

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>

Photopolymerization kinetics and phase behaviour of acrylate based polymer dispersed liquid crystals

Frederick Roussel; Jean-Marc Buisine; Ulrich Maschke; Xavier Coqueret

Online publication date: 06 August 2010

To cite this Article Roussel, Frederick , Buisine, Jean-Marc , Maschke, Ulrich and Coqueret, Xavier(1998) 'Photopolymerization kinetics and phase behaviour of acrylate based polymer dispersed liquid crystals', *Liquid Crystals*, 24: 4, 555 – 561

To link to this Article: DOI: 10.1080/026782998207028

URL: <http://dx.doi.org/10.1080/026782998207028>

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.

Photopolymerization kinetics and phase behaviour of acrylate based polymer dispersed liquid crystals

by FREDERICK ROUSSEL*, JEAN-MARC BUISINE

Laboratoire de Dynamique et Structure des Matériaux Moléculaires,
Equipe de Thermophysique de la Matière Condensée—CNRS (URA 801),
Université du Littoral, MREID, 145 Route du Pertuis d'Amont,
59140 Dunkerque, France

ULRICH MASCHKE and XAVIER COQUERET

Laboratoire de Chimie Macromoléculaire—CNRS (URA 351),
Université des Sciences et Technologies de Lille, Bât C6,
59655 Villeneuve d'Ascq Cedex, France

(Received 28 May 1997; in final form 14 October 1997; accepted 21 October 1997)

Polymer dispersed liquid crystal (PDLC) materials were prepared by a polymerization induced phase separation (PIPS) process using UV radiation. The samples were obtained from the liquid crystalline component E7 and a blend of monofunctional (2-ethylhexyl acrylate) and difunctional (1,6-hexane diol diacrylate) monomers as precursors of the matrix. Polymerization energetics and thermodynamic properties of PDLC materials were studied by differential scanning calorimetry. Photopolymerization kinetics and phase behaviour of the PDLC are presented and discussed as a function of UV polymerization conditions (UV light intensity, UV time exposure and isothermal curing temperature).

1. Introduction

Polymer dispersed liquid crystal (PDLC) materials consist commonly of low molecular mass liquid crystals dispersed as micron sized droplets in a solid polymer binder [1–3]. These materials have received considerable attention, because of their great potential for electro-optical applications such as flexible information displays and light shutter devices [2]. Most of the systems studied in the literature are prepared by phase separation of liquid crystal domains from a polymer matrix induced by polymerization and cross-linking of the polymer precursors using UV irradiation [1]. A good understanding of the polymerization induced phase separation (PIPS) process is important because of the close dependence between electro-optical properties and morphology of the PDLC films [4–7], and useful information on the phase separation process can be obtained by investigations of cure parameters and phase behaviour of LC/polymer dispersed materials.

In the present work, photocalorimetric and scanning calorimetric features have been investigated for an ultra-violet-cured PDLC prepared from precursors of simple chemical structure. The reactive starting mixture includes

a monofunctional acrylate monomer, a difunctional acrylate monomer and a nematic liquid crystal component [8, 9]. We report a study on the influence of polymerization conditions on kinetic parameters and phase behaviour of these particular acrylate based PDLC materials.

2. Experimental

2.1. Materials

The liquid crystalline mixture E7 (Merck Ltd, GB) was used during this work; it exhibits a nematic phase at room temperature, which easily forms a glassy nematic upon cooling; crystallization does not readily occur upon rearming. The glass gradually becomes a fluid nematic at $T_g = -62.0^\circ\text{C}$ with $\Delta C_p = 0.48 \text{ mJ mg}^{-1} \text{ }^\circ\text{C}^{-1}$. The nematic–isotropic transition of E7 occurs at $T_{NI} = 59.0^\circ\text{C}$ with $\Delta H_{NI} = 4.4 \text{ J g}^{-1}$. The precursors of the matrix consist of 2-ethylhexyl acrylate (EHA) and 1,6-hexane diol diacrylate (HDDA). HDDA (commercial grade) was purchased from UCB Chemicals (Drogenbos, Belgium). EHA (purity 98%) was obtained from Aldrich (Saint Quentin Fallavier, France). Both monomers were used as received. The UV polymerization was induced by 0.8 wt % of 2-hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173, Merck Darmstadt, Germany).

* Author for correspondence.

2.2. Preparation of PDLC samples

Previous studies [8, 9] have shown that the starting formulation EHA:HDDA:E7 (10:30:60) is suitable for obtaining liquid crystal dispersions in the cured polymer matrix. The monomers and the liquid crystal were mixed together at room temperature until the mixture became homogeneous. Samples were prepared by introducing 2.9 ± 0.1 mg of PDLC precursors into an aluminium DSC pan. The low viscosity of the compounds led rapidly to the formation of a thin film in close contact with the pan bottom allowing performance of reproducible measurements. DSC pans of cured samples were sealed to avoid evaporation during the temperature treatment. Both photocalorimetric and scanning calorimetric investigations were carried out on the same sample in order to study the influence of the polymerization process on the PDLC phase behaviour.

2.3. Calorimetric techniques

2.3.1. Isothermal photocalorimetry

Isothermal photocalorimetry [10–12] was used to determine cure energetics and kinetics. Photopolymerizations were initiated inside the DSC furnace under a nitrogen atmosphere (N_2 , 50 ml min^{-1}) with a SEIKO UV1-Unit. A purge time of 5 min was applied before starting irradiation. The source consisted of a 200 W mercury–xenon Hg–Xe lamp (UXM-200YA). The UV light intensity was fixed by neutral density filters (LOT-ORIEL). The wavelength of the UV radiation was set at $\lambda = 365 \text{ nm}$ using an interferential filter (LOT-ORIEL). During photopolymerization, the calorimetric response is characterized by an exothermal peak. In order to check for complete reaction and avoid baseline shifts (difference of light absorption between sample and reference cells), a second scan was carried out and then subtracted from the previous one. The heat of polymerization ΔQ_{pol} was determined by integration of the resulting heat release curve. The relative rate of polymerization was calculated as a normalized rate where the absolute rate is divided by the initial monomer concentration [11, 13]:

$$\text{Rate} = \frac{QM}{m\Delta H_{\text{pol}}} \quad (1)$$

where Q is the heat flow per second (J s^{-1}), M is the acrylate equivalent weight, i.e. the mass of monomer mixture containing one mole of acrylate function ($M = 122 \text{ g mol}^{-1}$ for the precursor blend EHA:HDDA 1:3), ΔH_{pol} is the molar enthalpy of polymerization (for acrylates $\Delta H_{\text{pol}} = 80 \text{ kJ mol}^{-1}$ [14]) and m is the mass of monomers in the sample. Double bond conversion is calculated by integrating the rate of polymerization as a function of time.

2.3.2. Scanning calorimetry

Investigations on the phase behaviour of UV cured PDLC samples were carried out using a SEIKO DSC 220C calorimeter. A liquid nitrogen circulation device allowed cooling experiments. The DSC cell was purged with 50 ml min^{-1} of nitrogen. The calorimeter was calibrated with indium and adamantane standards. Rates of $10^\circ\text{C min}^{-1}$ (heating) and $30^\circ\text{C min}^{-1}$ (cooling) were used in the temperature range from -120 to $+100^\circ\text{C}$. The programme consisted first in cooling the sample followed by several heating and cooling cycles. Data analysis was carried out on the second heating ramp.

3. Results and discussion

Photopolymerization kinetics and phase behaviour of PDLC samples are presented and discussed as a function of UV cure conditions, i.e. UV light intensity, UV exposure time and isothermal curing temperature.

3.1. Effects of UV light intensity on polymerization and phase behaviour

Five different neutral density filters were used to set the UV light intensity at $I_{\text{UV}} = 0.47, 0.94, 4.7, 9.4$ and 94 mW cm^{-2} . In order to keep the same UV dose for each of the samples, the UV exposure time t_{UV} was increased with decreasing I_{UV} . The isothermal curing temperature was fixed at $T_{\text{curing}} = 30^\circ\text{C}$. Polymerization parameters for the ‘pure’ monomers (without LC), denoted ‘pm’, and PDLC precursors are summarized in table 1. It can be seen that the heats released during polymerization $\Delta Q_{\text{pol}}^{\text{pm}}$ and $\Delta Q_{\text{pol}}^{\text{PDLC}}$ are proportional to reacted double bonds introduced in the formulation:

$$\Delta Q_{\text{pol}}^{\text{PDLC}} \sim \Delta Q_{\text{pol}}^{\text{pm}} \times 40\%. \quad (2)$$

These results account for the diluting effect of the liquid crystal on the reactive mixture [5, 13]. To examine the curing effects, both normalized polymerization rate (figure 1) and double bond conversion (figure 2) were monitored as a function of time. In figure 1, the maximum rate is reached for the shortest time period with the highest UV light intensity (94 mW cm^{-2}). Compared with the pure matrix, the time of peak maximum τ is slightly increased (5.4 s for the ‘pure’ monomers compared with 6.1 s for PDLC—table 1) due to dilution (60% LC) reducing the polymerization rate. However, τ^{pm} and τ^{PDLC} vary with I_{UV} in the same way, showing that the presence of the LC does not seem to affect drastically the polymerization process. The dependence of the polymerization rate on the light intensity was examined by plotting the maximum rate value $R_{\text{p,max}}$ as a function of $(I_{\text{UV}})^n$ for various simple hypothetical values of n . As shown in the inset of figure 1, the expected linear variation with $(I_{\text{UV}})^{0.5}$ [15], corresponding to a bimolecular termination for the kinetic chain, is

Table 1. Dependence of polymerization parameters for the pure monomers and PDLC materials on UV light intensity I_{UV} ($mW\ cm^{-2}$). ΔQ_{pol}^{pm} ($J\ g^{-1}$) = heat released by pure monomers; ΔQ_{pol}^{PDLC} ($J\ g^{-1}$) = heat released by PDLC precursors; τ^{pm} (s) and τ^{PDLC} (s) = time at peak maximum for pure monomers and PDLC, respectively; conversion (%) = final acrylate conversion in PDLC samples; $R_{p,max}$ (s^{-1}) = maximum rate of polymerization (PDLC).

I_{UV}	Parameter					
	ΔQ_{pol}^{pm}	ΔQ_{pol}^{PDLC}	τ^{pm}	τ^{PDLC}	Conversion	$R_{p,max} \times 10^2$
0.47	-506.0	-207.3	10.2	21.5	78	0.55
0.94	-506.4	-206.9	8.1	16.0	81	0.71
4.7	-507.8	-210.6	6.8	10.0	82	1.31
9.4	-514.5	-210.8	6.1	8.7	83	1.66
94	-508.9	-220.7	5.4	6.1	85	2.89

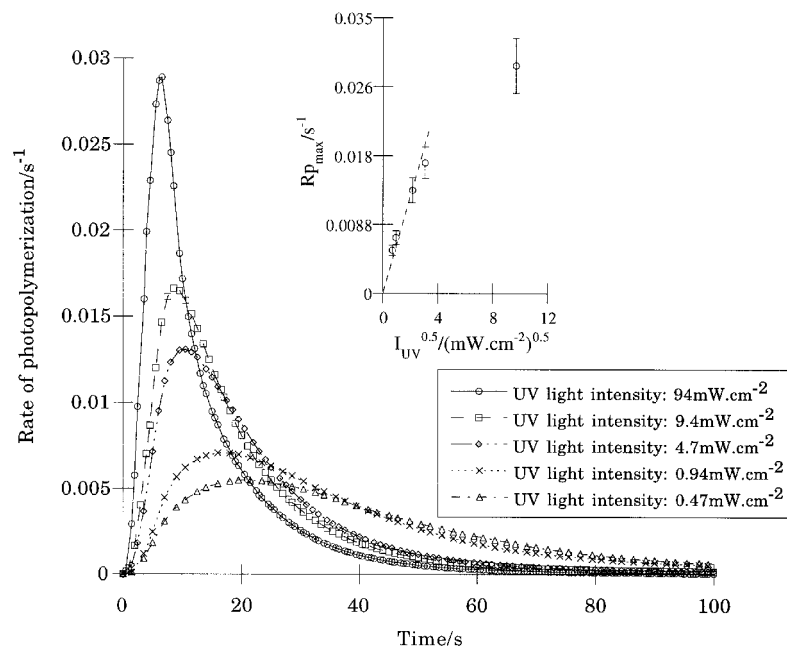


Figure 1. Normalized rate of polymerization versus time for different UV light intensity values. Inset: maximum rate of polymerization as a function of the square root of the UV light intensity.

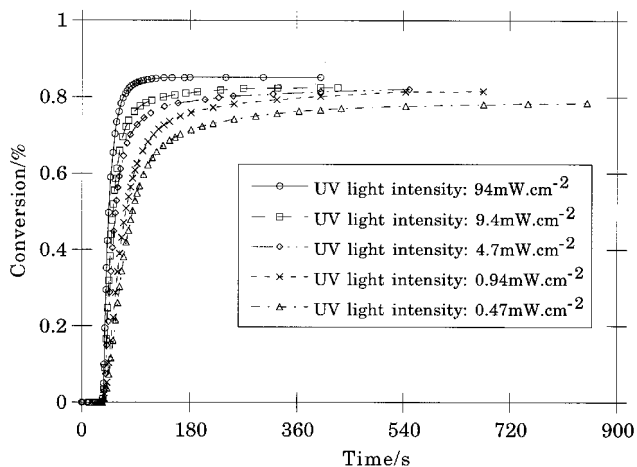


Figure 2. Double bond conversion as a function of time for different UV light intensity values.

approximately obeyed for the photopolymerization carried out with the four lowest light intensities. The rate measured with the highest value of I_{UV} is noticeably below the linear curve. The reason for this non-ideal behaviour is unclear; however the deviation is observed for a wide range of I_{UV} covering more than two decades. Under such conditions, some other parameters having a determining influence on the kinetic model may alter the course of the crosslinking polymerization process. The double bond conversion is plotted as a function of UV light intensity in figure 2. The maximum conversion of 85% is obtained with the highest UV light intensity ($94\ mW\ cm^{-2}$) (table 1), lower I_{UV} values leading to a lower extent of polymerization. However, the final conversions of the samples prepared are found to be in the same range as for high UV energy, but on different time scales: 85% conversion at $t = 180\ s$ ($I_{UV} = 94\ mW\ cm^{-2}$) and 78% conversion at $t = 850\ s$ ($I_{UV} = 0.47\ mW\ cm^{-2}$).

Therefore, it can be anticipated that the morphologies of the PDLC materials change with the UV light intensity. SEM studies are currently in progress to characterize this phenomenon.

The phase behaviour of PDLC samples prepared with five different UV light intensities was studied by DSC. A typical curve is presented in figure 3. The five corresponding thermograms of cured dispersed systems exhibit two transitions: a glass transition at $T_g = -60^\circ\text{C}$, and an endothermic peak at $T_{\text{NI}} = +52^\circ\text{C}$. These transitions can be assigned to the transformations of the segregated liquid crystalline phase [5, 8, 9]. The transition temperatures are almost identical to those of pure E7 and remain independent of the UV light intensity. The slight difference between $T_{\text{NI}}^{\text{pure E7}}$ and $T_{\text{NI}}^{\text{PDLC}}$ is probably due to the presence of trace amounts of contaminants in the PDLC-segregated nematic phase which contribute to a decrease of the N-I transition temperature. The pure matrix presents no particular thermal event [8, 9]. The enthalpy change at the nematic-isotropic transition $\Delta H_{\text{NI}}(T_{\text{NI}} = +52^\circ\text{C})$ increases with I_{UV} until reaching a plateau (figure 4). These data can be interpreted as

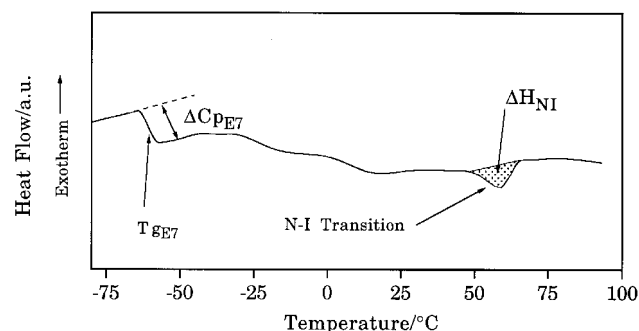


Figure 3. Typical thermogram for the cured mixture EHA:HDDA:E7 (10:30:60).

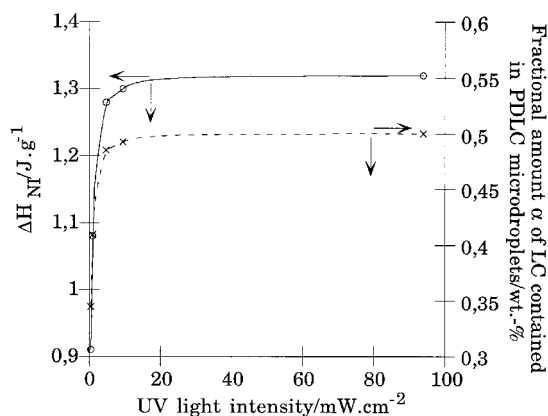


Figure 4. Enthalpy changes ΔH_{NI} at the nematic-isotropic transition, and fractional amounts α of LC contained in microdroplets for PDLC samples prepared at different UV light intensity values.

the result of a lower extent of phase separation for the networks of lower crosslink density obtained under weaker UV light intensities; lower double bond conversion leads to higher solubilities between matrix and LC. The fractional amount α of liquid crystal contained in the PDLC microdroplets has been determined [16, 8, 9] by using:

$$\alpha_{\text{exp}} = \frac{m_{\text{LC}}^{\text{D}}}{m_{\text{LC}}} = \left(1 + \frac{m_{\text{P}}}{m_{\text{LC}}} \right) P(x) \quad (3)$$

and

$$P(x) = \frac{\Delta H_{\text{NI}}(x)}{\Delta H_{\text{NI}}(\text{LC})}, \quad \text{or} \quad \frac{\Delta C_{\text{p}}(x)}{\Delta C_{\text{p}}(\text{LC})} \quad (4)$$

where m_{LC}^{D} represents the mass of LC included in the droplets, and m_{P} and m_{LC} are the masses of the polymer matrix and of the LC in the sample, respectively. $P(x)$ represents the ratio of the N-I transition enthalpy (or the heat capacity increment) for a LC/polymer material to the equivalent value for the pure LC.

α has been calculated from ΔH_{NI} to be in the region 0.50 for I_{UV} values superior to 20 mW cm^{-2} (figure 4); the remaining 50% of LC is plasticized in the matrix. ΔC_{p} values were not used for the calculation due to possible errors resulting from the presence of contaminants (especially at low I_{UV} values) quenched in the LC phase at low temperature. Therefore, in order to improve the phase separation process and PDLC properties, the UV light intensity should be set at least at $I_{\text{UV}} = 20 \text{ mW cm}^{-2}$.

3.2. Effects of UV exposure time on polymerization and phase behaviour

In order to examine the thermophysical characteristics of the sample at various points in time during the isothermal polymerization at $T_{\text{curing}} = 30^\circ\text{C}$ and under the highest UV light intensity ($P_{\text{UV}} = 94 \text{ mW cm}^{-2}$), five UV doses were applied by setting the UV exposure time at $t_{\text{UV}} = 1.2, 1.8, 2.4, 6$ and 180 s . As indicated by the plots of figure 5, the variation of the polymerization rate computed from the heat flux exhibits a change of slope, but does not decrease until a maximum is reached at $\tau = 5.25, 5.35, 5.50, 5.90$ and 6.10 s for the series of five increasing exposure times, respectively. It appears from examination of the value of τ for the three shortest exposure times, that the polymerization rate keeps on increasing for relatively long periods of time following shutter closing. The crude records of the heat flux were indeed not corrected from the time constant of the instrument [17]. This leads to an apparently delayed initiation and causes underestimation of the instant conversion computed by integration of the rate curve (figure 6), until the limiting value is reached. The

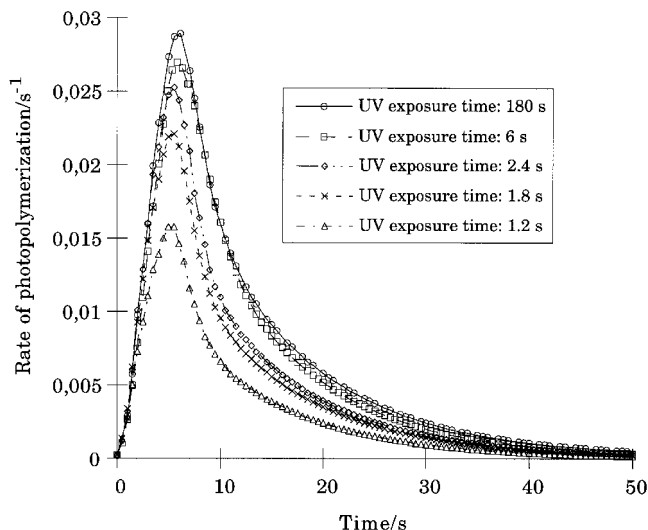


Figure 5. Normalized rate of polymerization versus time for different UV exposure times.

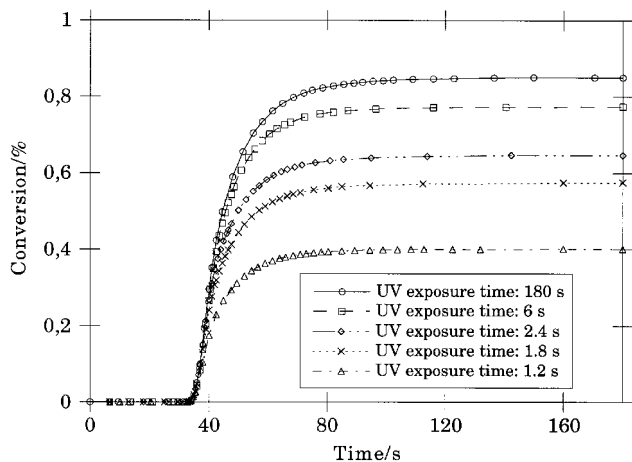


Figure 6. Double bond conversion as a function of time for different UV exposure times.

efficiency of the polymerization process is thus higher than the estimation given by the plots of figure 5. The maximal attainable conversion (85%) is almost reached after the 6·1 s long photoinitiation and subsequent dark polymerization (76%), confirming the very high polymerizability of the acrylate mixture that probably does not offer equilibrium conditions for the monomer-E7 mixture when submitted to a brutal change of constitution.

The PDLC materials prepared with different conversion ratios were studied by DSC; thermograms are reported in figure 7. For conversion ratios lower than 65·5%, the thermophysical properties of the segregated liquid crystalline phase cannot be accurately characterized. The nematic–isotropic transition occurs at a lower temperature and over a larger temperature scale than

for pure E7. Higher ΔC_p values at T_g ($T_{\text{curing}} = -65^\circ\text{C}$) show the presence of more significant quantities of quenched phases resulting from rapid cooling of the sample. As written in the previous section, these results can be explained by a lower extent of phase separation for the networks of lower crosslink density (lower conversions leading to larger residual monomer ratios). Therefore, in order to reduce the amount of contaminants in the LC phase, the double bond conversion should be as high as possible; the phase separation process would then be improved.

3.3. Effects of isothermal curing temperature on polymerization and phase behaviour

The reactive mixture was polymerized at five different temperatures: $T_{\text{curing}} = -50, 0, 30, 45, 75^\circ\text{C}$ ($\lambda = 365\text{ nm}$, $P_{\text{UV}} = 94\text{ mW cm}^{-2}$ and $t_{\text{UV}} = 3\text{ min}$). The normalized rates of photopolymerization are plotted versus time in figure 8. The shapes of the curves obtained are comparable except at low temperatures. The maximum rate is reached at shorter times with increasing curing temperatures (inset in figure 8). This effect results from a thermal activation of the polymerization propagation process and/or an enhanced mobility of reacting species at higher temperatures [5]. The double bond conversion is examined as seen in figure 9. At low temperature, $T_{\text{curing}} = -50^\circ\text{C}$, the reduced mobility of the reacting species [5] leads to a lower extent of reaction (65%). The maximum conversion, i.e. 85%, is obtained at $T_{\text{curing}} = 0$ and 30°C . This phenomenon is probably due to an earlier phase separation process which increases the local concentration of each of the phases (LC/matrix). The polymerization of the segregated acrylate rich phase is then improved, leading to higher conversions. At $T_{\text{curing}} = 45^\circ\text{C}$, the temperature of the reactive mixture is close to the nematic–isotropic transition ($T_{\text{NI}} = 52^\circ\text{C}$). Therefore, the liquid crystal microdroplets appear only at high crosslink density of the macromolecular network. The phase separation occurs too late to induce an enriched local concentration in monomers. The polymerization is then limited by diffusion processes and trapped double bonds are unable to react [13], so that lower conversions are found. At $T_{\text{curing}} = 75^\circ\text{C}$, this phenomenon is emphasized because the mixture remains in the isotropic state during the complete reaction.

As in previous sections, the PDLC samples were studied by DSC; the thermograms are similar to those presented in figure 3. The transition temperatures, i.e. glass transition T_g and nematic–isotropic transition T_{NI} , versus isothermal curing temperatures are reported in table 2. The nematic–isotropic transition temperature T_{NI} can be found in the same range, except for the sample prepared at $T_{\text{curing}} = -50^\circ\text{C}$. This behaviour can

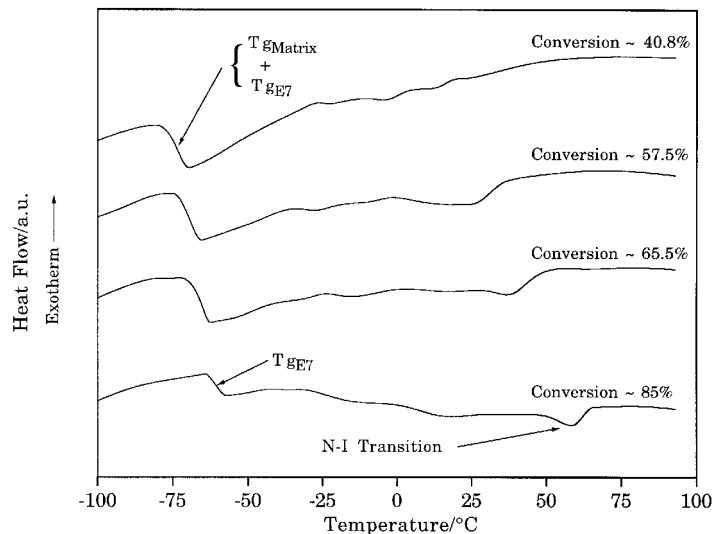


Figure 7. DSC curves of PDLC samples EHA:HDDA:E7 (10:30:60) prepared with different UV exposure times, i.e. different conversion ratios.

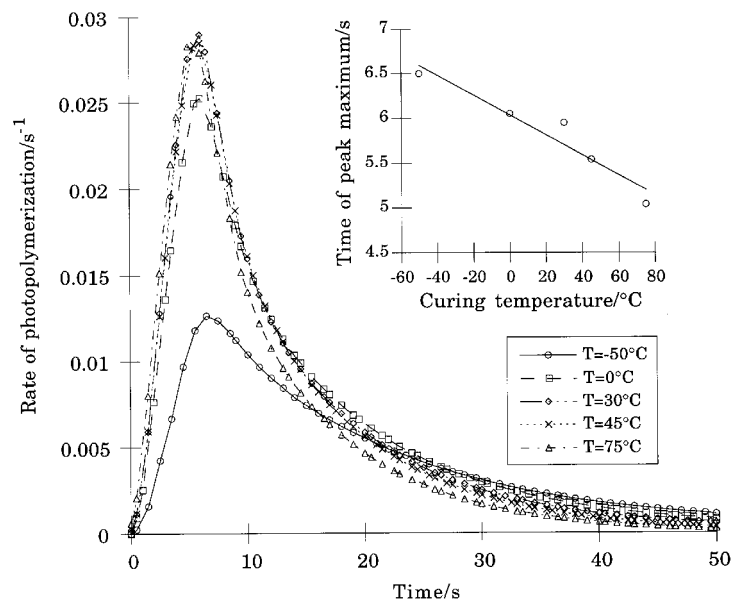


Figure 8. Normalized rate of polymerization versus time for different isothermal curing temperatures. Inset: influence of isothermal curing temperatures on the time of peak maximum.

Table 2. Influence of the isothermal curing temperature T_{curing} (°C) on the transition temperatures T (°C) of the segregated LC phase. NI = nematic–isotropic transition; g = glass transition.

T_{curing}	Transition temperatures	
	T_{NI}	T_{g}
-50	47.2	-63.0
0	51.0	-61.4
30	51.8	-61.4
45	53.2	-61.8
75	52.4	-61.3

be explained by the presence of unreacted monomers (65% conversion) dissolved in the LC phase. The presence of such contaminants contributes to a slight decrease of the glass transition temperature of the glassy nematic ($T_{\text{g}} = -63^{\circ}\text{C}$). However the glass transitions of the samples cured at higher temperatures remain nearly unchanged, meaning that the segregated LC phase is essentially pure. The enthalpy changes at the N–I transition ΔH_{NI} and the fractional amounts α of LC contained in the PDLC microdroplets are plotted versus isothermal curing temperature in figure 10. The highest ΔH_{NI} and α values are measured for the samples cured at $T_{\text{curing}} = 0$ and 30°C , i.e. with the maximum double

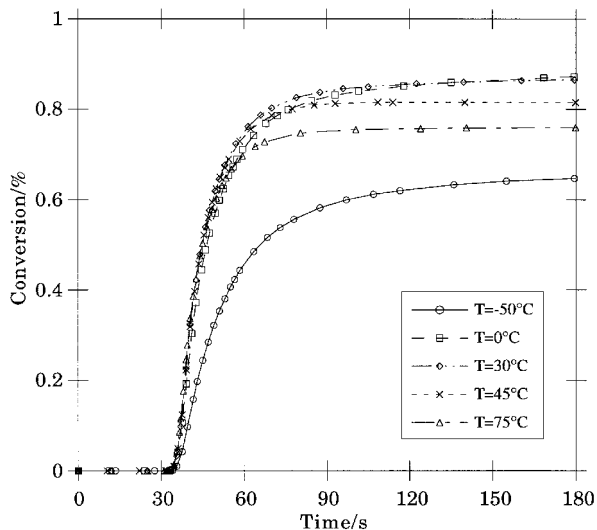


Figure 9. Double bond conversion as a function of time for different isothermal curing temperatures.

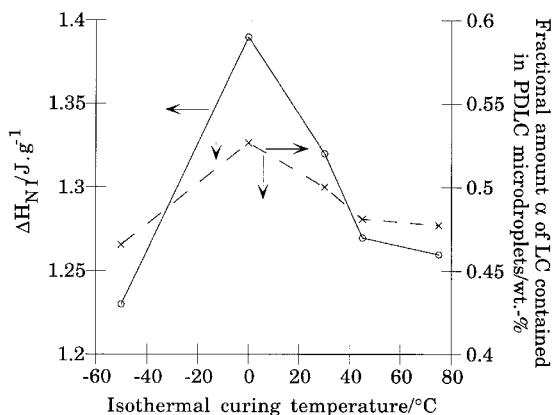


Figure 10. Enthalpy changes ΔH_{NI} at the nematic–isotropic transition, and fractional amounts α of LC contained in microdroplets for PDLC prepared at different isothermal curing temperatures.

bond conversion. Therefore the phase separation process is improved when the isothermal curing temperature is kept between $T_{\text{curing}}=0$ and 30°C .

4. Conclusion

Photopolymerization kinetics and the phase behaviour of acrylate based PDLC materials [initial composition

EHA:HDDA:E7 (10:30:60)] have been studied as a function of UV curing conditions. In order to improve the phase separation process, the double bond conversion should be as high as possible. To reach this goal, the cure parameters have been set for the system studied such that: UV light intensity $I_{\text{UV}}=94\text{ mW cm}^{-2}$, UV exposure time at least 15 s and isothermal curing temperature between $T_{\text{curing}}=0$ and 30°C . Further experiments are currently in progress to characterize the influence of curing conditions such as I_{UV} and T_{curing} on the morphology of the PDLC samples.

The authors gratefully acknowledge the support of the Ministère de l'Enseignement Supérieur et de la Recherche, the Région Nord-Pas de Calais and the CNRS.

References

- [1] DOANE, J. W., 1990, *Liquid Crystals—Applications and Uses*, Vol. 1, edited by B. Bahadur (Singapore: World Scientific), pp. 361–395.
- [2] KITZEROW, H. S., 1994, *Liq. Cryst.*, **16**, 1.
- [3] DRZAIĆ, P. S., 1995, *Liquid Crystal Dispersions* (Singapore: World Scientific).
- [4] SMITH, G. W., 1991, *Mol. Cryst. liq. Cryst.*, **196**, 89.
- [5] SMITH, G. W., 1994, *Mol. Cryst. liq. Cryst.*, **241**, 77.
- [6] BOOTS, H. M. J., KLOOSTERBOER, J. G., SERBUTOVIEZ, C., and TOUWSLAGER, F. J., 1996, *Macromolecules*, **29**, 7683.
- [7] SERBUTOVIEZ, C., KLOOSTERBOER, J. G., BOOTS, H. M. J., and TOUWSLAGER, F. J., 1996, *Macromolecules*, **29**, 7690.
- [8] ROUSSEL, F., 1996, PhD thesis, Université du Littoral, Dunkerque, France.
- [9] ROUSSEL, F., BUISINE, J. M., MASCHKE, U., and COQUERET, X., 1997, *Mol. Cryst. liq. Cryst.*, **299**, 321.
- [10] MOORE, J. E., 1978, *UV Curing Science and Technology*, edited by P. Pappas (Stanford), p. 133.
- [11] COOK, W. D., 1993, *J. Polym. Sci. A*, **31**, 1053.
- [12] HOYLE, C. E., and Watanabe, T., 1994, *Macromolecules*, **27**, 3790.
- [13] GUYMON, C. A., HOGGAN, E. N., WALBA, D. M., CLARK, N. A., and BOWMAN, C. N., 1995, *Liq. Cryst.*, **19**, 6.
- [14] TRYSON, G. R., and SHULTZ, A. R., 1979, *J. Polym. Sci. B*, **17**, 2059.
- [15] BURNETT, G. M., and MELVILLE, H. W., 1947, *Proc. Royal Soc.*, **A189**, 456.
- [16] SMITH, G. W., and VAZ, N. A., 1988, *Liq. Cryst.*, **3**, 543.
- [17] FISCHER, E. W., and KUNZE, W., 1989, *Proceedings RadTech Europe '89 Conference*, p. 669.