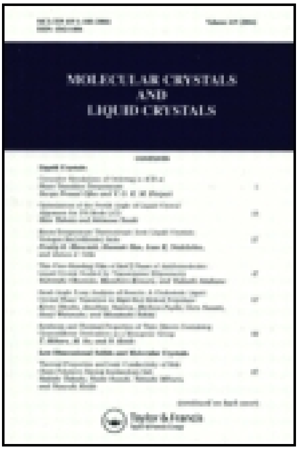

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

A Novel Study of the Polymerisation Process Involved in the Formation of the Network Component of Polymer-Stabilised Liquid Crystals Within Electro-Optic Cells Using High Performance Liquid Chromatography

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A Novel Study of the Polymerisation Process Involved in the Formation of the Network Component of Polymer-Stabilised Liquid Crystals Within Electro-Optic Cells Using High Performance Liquid Chromatography

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Polymer-stabilised liquid crystals are systems in which a small amount of monomer is dissolved within a liquid crystalline host, and then polymerised *in situ* to produce a network. The progress of the polymerisation, performed within electro-optic cells, was studied by establishing an analytical method novel to these systems. Samples were prepared by photopolymerisation of the monomer under well-defined reaction conditions; subsequent immersion in acetone caused the host and any unreacted monomer to dissolve. High performance liquid chromatography was used to separate and detect the various solutes in the resulting solutions, enabling the amount of unreacted monomer for a given set of conditions to be quantified. Longer irradiations cause a decrease in the proportion of unreacted monomer since more network is formed, while a more uniform LC director alignment (achieved by decreasing the sample thickness) or a higher level of order (achieved by decreasing the polymerisation temperature) promotes faster reactions.

Keywords: Polymer-stabilised liquid crystals; high performance liquid chromatography; photopolymerisation; network formation

INTRODUCTION

Polymer-stabilised liquid crystals (PSLCs), materials originally described as anisotropic gels,$^{(1-3)}$ are composite systems formed by dissolving a small amount of

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a monomer (typically, less than 5 wt % of the system) in a LC host, and then photopolymerising the monomer *in situ* within the LC phase. The monomer must have more than one reactive group (*e.g.* a diacrylate) in order to produce a cross-linked network, as opposed to discrete polymer chains.

The state of the network in a PSLC is dependent on the phase of the LC host during polymerisation. Once formed, the network is permanent and exerts aligning forces on the host, despite being present in low concentration. The aligning forces can be overcome by a sufficiently strong external field, but once the field is removed, the director pattern returns to the original orientation due to the presence of the network. Hence, these materials have attracted much interest with regard to display applications since they were first developed by Hikmet.(4) However, there remain fundamental questions regarding the nature and formation of these materials. For example, there are relatively few publications which concentrate on the polymerisation process, which is central to determining the nature and properties of a PSLC.

The general practice for making a PSLC has been to irradiate a suitable mixture of host, monomer and photoinitiator for several minutes. However, since the development of the network has not been studied to any great extent, in the majority of the work reported it is unclear how much of the monomer does not react due to an insufficient irradiation time. Of the work which has looked at network development, irradiation time has been shown to be an important factor,(5–8) with larger and more complicated cross-linked structures resulting when a longer irradiation period has been used. This can be attributed to the polymerisation of greater numbers of molecules over longer irradiation times.

Monitoring of the polymerisation process using UV-modified differential scanning calorimetry (DSC-UV) has revealed that for a UV intensity of 0.2 mW cm^{-2}, and using similar materials to those in the current work, it takes several minutes for the bulk of the monomer to polymerise.(9) However, in these experiments, the detection limit of the machine was such that the reaction could not be followed beyond ~70% monomer depletion, and the orientation of the LC director was not well-defined. We present a new approach for studying the progress of the polymerisation reaction. This involves measuring the amount of monomer which remains unreacted after irradiation of samples under a series of well-defined experimental conditions. Possibly the most important aspect of this method is that the reactions being studied take place within treated glass cells, within which the alignment of the LC director is well-defined throughout. This is typical of the environment in which PSLCs are formed for use in their primary application, LC displays. Employing this technique has made it possible to deduce the amount of monomer present within the network structures produced, and therefore to determine how the amount of monomer which polymerises influences these structures. In addition, the effect of varying the reaction parameters (*e.g.* irradiation time, polymerisation temperature, surface alignment, sample thickness) on the progress of the polymerisation can be deduced.

The particularly challenging feature of any analysis is that the residual monomer is present in low concentrations (a fraction of 1% of the original mixture) in a large excess of a chemically similar material, the LC host. As a consequence, direct spectroscopic analysis of samples is not feasible, and separation of monomer and host is required prior to analysis. Since the quantity of the residual monomer is small, any realistic analytical procedure will involve separation from the network. This can be achieved by dissolving the soluble material (host and unreacted monomer) by immersion of samples in an organic solvent. This method was originally described in the literature for the preparation of networks for evaluation by SEM;(10) it has been further developed in the present work to include analysis of the resulting solutions. This was achieved using high performance liquid chromatography (HPLC). The information obtained through analysis allowed the stated objectives to be achieved, *i.e.* to follow the progress of the polymerisation process within the environment of an electro-optic cell, and to quantify the effect of changing the polymerisation conditions.

EXPERIMENTAL

PSLCs were prepared from mixtures comprising the nematic host BL087 (a cyanobiphenyl and terphenyl-based mixture of high birefringence), the terphenyl-based LC diacrylate monomer RM60 (see Figure 1) and the photoinitiator Irgacure 651. Both the monomer and host were supplied by Merck R&D UK, while the initiator was supplied by Ciba-Geigy. The monomer concentration was 1.00 wt %, while the initiator concentration was 0.20 wt %. The homogeneous mixture, which had a nematic-to-isotropic transition temperature (T_{ni}) of 87.8°C, was introduced into glass sandwich cells, the internal surfaces of which had been coated with rubbed polyimide layers to promote uniaxial director alignment parallel to the glass surfaces. The glass was separated by Kapton spacers, the thickness of which was varied from 12.5 to 50 μm. Prior to polymerisation, the mass of mixture inside each cell was measured; samples were then irradiated for given periods of time using a mercury lamp (Blak-Ray B100 AP, UVP Inc.) emitting strongly (~25 mW cm^{-2}) over a wavelength region centred around 366 nm. The samples were held in a temperature-controlled stage during irradiation, which allowed the polymerisation process to be performed at constant temperatures (to ± 0.5°C). Following reaction, the irradiated samples within their glass cells were immersed in sealed jars containing 35 cm^3 of acetone for four days. During this time, the unpolymerised material was dissolved, while the network was left behind on the glass surfaces. The cells were then removed from these acetone "baths", and fresh acetone was added to the resulting solutions, giving each a volume of 100 cm^3. The dilute nature of the solutions meant that possible detrimental effects (such as complexation of solute molecules) in the subsequent analysis, carried out using reverse phase HPLC, were eliminated. The separated network material obtained by this route can be used to provide a detailed view of the network structure and morphology.(11,12)

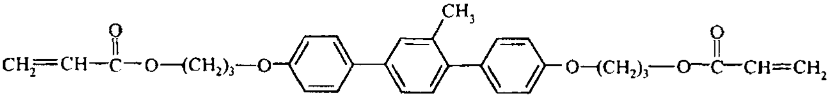

FIGURE 1 The molecular structure of the LC diacrylate monomer RM60

HPLC was carried out using a variety of columns and eluants in order to establish a suitable set of conditions for separating out the various materials present in solution. Eventually, baseline separation of the solutes was achieved using a 5 μm particle size column (HI-5C18–250A, Hichrom Ltd.) of 25 cm length and 4.6 mm internal diameter, along with an eluant consisting of 80 vol % HPLC grade acetonitrile (Aldrich Chemical Co.) and 20 vol % demineralised water. The eluant and the acetone-based test solutions were completely miscible. Samples (0.02 cm^3) were introduced using a sample loop, and the pump unit was a Gilson 302, pumping at 1.0 cm^3 min^{-1}. Solutes were detected by their ultraviolet (UV) absorptions, using a Pye-Unicam LC3 UV detector set to 273 nm; this corresponds to the λ_{max} of both the host and monomer. Retention times and peak areas were recorded on a Hewlett-Packard 3390A plotter/integrator.

Standard solutions containing known amounts of the host or monomer were prepared and analysed by HPLC, in order to establish the retention times of each solute (see Figure 2 and Table I), and to calibrate the response of the detector to the amount of material (see Figures 3 & 4). Thus, the amount of unreacted material after the formation of a PSLC could be accurately determined, and as the mass of material present before polymerisation is known, the proportion of unreacted material could also be determined.

Reproducibility in peak areas was tested by running a standard sample three times. There was some variation between the peak areas for each run; this was estimated to be (± 3%). Therefore, a maximum error of (± 3%) was associated with all peak areas in subsequent calculations. The other main source of uncertainty was in the calibration graphs (Figures 3 & 4). Linear regression lines were

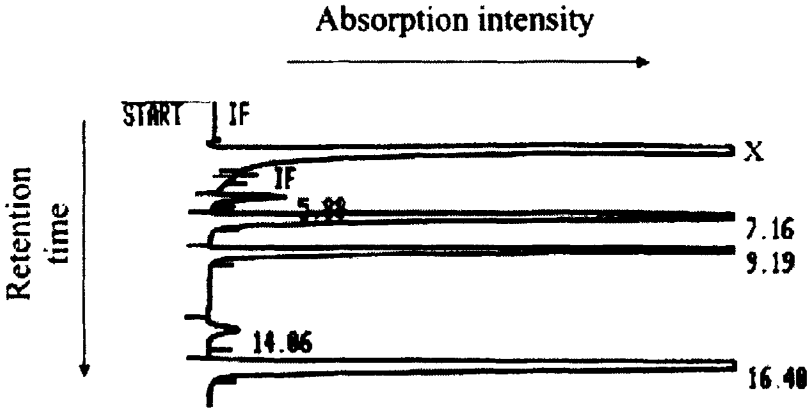

FIGURE 2 HPLC trace for an unpolymerised mixture (1 wt % RM60 in BL087), using an HI-5C18-250A column and a mixture of 80 vol % acetonitrile: 20 vol % water as the mobile phase. The numbers shown are the retention times of each component in minutes. The identity of each peak is given in Table I

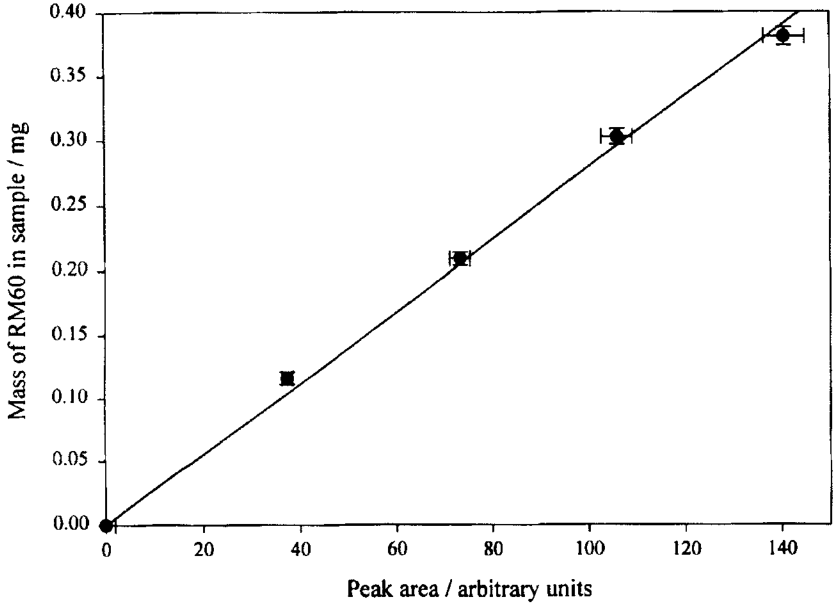

FIGURE 3 HPLC calibration graph for RM60, obtained by analysing standard solutions using a detection wavelength of 273 nm

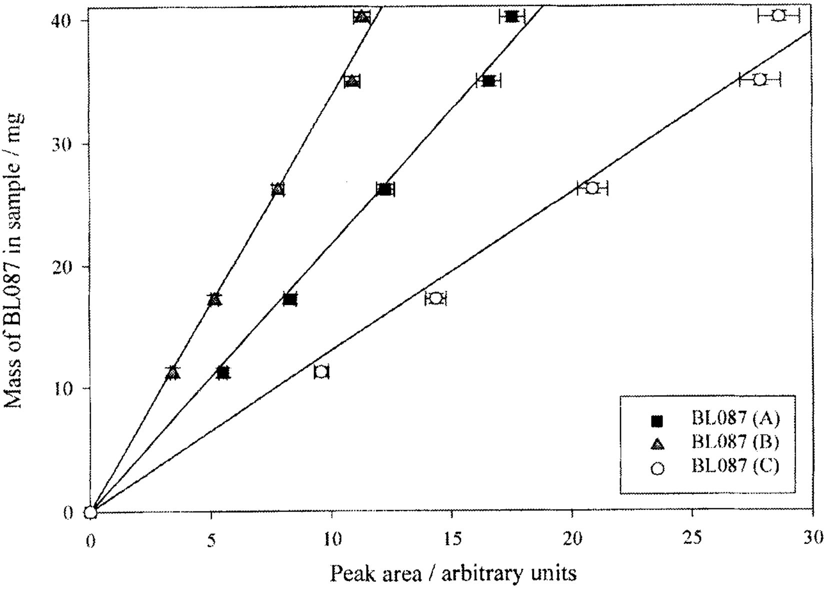

FIGURE 4 HPLC calibration graph for BL087, obtained by analysing standard solutions using a detection wavelength of 273 nm. The labels A, B and C relate to different components of BL087, as denoted in Table I

fitted to the data, with 95% confidence intervals used to represent the uncertainty in the gradient of the "best fit" lines. The total uncertainty in calculating the amount of material present in test samples can be observed in the error bars for each point in Figures 5 to 9.

TABLE I Table to show the identity of each peak in the HPLC trace shown in Figure 4

Stated retention time / minutes	*Substance*
X	Acetone
5.88	BL087 (component A)
7.16	BL087 (component B)
9.19	BL087 (component C)
14.06	RM60
16.40	BL087 (component D)

RESULTS

Using the HPLC parameters described in the previous section, a solution of the nematic host material in acetone was analysed. Of all the various compounds present, four major components were detected, each giving a significant peak. The monomer was a single component, and in mixed solutions with the host was sufficiently separated to be determined with an acceptable degree of accuracy (see Figure 2 and Table I).

Variation of irradiation time

A series of samples was examined using a cell thickness of 50 μm and a polymerisation temperature of 39°C, with different irradiation times. The reaction temperature ensured that polymerisations occurred in the nematic phase of the mixture. These results are presented in Figure 5. Those for the LC host show that for each component, the results for each particular sample are very similar. The results are also similar between samples, with approximately 100% (within experimental uncertainty) detected for each experiment. This was expected since the host molecules do not contain polymerisable groups, and so should in general be completely removed from samples by their immersion in acetone. However, there is the possibility that a small fraction of the host could be "locked in" to the network, which cannot be completely discounted by these experiments. Another possibility is that some of the host molecules may have hydrogen atoms abstracted from them by radicals present in the system, thereby altering their structure. This would mean that these molecules would not be identified as host because they would have a different retention time.

The results obtained for the monomer differ from those relating to the host. The proportion of unreacted monomer decreased with increasing irradiation time, following the trend shown in Figure 5. This gradual decrease is due to the incorporation of more monomer into the network as the irradiation time increased. The data were fitted to an exponential decay function of the form $y = y_0 + ae^{-bx}$, where y represents the proportion of unreacted monomer, x represents the irradiation time, a is a proportionality constant and b is the rate constant. For the purposes of data fitting, the proportion of unreacted monomer for an irradiation time of zero was assumed to be 100%. The fit to the data was reasonable, but not exact. Nevertheless, it provides a good approximation to the observed trend, and allows comparison with data acquired using different polymerisation conditions. For the particular set of data shown in Figure 5, the rate constant, b, was $(2.5 \pm 0.6) \times 10^{-2}\ \mathrm{s}^{-1}$.

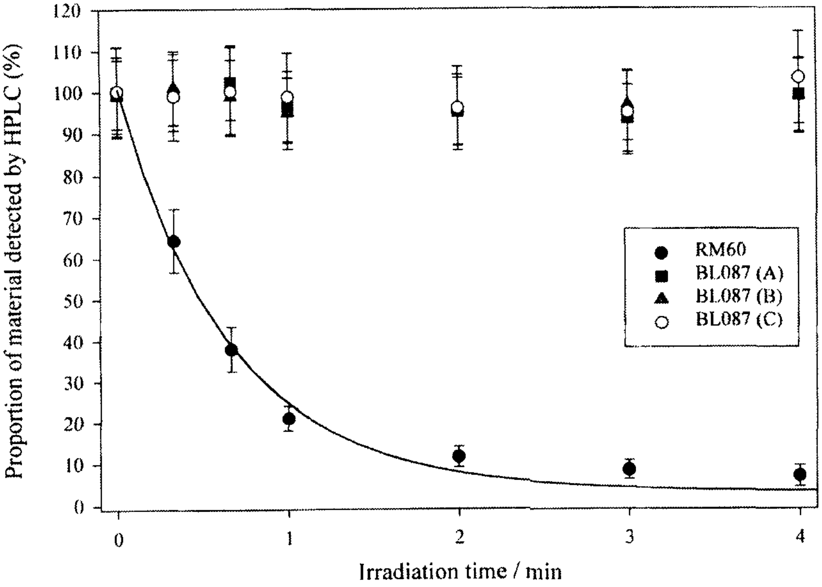

FIGURE 5 Graph of proportion of material detected against irradiation time for samples formed in the nematic phase using a polymerisation temperature of 39°C and a cell thickness of 50 μm. The curve through the data for this and subsequent figures is an exponential decay curve approximating the pattern of monomer depletion over time

Variation of cell thickness

Two further groups of samples were investigated, also using a polymerisation temperature of 39°C, but using cell thicknesses of 25 and 12.5 μm (see Figures 6 & 7 respectively). In addition, a limited number of samples were prepared using an intermediate cell thickness of 37.5 μm. Similar results were obtained compared to the 50 μm samples, but the depletion of monomer occurred faster, and higher rate constants were calculated. A summary of the rate constant values is presented in Table II.

Variation of polymerisation temperature

A series of samples was examined using a cell thickness of 50 μm, with a polymerisation temperature of 96°C, and different irradiation times. The temperature was such that samples were in the isotropic phase during each irradiation. Results (see Figure 8) were similar to the previous sets of samples formed in the

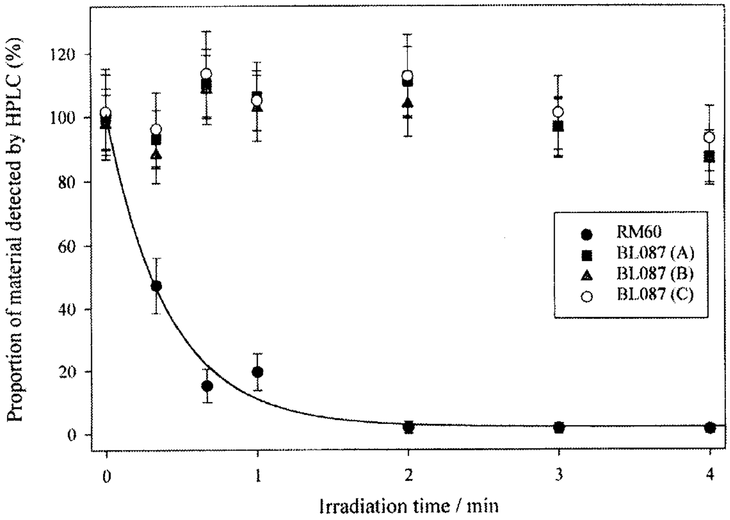

FIGURE 6 Graph of proportion of material detected against irradiation time for samples formed in the nematic phase using a polymerisation temperature of 39°C and a cell thickness of 25 μm

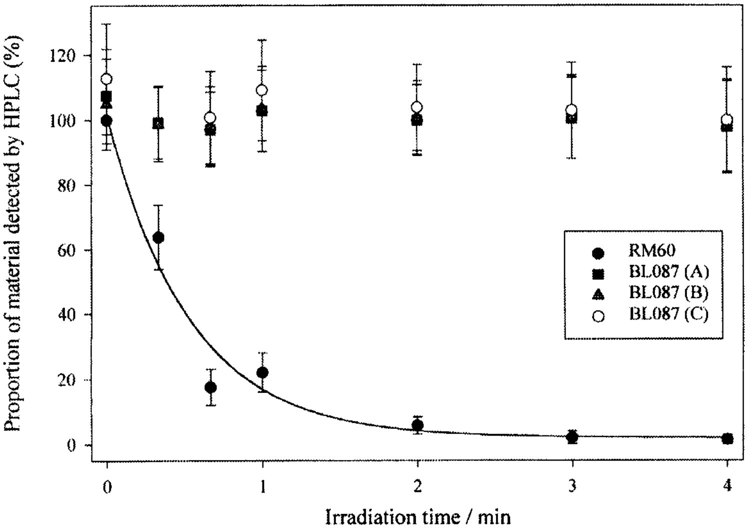

FIGURE 7 Graph of proportion of material detected against irradiation time for samples formed in the nematic phase using a polymerisation temperature of 39°C and a cell thickness of 12.5 μm

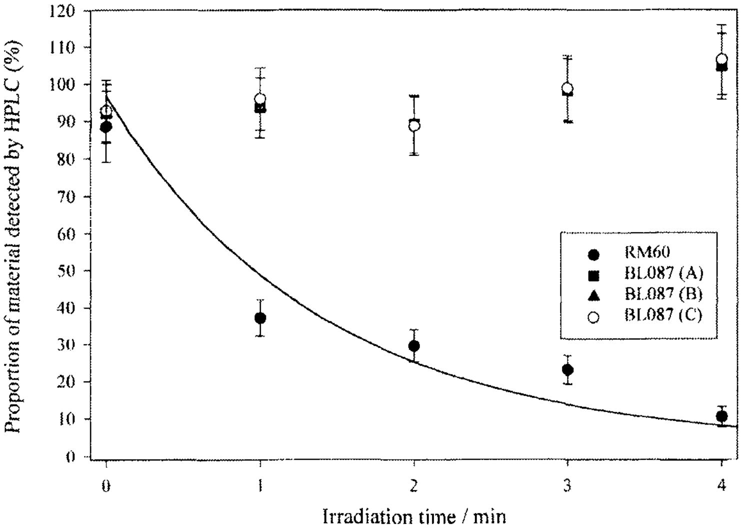

FIGURE 8 Graph of proportion of material detected against irradiation time for samples formed in the isotropic phase using a polymerisation temperature of 96°C and a cell thickness of 50 μm

nematic phase, although the reaction was considerably slower, with a rate constant of (1.2 ± 0.6) × 10^{-2} s^{-1} (*c.f.* the corresponding nematic series, which gave a rate constant of (2.5 ± 0.6) × 10^{-2} s^{-1}).

TABLE II Table summarising the rate constant values and estimated uncertainties obtained from data sets acquired from samples prepared using different cell thicknesses

Cell thickness / μm	*Rate constant / 10^{-2} s^{-1}*
12.5	3.2 ± 0.6
25	4.0 ± 0.6
37.5	3.3 ± 0.6
50	2.5 ± 0.6

A further series of samples was prepared using a cell thickness of 50 μm and irradiated for 1 minute at different polymerisation temperatures. Irradiation for 1 minute was chosen since, on the basis of the previous experiments, there was a significant amount of unreacted monomer remaining after this period. These results are presented in Figure 9. As for the previous sets of data, the proportion of the host detected was ~100% for each sample. In terms of the monomer, the

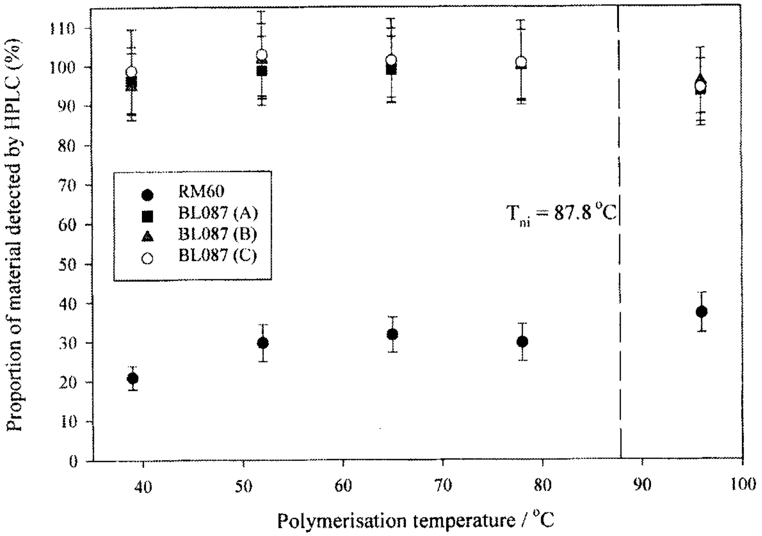

FIGURE 9 Graph of proportion of material detected against polymerisation temperature for samples formed using an irradiation time of 1 minute and a cell thickness of 50 μm

proportion detected was appreciably less than 100% since most was polymerised, leaving around 20–40% unreacted in these samples. The variation in the amount of unreacted monomer between different samples was small, but there was a slight and continuous increase with increasing polymerisation temperature. This increase continued into the isotropic phase, but there was no marked discontinuity at the T_{ni}. The results suggest that for a given time interval, less material polymerises at higher temperatures and, therefore, that the reaction is faster at lower temperatures. However, the lack of any significant discontinuity at the T_{ni} means that the temperature, not the phase of the host, is important. Previously, enhanced reaction rates have been reported for polymerisations within mesogenic hosts compared to isotropic ones,(13,14) and also in the bulk polymerisation of mesogenic acrylates.(15–17) However, as pointed out by Broer *et al*,(18) decreased polymerisation rates have also been reported in LC phases, meaning that each particular system must be treated separately.

In addition to the 50 μm samples, two samples of 25 μm thickness were irradiated for 1 minute at 39 and 96°C. For these samples, the increase in the amount of unreacted monomer with polymerisation temperature was more marked than for a cell thickness of 50 μm, since the sample irradiated at 39°C had less monomer remaining when using the thinner cell (~10% compared with ~20%). The sample irradiated at 96°C gave similar results with both thicknesses, suggesting that sample thickness is only an important factor in the nematic phase, not the isotropic phase.

DISCUSSION

The purpose of the work described in this paper was to establish a technique for determining the proportion of monomer which is used to form a network for a given set of conditions. This proved to be a challenging task, since the initial mass of monomer in a typical sample was of the order of 10^{-4} g, and this was present as a 1 wt % concentration within a LC host which was chemically similar to the monomer. Furthermore, after a polymerisation, the amount of monomer remaining was significantly less than that originally present. Using HPLC as the analytical technique, the separation of materials prior to their detection solved the problem of chemical similarity. In addition, the high sensitivity of the technique allowed detection of the monomer at low concentrations.

In order to perform an analysis, the soluble component had first to be separated from the network. Therefore, this is an *ex situ* technique. This has the disadvantage that the removal of the LC host and unreacted monomer by acetone causes significant changes to the network.(11) However, the technique serves its intended purpose, to quantify the unreacted material.

Within experimental uncertainty, the proportion of host detected was 100% of the original amount used for all samples investigated. It should be noted that the uncertainties present mean that the possibility that some host molecules could be trapped within the network, and hence not extracted into the analyte, cannot be ruled out from these measurements. However, transmission electron microscopy studies of sections taken from the network have revealed solid fibrillar structures, with no evidence for trapped host material.(12) For samples which were irradiated, the proportion of monomer remaining was less than 100%, since some had polymerised to give a network; the actual amount remaining depended on the reaction conditions. As would be expected, increasing the irradiation time caused greater numbers of molecules to be polymerised, which concurs with the DSC-UV experiments reported in the literature,(9,13,14,19,20) and morphological studies which show that the networks produced are more extensive for longer irradiations.(5–8) This demonstrates that the polymerisation requires a finite period for most of the molecules to react. If the irradiation is stopped after a time *t*, the free radicals present, which are responsible for building up the network, are quickly terminated. Any unreacted monomer present at this time will remain unreacted, not becoming part of the network. Therefore, to polymerise as many units as possible, the irradiation must continue in order to produce new radicals to replace those which have been terminated.

The proportion of monomer which remained unreacted decreased over time, but the decay pattern could not be fitted exactly to an exponential decay curve, or indeed to any simple kinetic process. This is due to the complicated nature of the reaction: the ability of each monomer molecule to react twice, the phase-separation of the growing network from the LC medium, and local increases in viscosity occurring around areas containing network are all factors which can markedly affect the process. However, the curves fitted to the data were useful guidelines for comparing the various sets of experimental data.

The reaction studied at 96°C (in the isotropic phase) gave a much lower rate constant than those at 39°C (in the nematic phase). This decrease in the polymerisation temperature, promoting a faster reaction, was confirmed by determining the amount of unreacted monomer after an irradiation period of 1 minute over a series of temperatures. The variation in the amount of unreacted monomer over the temperature range studied was relatively small, but revealed that as the temperature increases, the polymerisation takes longer to complete. The lack of a discontinuity at the T_{ni} suggests that temperature is also important in determining reaction rate in this system. The observations indicate that, at lower temperatures, the more anisotropic arrangement of the monomer molecules makes reaction more likely, and overcomes any possible increase in reaction rate which might be expected to occur due to an increase in thermal energy.

Reactions at 39°C using various sample thicknesses revealed a general feature of slower reaction for increasing sample thickness. This trend was, however, not applicable for a polymerisation temperature of 96°C (in the isotropic phase), where sample thickness did not significantly affect the overall rate. These observations can be related to the director pattern of the system, since material inside thicker cells is, on average, further away from the aligning surfaces. Therefore, for a nematic sample, there will be a broader distribution in director alignment for increasing cell thickness, leading to increased light scattering, a decrease in UV absorption, and a slower reaction. This feature does not apply in the isotropic phase, since the molecules are disordered throughout a sample, irrespective of cell thickness.

The results obtained have made it possible to quantify for the first time how much monomer goes into forming the network component of PSLCs under various experimental conditions, and reveal how long an irradiation period is required for the polymerisation process to go to completion. As well as being interesting from a fundamental point of view, this information is also important with regard to applications. The central function of PSLCs is their use in LC displays. It is therefore very useful to know how long an irradiation is required under a particular set of conditions to polymerise a certain amount of monomer to give a material with well-defined and reproducible electro-optic properties. For example, when a relatively large proportion of monomer is polymerised, more network is obtained and the threshold voltage for electro-optic switching will tend to be larger, while the decay time on removal of the switching voltage will tend to be shorter. The amount of monomer which polymerises also affects the morphology of the network. For example, relatively low irradiation times produce a network consisting of isolated droplets, while longer irradiations produce greater numbers of droplets, which aggregate into fibrillar structures. A detailed study on network morphology will be presented in a forthcoming paper.(21)

The ideal way of monitoring the polymerisation process in PSLCs would be to use an *in situ* technique, so as not to disturb the material. DSC-UV is such a technique, the basis of which lies in measuring the heat evolved from a reaction as a result of UV irradiation at constant temperature.(9) There are relatively few reports in the literature dealing with the polymerisation process, and those published have used DSC-UV. Results obtained have given important insights into the polymerisation reaction, but the main drawback of the technique is that samples are formed in aluminium pans. This is a very different environment to the glass cells in which PSLCs would be generated for use in displays (the primary application of these materials), and one in which the sample thickness cannot be accurately controlled. The most important difference is that the enforced global director alignment produced inside cells would not be reproduced inside the aluminium pans. For a nematic sample, this would mean that a polydomain texture would exist instead of a monodomain, and this could affect the polymerisation behaviour in a similar way to that seen for the glass cells when their thickness is increased. For example, the broader distribution of director alignments may produce a slower reaction rate, while light scattering from domain boundaries would have the same effect by scattering UV radiation out of samples, leading to an effective decrease in UV intensity.

In addition to DSC-UV, another *in situ* technique which has been applied to PSLCs is IR spectroscopy.(9) However, the amount of monomer used in such experiments was 10 wt % or more, significantly greater than the 1 wt % used for the experiments in this study. As part of the work described in this paper, FTIR spectra of the host/monomer mixture were taken, and the monomer could not be detected due to the very small amount present relative to the host. The use of multiple internal reflectance spectroscopy (MIRS) could potentially improve the situation, but the host may still obscure the monomer, especially when very little monomer remains after an irradiation. Another factor is that samples for IR spectroscopy tend to be formed between salt discs since glass does not transmit in the infrared region of the spectrum. To date, no *in situ* techniques have been applied for monitoring the polymerisation process of PSLCs in their "natural environment".

The main advantage of the procedure developed in this work using HPLC is that, while being an *ex situ* technique, it does allow monitoring of the results of a polymerisation in a treated glass cell, which DSC-UV cannot. Furthermore, in the DSC-UV experiments reported by Hikmet,(9) the progress of the polymerisation could not be followed beyond ~70% monomer depletion, while the maximum conversion reported by Guymon *et al*(13,14) was 90%. In the study described here, HPLC has been used to monitor the polymerisation beyond these limits.

Recently, DSC-UV experiments performed by Guymon *et al*(13,14,19,20) have concentrated on ferroelectric PSLCs. This work has involved the nematic phase, however, and comparisons can be made between these results and the HPLC data generated in this study. In the earlier studies, a variety of diacrylate monomers was investigated, and the general trend was for the polymerisation rate to increase with decreasing temperature, as observed in this work. The rate increases were attributed to enhanced orientation and segregation of the polymerisable bonds. However, one monomer exhibited the opposite behaviour,(19) possibly due to factors such as molecular bulkiness and steric hindrance overcoming the orienting effects of the LC host. Maximum polymerisation rates for the nematic phase reported by Guymon were ~10^{-3} s^{-1}, which is an order of magnitude lower than those calculated from the present study. This difference may be explained by the factor of ten difference in UV intensity between the two sets of experiments (2.5 mW cm^{-2} compared to ~25 mW cm^{-2} for the experiments presented in this paper). Furthermore, the difference in reaction rate between the nematic and isotropic phases was found to be much greater than previously reported.

The various differences between results from the HPLC and DSC-UV experiments are probably due to the use of different materials with somewhat different properties. It should be noted that there have been no previous reports on the particular chemical systems of the current work. Thus, attempts to draw exact comparisons between the different systems will be subject to a considerable degree of uncertainty. For example, C6M (see Figure 10) is a common LC diacrylate used in many literature studies; this has notable structural differences from the diacrylate used in the present study. Differences in chemical structures are even more marked for the LC host: while BL087 contains simple cyanobiphenyls and terphenyls, the ferroelectric materials used by Guymon *et al* are considerably more complex in composition. Hence, the phase behaviour of the systems is different, and this would lead to variations in the polymerisation behaviour.

Ultimately, HPLC has been shown to be a useful and valuable tool for monitoring the polymerisation process in PSLCs, and provides a realistic alternative to the DSC-UV method.

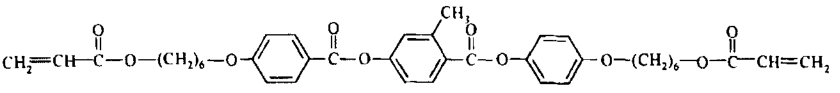

FIGURE 10 The molecular structure of the diacrylate monomer C6M

CONCLUSION

The progress of the polymerisation reaction in which the network component of PSLCs is formed was successfully monitored by HPLC, which, for the first time, has been established as a viable technique for studying these materials. In addition, this method made it possible to monitor the polymerisation process inside a realistic environment, *i.e.* an electro-optic cell. Results showed that the proportion of monomer which was consumed by the process was crucially dependent upon the reaction conditions. Longer irradiation times caused greater numbers of molecules to polymerise, while the reaction was found to be faster for lower polymerisation temperatures. Sample thickness was unimportant for samples polymerised in the isotropic phase, but in the nematic phase, the reaction was faster in thinner cells. This can also be attributed to the director pattern of the host, with material in the nematic phase having a more uniform director pattern within a thinner cell, while material in the isotropic phase always shows a random arrangement, regardless of cell thickness. Monitoring of the polymerisation process showed that the kinetics were complicated, with no simple kinetic scheme being applicable.

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