Infra-red Study on the Evolution of the Polymerization of Mesogenic Diacrylates in a Low Molecular Mass Liquid Crystal Matrix

Pascal Gautier [a] [c] , Monique Brunet [a] , Naci Basturk [b] & Joachim Grupp [b]

[a] GDPC Université Montpellier II, c.c. 026, F-34095, Montpellier, France

[b] ASULAB S.A., rue des Sors 3, CH-2074, Marin-Epagnier, Switzerland

[c] ASULAB., rue des Sors 3, CH-2074, Marin

PLEASE SCROLL DOWN FOR ARTICLE

Infra-Red Study on the Evolution of the Polymerization of Mesogenic Diacrylates in a Low Molecular Mass Liquid Crystal Matrix

PASCAL GAUTIER[*][¶], MONIQUE BRUNET[*], NACI BASTURK[b] AND
JOACHIM GRUPP[b]

[*]GDPC Université Montpellier II, c.c. 026, F-34095 Montpellier, France;
[b]ASULAB S.A., rue des Sors 3, CH-2074 Marin-Epagnier, Switzerland

Infra-red spectroscopy has been used to follow the evolution of the photopolymerization of mesogenic diacrylates in a liquid crystal matrix. The kinetic is a first order one as in isotropic solvents. The rate constant and the final conversion ratio depend on the monomer concentration. The order parameter of the liquid crystal decreases during polymerization due to reorganization. The electro-optical characteristics of a gel depend on the nature of the monomer and on the density of cross-linked bonds. A reversible electro-optical behaviour is observed with a high density of cross-linked bonds. Gels with low densities of cross-linked bonds exhibit a memory effect.

<u>Keywords</u> gel; diacrylates; polymerization; infra-red; kinetic; electro-optic

INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) are of considerable interest for a large number of display applications, because of the high transmittance in the clear state which is due to the operation without polarizers. The disadvantages of PDLCs are their high operating voltage, their slow response time and a residual scattering, called haze, which stays in the clear state [1]. New gels made from reactive mesogenic diacrylates and low molecular

¶ Author for correspondence, current address ASULAB., rue des Sors 3, CH-2074 Marin

mass cyano-biphenyl liquid crystal overcome some of these drawbacks [2]. However, the preparation parameters must be controlled in order to optimize the electro-optical properties of these gels such as memory effect, contrast ratio, switching voltages, etc.

The anisotropic gels are interconnected two-phase systems of free low molecular mass liquid crystals molecules and cross-linked polyacrylate molecules [2]. The gels are obtained by in-situ photopolymerizing a mixture of non reactive liquid crystals molecules and diacrylate molecules in a cell with alignment layers. The network in the gels possesses the structure of the initial mixture [3]. The liquid crystals molecules are not chemically attached to the polymer network. There are no long range fluctuations in the refractive indices within the gel, so no light scattering is observed [2], but the application of an electric field can induce light scattering [3].

We use infra-red spectroscopy to investigate the influence of the polymerization process on the light scattering as function of the applied voltage (electro-optical properties) in the anisotropic gels, in the confined geometry of a liquid crystal cell.

EXPERIMENTS

Samples

In this study, a diacrylate monomer (either RM1 modified which is a mesogen or RM249 which is not a mesogen) is dissolved at different concentrations in a nematic cyanobiphenyl mixture (E7) doped with the photoinitiator Irgacure 369 (Ciba Geigy).

MONOMER A   **RM1®**   ®MERCK Ltd·
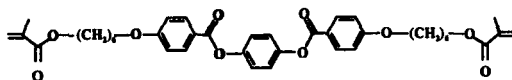
MONOMER B   **RM 249®**

LIQUID CRYSTAL   Principal constituent of E7®

The usable concentration range of monomers is limited at high concentration by the solubility limit in E7 and at low concentration by the sensitivity of the FTIR spectrometer (Perkin Elmer 1725X).The filled sample

cells are illuminated with a tungsten mercury lamp (1.69mW/cm² at 50 cm). The cells are made of calcium fluoride which is transparent to UV radiations, needed for the photopolymerization, and to IR l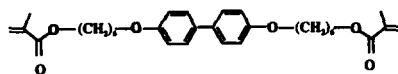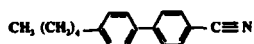ight used for the measurements, figure A. The alignment layer is a rubbed polyimide which is transparent to infra-red due to its low thickness of 100 Å. The cell gap is controlled by 9 μm spacers.

Calcium fluoride

9 μm spacers

Rubbed polyimide alignement layer
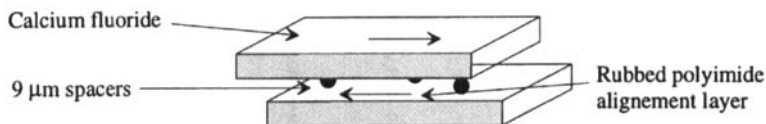
FIGURE A   Cell for infra-red measurements

Infra-red measurements

The monomers are linked to each other through the opening of the double bond C=C of the acrylate group caused by the decomposition of the initiator. The progress of the polymerization of acrylates is normally measured by a decrease in the absorbance of the double bond C=C (1640 cm^{-1}). But this absorption is too weak to be a convenient probe, because of the low concentrations of the monomer and the small sample volume, figure 1a.

FIGURE 1a Infra-red spectra of LCDP with 1.5% mol. of monomer A
Before polymerization ———— and after ....

The double bonds C=C and C=O of the acrylate group are conjugated. The double bond C=C, and consequently the conjugation, disappears after polymerization, figure B.

Before polymerization   **After polymerization**
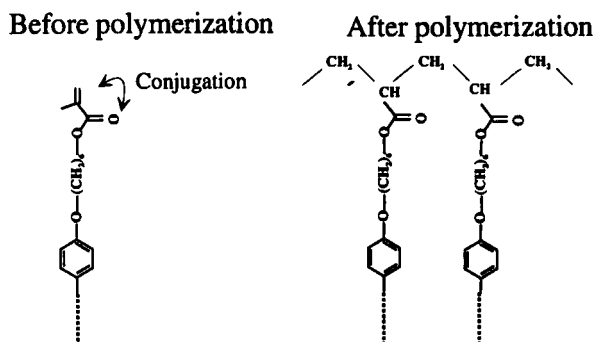
FIGURE B   Structure of polyacrylates
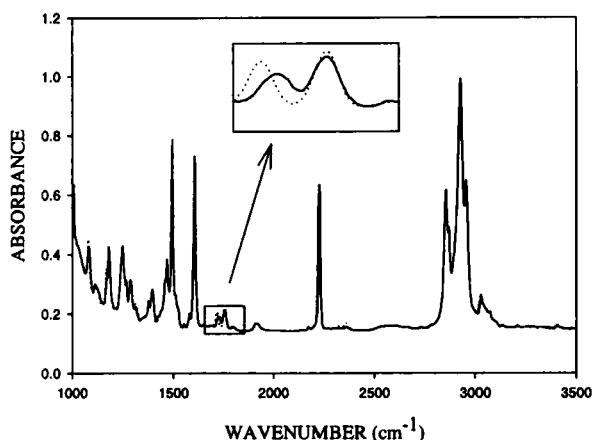
The absorption frequency of the conjugated C=O is lower than that of the non conjugated one. During the polymerization, a new peak appears at 1724 cm^{-1} while the conjugated C=O peak at 1716 cm^{-1} decreases, figure 1b. These two peaks are deconvoluted using a commercial software. The integrated area of the 1716 cm^{-1} peak is used to calculate the relative concentration of free monomers.

FIGURE 1b   Spectrum of a gel containing 1.5% mol. of monomer A after 5s under UV light.
——— Spectrum measured ······· Fitted spectrum —— Deconvoluated peaks

The order parameter $<P_2>$, equation (2), of the E7 liquid crystal in the gel is determined by the dichroic ratio D, equation (1), of the stretching vibration mode of the nitrile (CN) group (2226 cm^{-1}) [4].

$$D = \frac{A_\parallel}{A_\perp} \tag{1}$$

$$< P_2 >= \frac{gD-1}{gD+2} \times \frac{1}{1-\frac{3}{2}\sin^2\alpha} \tag{2}$$
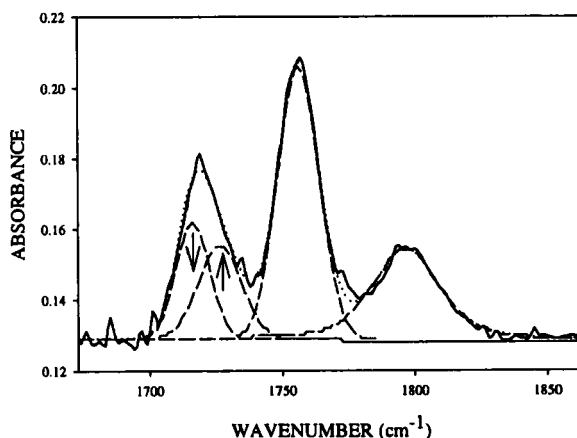
g is a local field correction factor which is 1.52 for cyanobiphenyl liquid crystals [4] and α is the angle between the transition moment and the molecular axis. The angle α is close to zero for the CN stretching mode [4]. We used a wire grid polarizer to measure absorptions parallel and perpendicular to the director of the liquid crystal. The cells were maintained at a constant temperature of 22 °C during the polymerization and the measurements. This insures that the measurements of the order parameter as well as the parameters of polymerization are not affected by environment temperature variations.

Electro-optical measurements
The electro-optical properties measured are the contrast ratio CR, equation (3), the threshold voltage and the memory parameter M.

$$CR = \frac{T_{10}}{T_{90}} \tag{3}$$

$$M = \frac{T_r - T_0}{T_0} \tag{4}$$

T_{10} is the 10% value of the initial transmission T_0 and T_{90} is the 90% transmission. T_r is the transmission at 0V after a scan of the applied voltage up to 60V. The electro-optical measurements were carried out using a waveform generator and a lock-in amplifier controlled by a computer.

RESULTS

Conversion ratio and kinetic of polymerization

We verified that the photopolymerization stops when UV light is removed and restarts with a new exposure. We measured the concentration of monomers between each exposure. In this way we followed the evolution of the polymerization as a function of the cumulate time t.

The conversion ratio Cvr is the proportion of the concentration of free monomers at a time t $[M]_t$ after the polymerization has started with the initial concentration of free monomers $[M]_{t=0}$, see equation (5).

$$Cvr(\%) = \frac{[M]_t}{[M]_{t=0}} \times 100 \qquad (5)$$

The concentration of free monomers is proportional to the absorption of the conjugated carbonyl group (C=O) at the wavenumber of $1716 \, cm^{-1}$.

The final conversion ratio reached in the gel depends on the initial concentration of monomers and on their nature, figure 2.
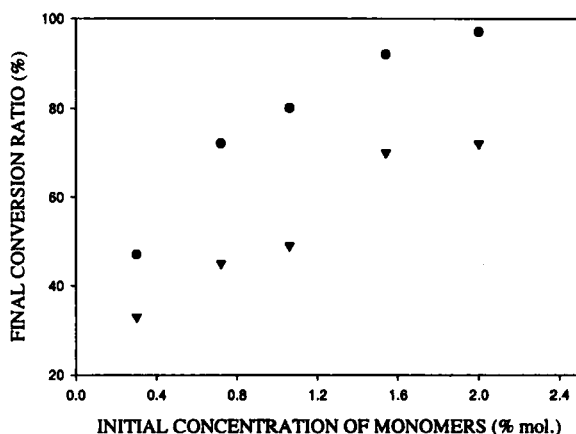

FIGURE 2 Plot of final conversion ratio versus initial molecular concentration of reactive monomers.   ● monomer A   ▼ monomer B

With an identical initial molar concentration, the conversion ratio reached for gels with monomer A is higher than that reached for gels with monomer B. This is probably due to their different chemical structure.

Two regimes are observed during the conversion. The first one lasts less than one minute and is characterised by a high conversion rate which is reaction limited or limited by the diffusion of the monomers. During this

regime a phase separation occurs between the low molecular mass liquid crystal and the polymer rich phase. During this phase separation, soluble micro-networks, the occurrence of which was introduced by C.V. Rajaram et al. to explain the results of morphology analysis [6], grow to become non soluble primary polymer particles. During the second regime, which lasts several hours, an aggregation process of the polymer particules leads to the formation of a network. The conversion rate of the regime is diffusion-limited by the primary polymer particles like in diffusion-limited aggregation found in colloid systems [6].

The polymerization of diacrylates in isotropic solvent obeys a first order kinetic [5] in diluted systems, equation (6).

$$[M]_t = [M]_{t=0} e^{-kt} \qquad\qquad (6)$$

An exponential fit of the conversion ratio versus time, represented by lines in figure 3 and 4, shows that the kinetic is also a first order one in a nematic medium during the first regime. We determine the rate constant k as a parameter of the fit. The molecular organization of the nematic phase seems not to affect the kinetic of polymerization. Such observations have already been reported by D.J. Broer in photo-DSC studies [8].
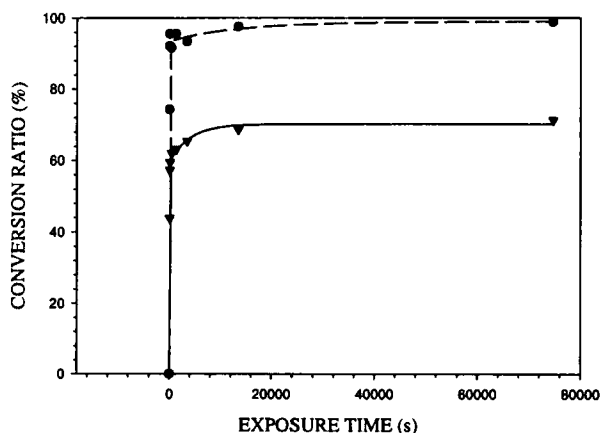

FIGURE 3   Plot of conversion ratio versus exposition time to UV light
for a concentration of 1.5 % mol. of   ●   monomer A   ▼   monomer B
——— Exponential fits
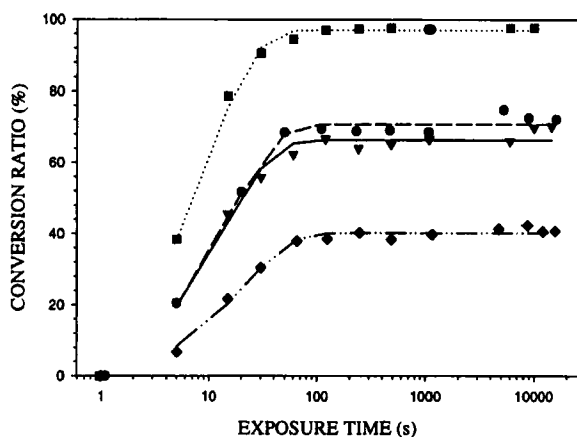— —

P. GAUTIER *et al.*

FIGURE 4   Plot of conversion ratio versus exposition time to UV light
for 2 concentrations: 2.0 % mol. of ■ monomer A ▼ monomer B
0.7 % mol. of ● monomer A ◆ monomer B

The rate constant of the first regime increases with the concentration of monomer due to the higher probability for a growing chain to find a monomer in the medium, figure 5. However, the rate constant decreases at high concentration. We attribute this to an increase of the viscosity, also named vitrification effect [5], which limits the diffusion of reactive species. At high concentration of monomer the first regime becomes a diffusion limited process like the second one.
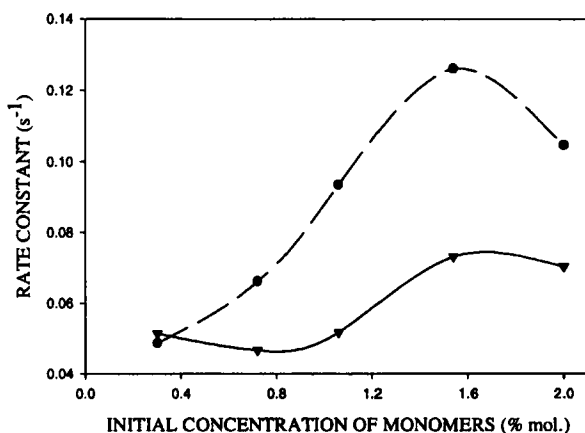

FIGURE 5   Plot of rate constants
versus initial concentration of monomers
—●- - monomer A   —▼— monomer B

Order parameter

The order parameter of the liquid crystal in the gel decreases during the exposure to UV light, figure 6, whereas the order parameter of the liquid crystal alone remains constant during the same exposure time. The exposure to UV light is sufficient to polymerize gels without damaging the liquid crystal. We attribute the decrease of the order parameter in the gel to the phase separation between the liquid crystal and the polymer particles. This is shown by the fact that the amplitude of the decrease is related to the conversion ratio, figure 7. We did not observe any significant variations of the order parameter during the second regime.
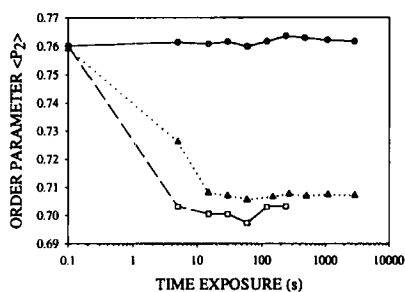

FIGURE 6   Plot of the order parameter
of the liquid crystal E7 versus exposition time to UV light.
The gels have an initial concentration
of 2 % mol. of monomers.
—●— Liquid crystal E7
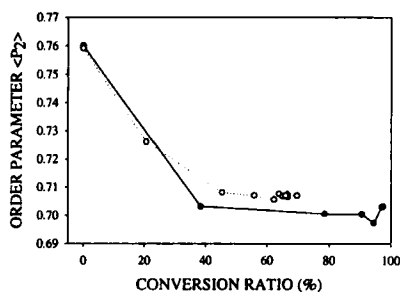—□— Gel with monomer A   ···▲··· Gel with monomer B

FIGURE 7   Plot of the order parameter
versus the conversion ratio.
the gel contains 2% mol. of monomer
—●— monomer A   ·○· monomer B

Electro-optical properties

The gels made with monomer A show a reversible electro-optical behaviour, figure 8, whereas the gel made with monomer B exhibits a memory effect, figure 9.
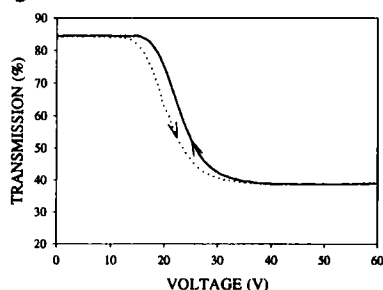

FIGURE 8   Plot of the transmission of the gel
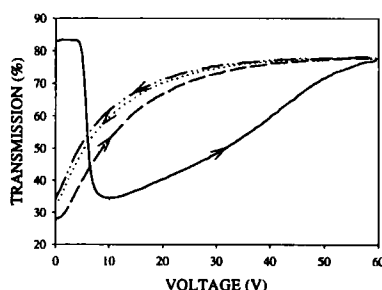versus the applied voltage.
1.5% mol. of monomer A.

FIGURE 9   Plot of the transmission of the gel
versus the applied voltage.
1.5% mol. of monomer B.

····· First scan   ═══·· Second scan

In figure 10 and 11, the electro-optical characteristics of the gel are plotted as a function of the relative density of cross-linked bonds which is the product of the conversion ratio and the initial monomer concentration.
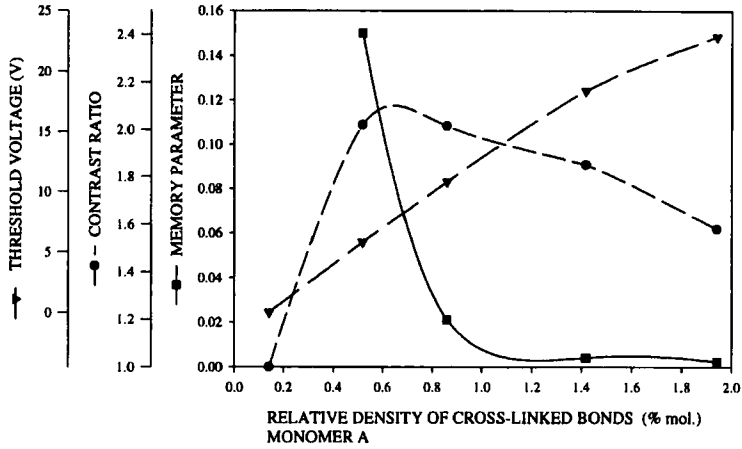

RELATIVE DENSITY OF CROSS-LINKED BONDS (% mol.)
MONOMER A

FIGURE 10 Plot of the electrooptical characteristics
versus molecular concentration of monomer A

RELATIVE DENSITY OF CROSS-LINKED BONDS (% mol.)
MONOMERS B
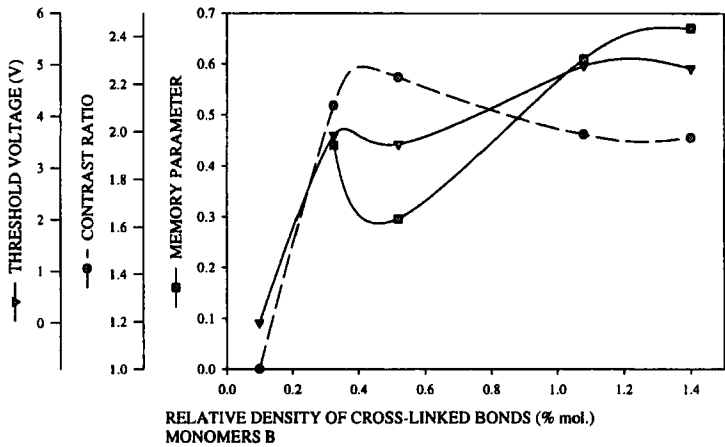
FIGURE 11 Plot of the electrooptical characteristics
versus molecular concentration of monomer B

For gels with both monomer A and B the maximum contrast ratio is reached at 0.5% of density of cross-linked bonds and decreases for higher densities, by about 20% for gels with monomer A and by 10% for gels with monomer B. The threshold voltage curve versus density of cross-linked bonds increases quasi linearly for gels with monomer A. The threshold voltage for

gels with monomer B increases weakly versus the relative density of cross-linked bonds. The threshold voltage is greater for gels with monomer A than for gels with monomer B. This is due to the differences in morphology and in interactions at the liquid crystal-polymer interface between both these types of gel. The memory parameter curve decreases to zero for gels with monomer A whereas it increases for gels with monomer B. These differences are related to the polymerization parameters and to the nature of the monomers.

The fact that the electro-optical characteristics of a type of gel, such as the contrast ratio and the threshold voltage, have an opposite dependence on the relative density of cross-linked bonds implies that a compromise must be chosen in order to optimise their performances. A gel with a high relative density of cross-linked bonds (monomer A) and a low memory parameter should be preferred for display applications whereas a gel with a low relative density of cross-linked bonds (monomer B) and a high memory parameter is more suitable for optical storage devices.

The conversion ratio reached with monomer A (95%) is higher than that reached with monomer B (70%). A high conversion ratio reduces the presence of polymer fragments inside the liquid crystal domains. These fragments induce the memory effect [7], see figure C.
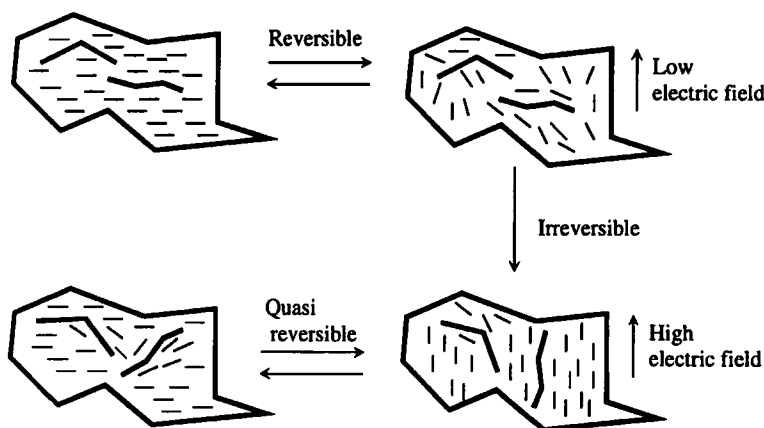

FIGURE C   Effect of electric fields on polymer fragments [7]

The irreversible behaviour is due to the fact that polymer fragments do not manage to relax back at their initial position after application of a high electric field. This is equivalent to a plastic deformation in solid materials.

P. GAUTIER *et al.*

CONCLUSION

Two different regimes are observed during polymerization. The first one is governed by a first order kinetic similar to that observed in isotropic solvent. The order of the liquid crystal decreases during the first regime and remains constant in the second one. The nature of the monomer and the control of the relative density of cross-linked bonds determine the electro-optical properties of nematic gels.

REFERENCES

[1] Yamada et al., *Eurodisplay 93 Conference Proceedings*, p.401

[2] R.A.M. Hikmet, *J. Appl. Phys.* 68(9), 1. Nov. 90, 4406-4412

[3] R.A.M. Hikmet, in *Liquid Crystals in Complex Geometries* edited by G.P Crawford and S. Zumer (Taylor & Francis Ltd, 1996), chap. 3

[4] I. Khoo & S. Wu in *Optics and non Linear Optics of Liquid Crystals* (Word Scientific Publishing Co 1993), p.64

[5] J.P. Mercier, *Polymérisation des monomères vinyliques* (Presses Polytechniques Romandes, Lausanne 1983), p.17

[6] C.V. Rajaram et al., Chem. Mater., 1995, **7**, 2300-2308

[7] L. Bouteiller et al., Liquid Crystals, 1994, **17**, No5, 709-716

[8] D.J. Broer, in *Liquid Crystals in Complex Geometries* edited by G.P Crawford and S. Zumer (Taylor & Francis Ltd, 1996), p.243-244