), (∇) were measured by DSC (see Figs. 3-4) and (○) by microscopic observations of ``gel melting´´. The symbol (▲) indicates the mesotectic 3-phase equilibrium $\{L_1\} = \{N+C_2\}$.

A (partial) phase diagram of the DBS/LC-E7 system is shown in Fig. 1, where the transition temperatures as observed by DSC are plotted *versus* the material composition (*w* is the weight fraction DBS). It should be noted that LC-E7 is a multicomponent mixture, and thus, an interpretation in terms of a binary phase diagram such as Fig. 1 is not strictly correct.

Nevertheless, the phase diagram provides essential insights justifying its use. As shown in Fig. 1, we have only examined the composition range $w \leq 0.35$ ($\equiv T \leq 200\ ^{\circ}\mathrm{C}$), because dissolving increased amounts of DBS requires heating to higher temperatures for which thermogravimetric analysis of the LC material shows significant weight-loss.

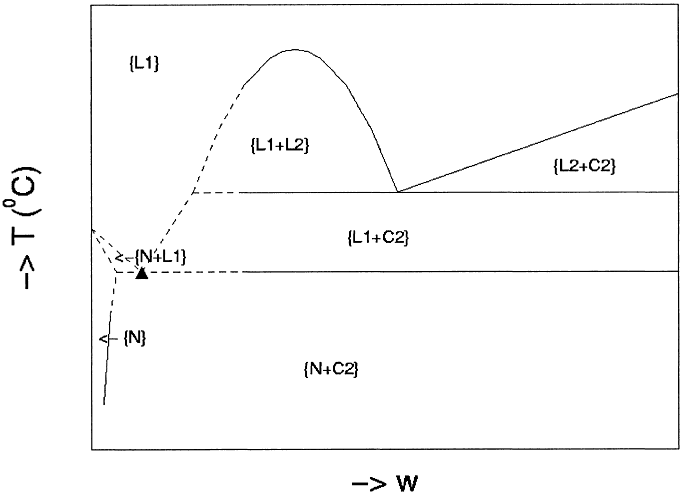

Figure 2: Schematic diagram of the DBS/LC-E7 phase behaviour. The mesotectic point is indicated by (▲). Dotted lines represent observed transitions as condensed in Fig. 1. Full lines are tentative extrapolations of the observed phase behaviour not confirmed by experiments.

In Fig. 1, which is based on the DSC melting traces shown in Figs. 3-4, four characteristic regions, $\{L_1\}$, $\{L_1+L_2\}$, $\{L_1+C_2\}$ and $\{N+C_2\}$, separated by three characteristic transitions (□), (● and ○) and (∇) are observed. In the region $\{L_1\}$, the DBS/LC-E7 system appears as an isotropic liquid. In the other regions two phases coexist: isotropic LC-rich and DBS-rich liquids in the $\{L_1+L_2\}$-region; an isotropic LC-rich liquid and a finely dispersed well-ordered network phase in the $\{L_1+C_2\}$-region (this is the isotropic gel region);[3,9-11] and a birefringent LC-rich liquid and the network in the $\{N+C_2\}$-region (this is the anisotropic gel region).[3,9-11] The transitions in Fig. 1 correspond to respectively the nematic-isotropic transition of the LC-rich phase (□), the sol-gel transition at which the DBS network is formed/broken (● and ○), and liquid-liquid phase separation (∇). The phase behaviour of the DBS/E7-system has also been studied by optical microscopy which, in fact, allowed detection of gelation in samples with weight fractions DBS as low as 0.3 wt % (DSC gave only signals down to 0.5 wt %; see Fig. 1).

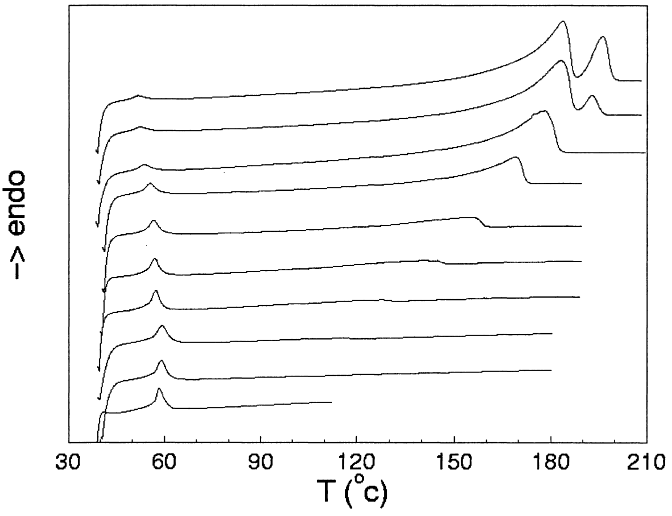

Figure 3: DSC thermograms of, from top to bottom, 36.3 wt % DBS/LC-E7; 32%; 25%; 13.9%; 7.5%; 4.5%; 2%; 1%; 0.5%; and 0% (neat E7).

As shown in Fig. 1, the phase separation in the $\{N+C_2\}$-region is nearly complete, i.e., a well-ordered sub-micron scale $\{C_2\}$-phase coexists with a $\{N\}$-phase, consisting of nearly pure LC material. In the $\{N\}$-phase, the environment of the LC molecules is liquid-like, allowing the LC molecules to maintain their (speed of) response to an electric field. Macroscopically, on the other hand, due to the $\{C_2\}$ network, the DBS/LC-E7 system behaves as a visco-elastic solid.

In Fig. 1 we have also marked the location of a mesotectic 3-phase equilibrium point $\{L_1\} = \{N+C_2\}$ (▲)[3] at $w \approx 0.003$ and $T = 58.5^\circ$C. The presence of this point in the phase diagram of DBS/LC-E7 may not be immediately obvious from the data displayed, but is a direct consequence of the indisputable existence of a $\{N+L_1\}$ coexistence region at low w, as is understood from the schematic picture in Fig. 2.

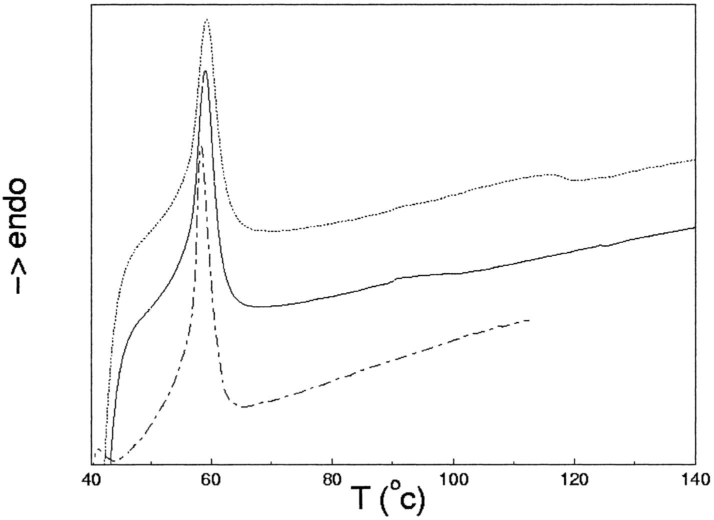

Figure 4: DSC traces of 1 wt % DBS/LC-E7 (dotted line); 0.5 wt % (solid line); and neat E7 (dash-dotted line). Thermograms are enlarged versions of traces shown in Fig. 3 to more clearly depict the weak signals associated with the sol-gel transition at $T \approx 115\ ^\circ C$ (1%; dotted line) and $T \approx 95\ ^\circ C$ (0.5%; solid line). The figure also shows the increased $T_{N/I}$ for the 1 wt % and 0.5 wt % DBS samples.

Since the mesotectic point is located very close to the $w = 0$ -axis, cooling of practically relevant material compositions, $0.005 \leq w \leq 0.05$, implies passing the point from the right hand side for which T_{SG} (•) > $T_{N/I}$ (□) (see Figs. 1-2). Thus, since the N/I-transition always occurs in a highly viscous (gelled) material, the LC-molecules can not be oriented by weak external forces such as polyimide (PI) orientation layers and macroscopically oriented structures (e.g., twisted nematic configurations) can not be obtained. Alternatively, the network causes μm-scale spatial director variations, resulting in a strongly enhanced light scattering when compared to neat LC-E7, which can be exploited in scattering-based display applications or projection systems.

In principle, refractive index differences between the network and (birefringent) liquid phase may also contribute to the scattering, However, since the material becomes perfectly transparent when heated into the isotropic gel state, we believe this to be a minor effect, as also follows from the typical size of the aggregates in DBS gels (<< 100 nm).[1,12]

When looking at the details of the DSC thermograms in Figs. 3-4, it is seen that $T_{N/I}$ initially rises about 1 °C with increase of DBS content, followed by a decrease of over 6 °C. Further, a broadening and weakening of the DSC-signals occurs. This is all in striking agreement with DSC traces of the LC-material p-azoxyanisole in contact with a range of well-defined porous materials.[13] Dadmun *et al.*[13] explain these phenomena in terms of a balance between surface-induced ordering of the LC material (important in materials with larger pores) and weakening of order due to pore-confinement in materials with small pores. Thus far, we adopt an identical explanation for the thermal behaviour of the current system, since pore sizes reported in Ref. 13 are commensurate with previously estimated mesh-sizes of DBS networks in ethylene glycol[12] and isotactic polypropylene,[1] and because work in progress on binary gels composed of 12-hydroxyoctadecanoic and 4-n-pentyl-4'-cyanobiphenyl (K15) shows the same trends, thus ruling out that the observations are caused by the multicomponent nature of LC-E7.

With regard to the mechanical properties of the gels, it was noticed that the gels produced show stable visco-elastic material behaviour. No weakening was observed over periods of several months. Gel strengths were found to be in the range 600 Pa - 2000 Pa (corresponding to loads of 6 - 20 g/cm^2) for samples containing 0.5 wt % - 3 wt % DBS. These values imply that gelled films can easily hold a top layer such as a a diacrylate coating which, in our opinion, is indicative of the potential that thermo-reversible LC-gels may have in large area applications.

In Fig. 5, a photograph of an 18 μm thick non-pixelated demonstrator cell with an area of 30 x 30 mm shows that the thermo-reversible gel concept indeed allows to create electro-optically active cells that are reversibly switchable at 80 V between a scattering-off and a transparent-on state. Clearly, both the clarity of the on-state and the amount of scattering in the off-state are promising with regard to application purposes. Benefits of the type of system explored by us, when compared to conventional PDLC systems, are its thermo-reversibility (that may be explored in a continuous production line), the very low amounts of gelling agent needed, and the ease of gel manufacturing (in contrast to diacrylate gels, no UV curing is needed). Additional benefits may lie in the large variety of gelling agents that have been discovered over the past years.[14] On the other hand, the operating voltage (80 V) that is currently required is high when compared to the15 V used in a 7 μm thick PDLC cell optimised at Philips Research.[15] (The difference is partially explained by the disparity in cell thickness, since $V_{appl} \sim d_{cell}$.)

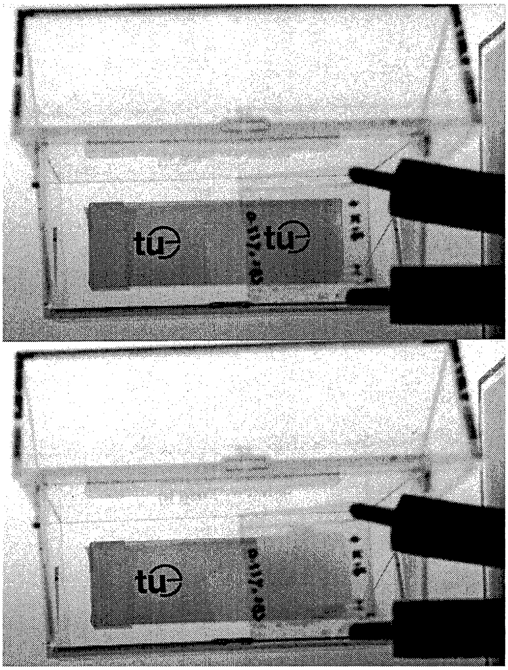

Figure 5: The transparent on- (top) and light scattering off-state (bottom) of a 30 x 30 mm cell filled with a 1 wt % DBS/LC-E7 mixture. In the on state an 80 V 100 Hz AC voltage was supplied with the aid of a Keithley Source Measurement Unit. In the photograph, the distance between the cell and the displayed symbol is approximately 10 cm.

Conclusions

The phase behaviour of the thermo-reversible LC-gel forming system comprising the commercially available ingredients 1,3:2,4-Di-O-benzylidene-D-sorbitol (DBS) and LC-E7 has been investigated by differential scanning calorimetry. It was found that the phase diagram displays a monotectic-type point, which we refer to as ‘‘mesotectic´´, at which a liquid is in equilibrium with a solid and a mesophase. Further, it was shown that the location of the mesotectic point at extremely low weight fractions of DBS, allows manufacturing of white light-scattering films at all practically relevant material compositions. Finally, a non-pixelated 30 x 30 demonstrator cell showed that DBS/LC-E7 is reversibly switchable to a clear state by AC electric fields.

Acknowledgements

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