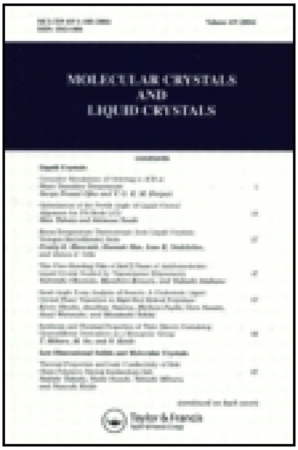


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Effects of Ultraviolet-curing conditions on the electro-optical behavior of polymer dispersed liquid crystal films

F. Z. Abdoune [a], L. Benkhaled [c], X. Coqueret [c], U. Maschke* [c] & L. Mechernene [d]

[a] Laboratoire de Chimie Macromoléculaire (UMR CNRS NO. 8009), France

[b] Laboratoire de Recherche sur les Macromolécules, Université Aboubakr Belkaïd, Tlemcen, Algeria

[c] Laboratoire de Chimie Macromoléculaire (UMR CNRS NO. 8009), Université des Sciences et Technologies de Lille, France

[d] Laboratoire de Recherche sur les Macromolécules, Université Aboubakr Belkaïd, Tlemcen, Algeria

Version of record first published: 18 Oct 2010

To cite this article: F. Z. Abdoune, L. Benkhaled, X. Coqueret, U. Maschke* & L. Mechernene (2004): Effects of Ultraviolet-curing conditions on the electro-optical behavior of polymer dispersed liquid crystal films, Molecular Crystals and Liquid Crystals, 422:1, 163-172

To link to this article: http://dx.doi.org/10.1080/15421400490502508

*Mol. Cryst. Liq. Cryst.*, Vol. 422, pp. 163/[433]–172/[442], 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490502508

# EFFECTS OF ULTRAVIOLET-CURING CONDITIONS ON THE ELECTRO-OPTICAL BEHAVIOR OF POLYMER DISPERSED LIQUID CRYSTAL FILMS

*F. Z. Abdoune,*
*Laboratoire de Chimie Macromoléculaire (UMR CNRS NO. 8009)*
*Bâtiment C6, Université des Sciences et Technologies de Lille*
*F-59655 Villeneuve d'Ascq Cedex, France*
*and*
*Laboratoire de Recherche sur les Macromolécules,*
*Faculté des Sciences, Université Aboubakr Belkaïd*
*BP 119, 13000 Tlemcen, Algeria*

*L. Benkhaled, X. Coqueret, and U. Maschke**
*Laboratoire de Chimie Macromoléculaire (UMR CNRS NO. 8009)*
*Bâtiment C6, Université des Sciences et Technologies de Lille*
*F-59655 Villeneuve d'Ascq Cedex, France*

*L. Mechernene*
*Laboratoire de Recherche sur les Macromolécules,*
*Faculté des Sciences, Université Aboubakr Belkaïd*
*BP 119, 13000 Tlemcen, Algeria*

*The electro-optical behavior of Polymer Dispersed Liquid Crystal (PDLC) films was studied to understand the relationship between the conditions of preparation in terms of the extent of curing, the morphology, and the response to an external electrical field. The PDLC films were prepared by phase separation of a diacrylate/nematic liquid crystal mixture induced by Ultraviolet (UV) curing for two irradiation doses, 50 mJ/cm$^2$ and 150 mJ/cm$^2$. The transmission vs voltage curves were investigated as a function of thickness and*

This work has been accomplished in the framework of a French–Algerian research program (Programme International de Coopération Scientifique). The authors gratefully acknowledge the support of the C.N.R.S. and the Ministère Algérien de l'Enseignement Supérieur et de la Recherche Scientifique. The SEM observations were made at the University of Picardie at Amiens and we would like to express our gratitude to Professor Jean-Marie Tarascon and to Dr. Lucas Sannier.

*Corresponding author. Tel.: 33 3 20 33 63 81, Fax: 33 3 20 43 43 45, E-mail: maschke@univ-lille1.fr

*show similar shapes, low transmission in the off-state and high transmission in the on-state in both cases. The results obtained for 150 mJ/cm$^2$ exhibit slightly lower switching voltages and in particular, the 50 mJ/cm$^2$ samples lead to relatively large dispersed data in terms of threshold voltages.*

*Keywords*: liquid crystal; polymer dispersed liquid crystal; ultraviolet curing

## 1. INTRODUCTION

Polymer Dispersed Liquid Crystal (PDLC) materials present a great interest for their practical applications in electro-optical devices such as optical shutters, large area displays and smart windows [1,2]. PDLC films consist of micron-sized nematic liquid crystalline (LC) droplets dispersed in a polymer binder. Since the LC molecules can change their orientation under the influence of an applied electrical field, the PDLC film switch under certain conditions between an opaque light scattering off-state to a transparent on-state.

In this work, PDLC films were prepared by ultraviolet (UV) irradiation induced polymerization from a homogeneous mixture of tripropyleneglycoldiacrylate monomer, nematic LC blend E7, and a photoinitiator. When the polymerization/cross-linking reactions occur, the LC phase separates from the growing polymer network, forming domains dispersed in the polymer matrix.

The electro-optical performance of PDLC films such as threshold and swiching voltages, off-state and on-state transmissions, response times, brightness, and contrast depend on many parameters such as size and shape of the droplets, and in particular the architecture of the polymer network [3–7]. These parameters are strongly determined by the UV irradiation conditions.

R. Yamaguchi et al. [8] investigated some monomer/LC systems in order to understand the electro-optical response of UV-cured PDLC materials. These authors used a static UV lamp and studied the electro-optical behavior as a function of the exposure time. In particular, UV-irradiated films of 50 s showed higher threshold and saturation voltages than samples cured for 500 s.

Other authors report on the dependence of the UV-curing conditions on morphology and electro-optical properties by varying both the UV lamp power and the curing time [9–10]. For example, Lackner et al. [9] described an investigation of transmission vs voltage curves of PDLC films obtained from various light intensities and irradiation times. The overal energy received by the sample was always kept constant. A shift to higher switching voltages was observed for higher UV-intensities applied during short exposure times. Small droplets were found in this case while large droplets were observed for low intensities and long irradiation periods.

To our knowledge, these studies do not rely on the relationship between the chemical stability and the UV-curing parameters mentioned above. However, the control of the extent of the polymerization/crosslinking reactions is of prime importance for good and reproducible electro-optical performance and also to avoid ageing effects due to dangling polymer chains and diffusion controlled processes of unreacted species or unsegregated LC molecules. It is, therefore, important to achieve complete conversion of the monomer to the polymer network independent of the particular choice of UV light intensities and exposure times.

In the present work, the conversion ratio of the monomer in the initial mixture was investigated as a function of the applied UV dose in order to analyse the extent of formation of the polymer network prior to study the electro-optical and morphological properties of the PDLC films. Selected results corresponding to two different UV-dose values are presented. The degree of curing was followed by means of Fourier Transform Infrared (FTIR) spectroscopy measurements by monitoring the disappearance of the absorption band of the carbon-carbon double bond related to the acrylate functions [11].

The electro-optical response in terms of the transmission as function of applied voltage and film thickness was obtained for the two chosen UV-curing doses. These results are discussed and compared to observations of the morphology obtained by Scanning Electron Microscopy (SEM) measurements.

## 2. EXPERIMENTAL PART

### a. Materials and Sample Preparation

Tripropyleneglycoldiacrylate (TPGDA) as monomer was obtained from UCB (Belgium). The nematic LC mixture E7 (Merck KGaA, Darmstadt, Germany) was employed in this work exhibiting a positive dielectric anisotropy and a nematic-isotropic transition temperature at $T_{\mathrm{NI}} = 61^{\circ}\mathrm{C}$. E7 is an eutectic mixture containing four cyanoparaphenylene derivatives. 30 weight-percent (wt-%) of TPGDA, 70wt-% of E7, and 2wt-% (of the acrylate mixture) of a photoinitiator (Lucirin TPO, BASF) were mixed together until the blend became homogeneous.

For electro-optical investigations, the initial reactive mixture was sandwiched between a glass plate (Balzers, Liechtenstein) and a 100 μm thick Polyethyleneterephthalate (PET) sheet (Renker, Germany), both coated with a thin transparent layer of conducting indium/tin oxide. The film thickness was measured by a micrometer calliper (Mitutoyo; uncertainty: ±1 μm). No temperature control during the irradiation processes has been performed. Samples for infrared spectroscopy were prepared in a similar way by replacing the glass by a NaCl plate.

## b. Ultraviolet Curing

The UV polymerization and cross-linking processes were induced by a Minicure Model MC4-300 (Primarc UV Technology) equipped with a medium pressure mercury arc lamp rated 80 W/cm. The samples prepared as described above were placed on a conveyor belt. The dose received by the sample was either 50 mJ/cm$^2$ or 150 mJ/cm$^2$. This was achieved by using a constant light intensity and changing the exposure time by varying the conveyor speed from 1.5 m s$^{-1}$ to 0.5 m s$^{-1}$, respectively.

## c. Electro-optical Measurements

A standard set-up including a laser, a sample holder and a photodiode together with a computer controlled data acquisition was employed for the analysis of the electro-optical properties. The transmission of unpolarized HeNe laser light ($\lambda = 632.8$ nm) passing perpendicular through the PDLC film was measured at room temperature without and upon application of an external electric field. Several sinusoidal voltage scan up and down cycles with appropriate maximum voltages were applied during a period of 120 s, using a frequency of 145 Hz.

## d. Scanning Electron Microscopy (SEM)

Sample morphologies were recorded in a Philips XL-30 electron microscope operating in the scanning mode with an acceleration voltage of 10 kV. After curing of the monomer/LC mixture, the PET sheet was removed and the LC was then extracted by immersing the sample in tetrahydrofuran. Dried films were coated by a thin platinum layer and investigated by SEM. A magnification of 20000x was used allowing to reveal the sample morphology.

## e. Infrared Spectroscopy

Infrared spectra of thin films (less than 10 μm) were recorded in the transmission mode with a Perkin Elmer 2000 model before and after curing. Each dose was applied only once at room temperature and the time interval between the end of exposure and the infrared analysis was kept constant (less than one minute). The number of accumulated scans was 16 with an spectral resolution of 4 cm$^{-1}$. In general, the same experiment was repeated five times to check the reproducibility of the results.

## RESULTS AND DISCUSSION

PDLC films were prepared by polymerization induced phase separation of an initially homogeneous monomer/LC solution. Important physical properties of PDLC films such as the electro-optical response and the mechanical behavior are directly related with the conditions under which the materials are obtained. In particular, the kinetics of photopolymerization and the phase separation behavior of the monomer/LC blend govern the architecture of the obtained polymer network. A difunctional acrylic monomer was used in this work giving rise to a chemically crosslinked polymer network. In order to analyse the extent of formation of the polymer network, the relationship between the conversion of the monomer and the curing conditions was investigated. It is evident that high monomer conversions should be reached to minimize undesired effects of unreacted monomers or dangling chains. FTIR spectroscopy was applied as a versatile method to investigate the extent of curing via carbon-carbon double bond conversion.

One of the most characteristic absorption bands which is quite often used in IR-analysis of acrylates is the one corresponding to the $-CH=CH-$ deformation vibration at 810 $cm^{-1}$ [11–14]. Unfortunately, the LC E7 exhibits a strong absorption band near 810 $cm^{-1}$ originating from the vibration

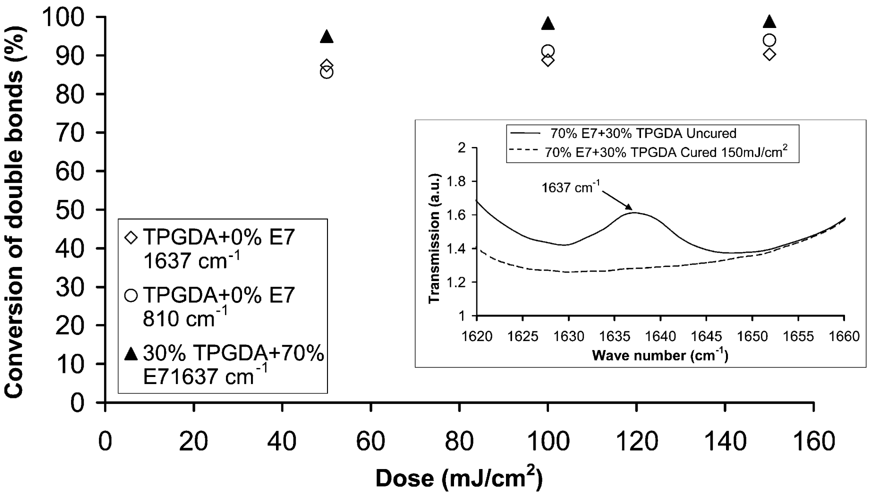
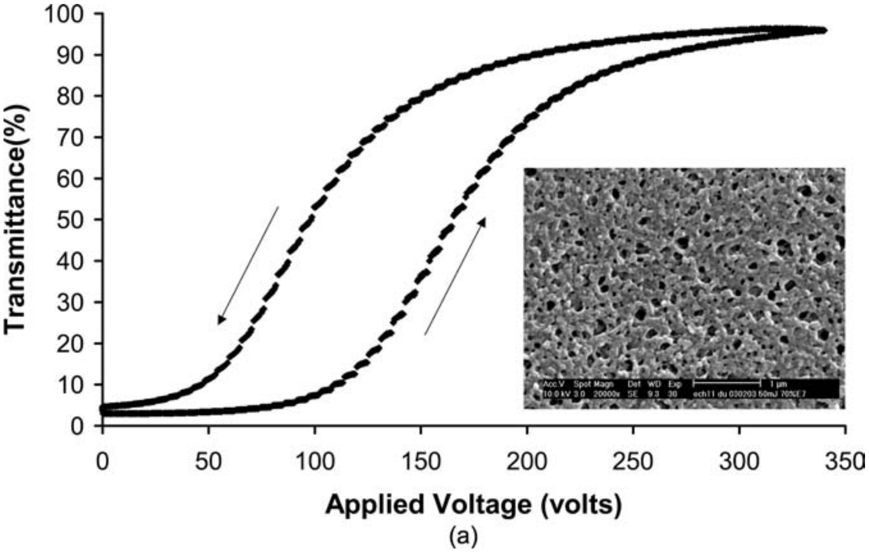


**FIGURE 1** Conversion of monomeric double bonds versus UV-dose obtained by FTIR analysis. The insert shows the decrease of the transmission at 1637 $cm^{-1}$ for the 30wt-% TPGDA/70wt-% E7 system due to the conversion of the double bonds of the acrylic functions.

of the phenyl group. To circumvent the difficulty coming from the overlap of the two bands, another band emerging at 1637 cm$^{-1}$ is used for the analysis of the TPGDA/E7 blend. The insert of Figure 1 indicates that the peak and area of this band decrease during the process of curing due to the conversion of double bonds. The calculation of the monomer conversion is made by considering the peak heights of the absorption bands at either 1637 cm$^{-1}$ or 810 cm$^{-1}$. Figure 1 represents the results of a FTIR spectroscopic analysis of two different systems : the pure monomer and a 30wt-% TPGDA/70wt-% LC blend. In the first case the conversion was calculated for both absorption bands while only the result from 1637 cm$^{-1}$ was available for the TPGDA/LC mixture. Consistent results were obtained for the conversion of the pure monomer. Values between 85% for a dose of 50 mJ/cm$^2$ and 90% for 150 mJ/cm$^2$ were obtained, roughly 5% less than the corresponding results for the 30wt-% TPGDA/70wt-% LC blend. These results show clearly that high conversions were achieved in all cases considered here and that, therefore, one of the conditions necessary for good performance of PDLC films are fullfilled.



(a)

**FIGURE 2** Electro-optical response of 25 μm thick UV-cured 30wt-% TPGDA/70wt-% E7 PDLC films ($\lambda = 632.8$ nm, sinusoidal voltage ramps of frequency 145 Hz at room temperature) a) 50 mJ/cm$^2$; b) 150 mJ/cm$^2$. The inserts exhibit the corresponding sample morphology obtained by SEM.

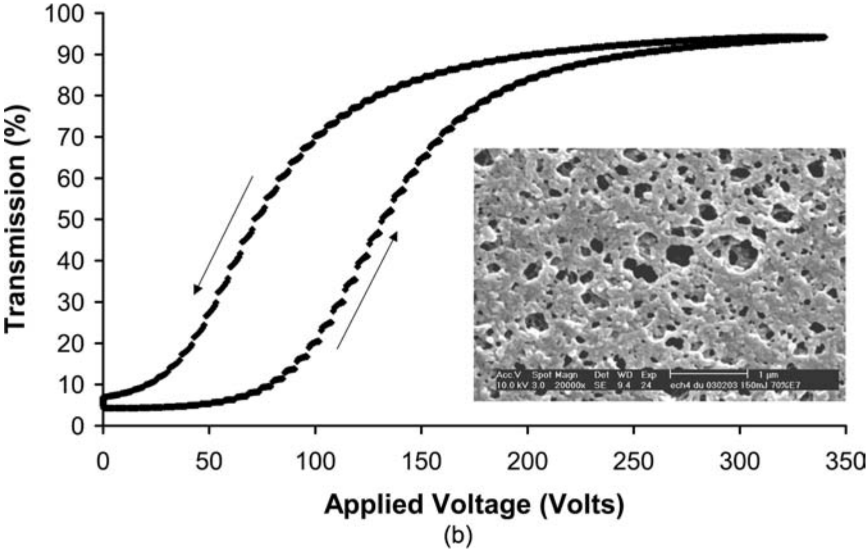


**FIGURE 2** Continued.

Figure 2a and 2b exhibit transmission vs. voltage curves of 25 µm thick PDLC films cured with 50 mJ/cm$^2$ and 150 mJ/cm$^2$, respectively. Both electro-optical response curves show low transmission values in the off-state, high transmissions in the on-state, and similar shapes characterized by a slow increase of the transmission upon application of an electrical field. Furthermore, the samples show a relatively large hysteresis i.e. in an increasing field, the transmission at a specific voltage is lower than the transmission at the same voltage in a decreasing electrical field.

The electrical field necessary to switch the 50 mJ/cm$^2$ film from an opaque to a transparent state is slightly higher than for the 150 mJ/cm$^2$ sample as can be seen by comparing the electro-optical response curves shown in Figure 2a and 2b. The electro-optical properties can be explained by the analysis of the corresponding sample morphologies which are displayed as inserts in these figures. Large size distributions of irregularly shaped domains were observed in both cases and are in good agreement with the slow response to the applied electrical field: LC molecules in larger droplets orient already at low electrical fields whereas LC molecules in smaller droplets need higher voltages to orient due to the higher curvature of these droplets. The morphology analysis reveals increased droplet sizes of the 150 mJ/cm$^2$ sample compared to 50 mJ/cm$^2$ which lead to the observed shift of the transmission vs. voltage curve to lower values.

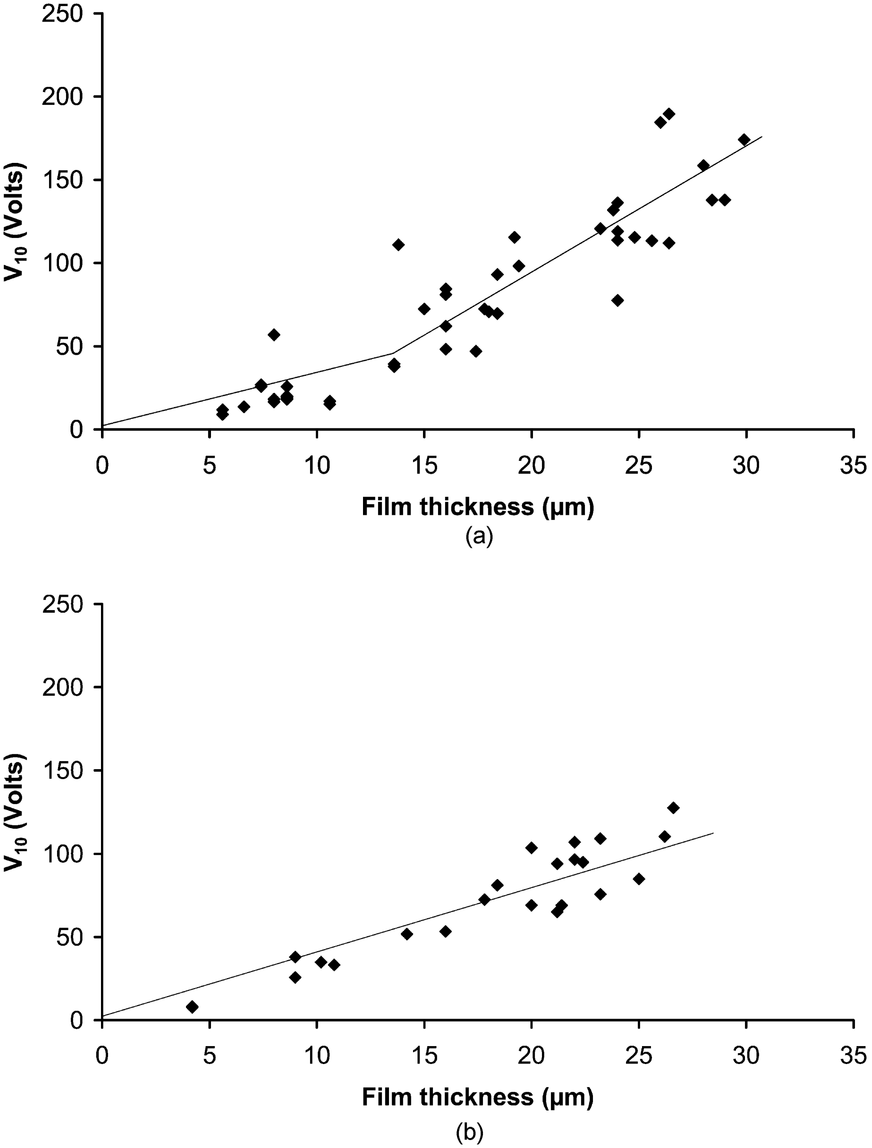


**FIGURE 3** Threshold ($V_{10}$) voltages as a function of film thickness for UV-cured samples a) 50 mJ/cm$^2$; b) 150 mJ/cm$^2$.

Figure 3 shows the threshold voltages as a function of film thickness for a) 50 mJ/cm$^2$ and b) 150 mJ/cm$^2$ samples. Widely dispersed results were found in the case of the lower UV-dose and the experimental data cannot be described by a linear relationship. However, the results can be fitted by a combination of two linear regression curves with a change of the slope around a film thickness of 14 μm. On the other hand, the results obtained for the 150 mJ/cm$^2$ sample can be described by a single linear fit.

## CONCLUSIONS

PDLC films prepared by UV-irradiation using a PIPS process were studied in order to understand the effect of UV-dose on electro-optical performances of these composite materials. The results obtained from infrared spectroscopic measurements indicate nearly complete monomer conversions for samples cured with 50 mJ/cm$^2$ and 150 mJ/cm$^2$. Nevertheless, morphologies and some electro-optical properties of these samples were different comparing the two doses. The transmission vs voltage curves show similar shapes which can be explained by a large droplet size distribution observed in both cases as shown by morphology analysis obtained by SEM. The threshold and saturation voltages are slightly higher for the lower UV-dose samples. This behavior was expected because the droplet sizes are smaller in comparison with those corresponding to higher doses. These results are in good agreement with the obtained film morphologies showing relatively small droplet sizes in the case of the lower dose. The dependence of the threshold voltage on the film thickness was found to be different for the two cases. The results obtained from the higher UV dose indicate, as expected, a linear variation of the threshold voltage as a function of the film thickness. On the contrary, the curves obtained for the lower dose exhibit an unusual behavior. The results are widely dispersed and cannot be fitted by a single linear slope. This effect is more pronounced for large film thicknesses. A possible explanation of this phenomenon could be the architecture of the polymer network that can be formed differently for the two doses.

## REFERENCES

[1] Doane, J. W., Vaz, N. A., Wu, B. G., & Zumer, S. (1986). *Appl. Phys. Lett.*, *48*, 269.

[2] Doane, J. W., Chidichimo, G., & Vaz, N. A. (1987). US Patent, 4,688,900.

[3] Smith, G. W. & Vaz, N. A. (1988). *Liq. Cryst.*, *3*, 543.

[4] Nazarenko, V. G., Sarala, S., & Madhusudana, N. V. (1994). *Jpn. J. Appl. Phys.*, *33*, 2641.

[5] Lovinger, A. J., Amundson, K. R., & Davis, D. D. (1994). *Chem. Mat.*, *6*, 1726.

[6] LeGrange, J. D., Carter, S. A., Fuentes, M., Boo, J., Freeny, A. E., Cleveland, W., & Miller, T. M. (1997). *J. Appl. Phys.*, *81*, 5984.

[7] Grand, C., Achard, M. F., & Hardouin, F. (1997). *Liq. Cryst.*, *22*, 287.
[8] Yamaguchi, R., Sudo, N., & Sato, S. (1995). *Mol. Cryst. Liq. Cryst.*, *262*, 119.
[9] Lackner, A. M., Margerum, J. D., Ramos, E., & Lim, K.-C. (1989). *SPIE*, *1080*, 53.
[10] Nastal, E., Zuranska, E., & Mucha, M. (1999). *J. Appl. Polym. Sci.*, *71*, 445.
[11] Rabek, J. F. (1993). Experimental and analytical methods for the investigation of radiation curing. In: *Radiation Curing in Polymer Science and Technology*, Fouassier, J. P. & Rabek, J. F (Eds.), Elsevier Applied Science: London.
[12] McFarland, C. A., Koenig, J. L., West, J. L. (1993).
(a) *Appl. Spectroscopy*, *47*, 321.
(b) *Appl. Spectroscopy*, *47*, 598.
[13] Bhargava, R., Shi-Qing, W., & Koenig, J. L. (1999).
(a) *Macromolecules*, *32*, 2748.
(b) *Macromolecules*, *32*, 8982.
(c) *Macromolecules*, *32*, 8989.
[14] Bentley, W. G. & Koenig, J. L. (1997). *Appl. Spectr.*, *51*, 1453.