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## Liquid Crystals

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# Copolymerizable initiator for improved polymer dispersed liquid crystal films

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The problems of photoinitiator contamination are addressed for the liquid crystal phase in polymer dispersed liquid crystal films formed by photopolymerization induced phase separation of liquid crystal from monomer solutions. Initiator contamination lowers the clearing point of the liquid crystal phase, and decreases the photostability and resistivity of the polymer dispersed liquid crystal. These problems are minimized by replacing the conventional photoinitiators with copolymerizable initiators which become incorporated in the polymer phase as it separates. Copolymerizable photoinitiators are studied and used to form polymer dispersed liquid crystals with higher clearing point liquid crystal phases, higher resistivity, and better photostability than polymer dispersed liquid crystals formed with conventional photoinitiators. These improvements provide very significant advantages for many polymer dispersed liquid crystal applications.

## 1. Introduction

The technique of forming polymer dispersed liquid crystal films by photopolymerization induced phase separation of liquid crystal monomer solutions [1, 2] using ultraviolet light exposure is convenient and has many advantages. The electro-optical properties of these polymer dispersed liquid crystals can be favourably affected by controlling the droplet size of the liquid crystal phase [2–4] and the off-state prealignment [5] during their formation. However, this process has also suffered from the problem of contamination of the liquid crystal phase by the conventional photoinitiators which are used. This is due to the greater solubility of these initiators in the mobile liquid crystal phase than in the cured solid polymer phase. Most of a conventional initiator is not used up photochemically during the polymer dispersed liquid crystal formation. Thus, the initiator ends up partitioned between the polymer phase and the liquid crystal phase, with a large part of it in the liquid crystal droplets. Such initiator contamination tends to lower the clearing point of the liquid crystal phase. As a typical example, a polymer dispersed liquid crystal made from a 50:50 solution of BDH-E7 in Norland NOA-65 showed a clearing point of about 56°C for its liquid crystal droplets [5], instead of the initial 60°C for the pure liquid crystal. Initiator contamination can also decrease the photostability and the resistivity of the polymer dispersed liquid crystal.

In this paper we present evidence that the usual decrease in the polymer dispersed liquid crystal clearing point is caused by initiator contamination of the liquid crystal phase. We show that this problem can be minimized by replacing conventional

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initiators with copolymerizable photoinitiators which become incorporated predominantly in the polymer phase as it separates, rather than in the liquid crystal phase. This technique resulted in superior polymer dispersed liquid crystals with higher clearing point liquid crystal phases, higher resistivity, and better photostability, all of which are major advantages for many polymer dispersed liquid crystal applications.

## 2. Experimental

### 2.1. *Materials*

The monomer system used was HRL-URC, which is a proprietary mixture of the multifunctional mercaptan trimethylolpropane tri-3-mercaptopropionate (TMPTMP) and multifunctional vinylurethanes (MVU) used together in the percentages or ratios indicated.

The liquid crystals used were obtained commercially from British Drug House, except for the proprietary mixture HRL–PD50 which contains cyanobiphenyl, cyanophenylcyclohexane, and cyanoterphenyl components [6]. HRL–PD50 has a nematic range of about −20 to 83°C, but with a broad clearing point range of 81–86°C.

The conventional photoinitiators were obtained commercially from the Aldrich Chemical Co., and experimental samples of the copolymerizable initiators [7] were obtained from E. Merck. The 'QC accelerator' used was Quantacure (ethyl 4-dimethylaminophenyl benzoate) from Ward Blenkinsop & Co., Ltd.

### 2.2. *Techniques*

The HRL-URC monomer system was prepared by mixing parts of TMPTMP and MVU, e.g., 120 : 100 (by weight), respectively, giving a mixture with a SH/C=C ratio of 1·5 in the monomer. Each monomer solution was mixed with the selected liquid crystal for example, on a 50 : 50 (by volume) basis with BDH-E7. The photoinitiator was dissolved in the overall monomer liquid crystal system in the selected percentage by weight indicated in the experiment.

The monomer/liquid crystal/initiator solution was placed between indium tin oxide coated glass electrodes separated by a 13 $\mu$m thick Mylar perimeter spacer. Ultraviolet exposures were made as in prior experiments [6] using a 350 W high pressure mercury arc lamp, yielding intensities at the cell surface of about 60 mW cm$^{-2}$ over the 300–500 nm range.

Photostability tests were carried out with exposures from a 1·6 kW xenon arc lamp giving intensities on the cell of about 2 W cm$^{-2}$ in the 372–750 nm range. This exposure system heated the polymer dispersed liquid crystal cell up to about 43°C.

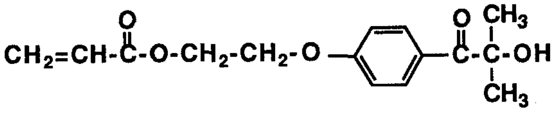
## 3. Results and discussion

We observed that the direct dissolution of conventional initiators in liquid crystals lowers their clearing points by about 3·7°C per 1 per cent of benzophenone added to BDH-E7 and by about 3·8°C per 1 per cent of 2,2-diethoxyacetophenone (DEAP) added to BDH-E9. In the ultraviolet-initiated polymer dispersed liquid crystal made from BDH-E7 and Norland-NOA65, the liquid crystal droplet phase would have a clearing point of 60°C if it separated out as pure E7, with all the components in the same ratio as formulated initially. However, as indicated above, typical polymer dispersed liquid crystal made from this system has a clearing point of about 56°C. If this 4° lowering of the clearing point is assumed to be entirely due to contamination from the photoinitiator, it would take only about a 1 per cent concentration of the initiator in the liquid crystal droplets to cause the effect.

We have studied the use of copolymerizable photoinitiators in place of conventional photoinitiators as a means of trapping most of the initiator in the polymer phase of the polymer dispersed liquid crystal as it separates, thereby preventing initiator from separating (or remaining) in the liquid crystal phase. The structures and names of the two copolymerizable initiators used are shown in figure 1. They were previously studied [7] within a polymer matrix to obtain higher quality and longer lasting polymer films, but they had not been investigated in phase separation systems such as the polymer dispersed liquid crystal formation experiments described here.

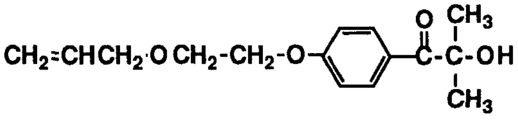
In one series of experiments, we studied polymer dispersed liquid crystals made from various concentrations of copolymerizable initiator **I** as compared to the same concentrations of benzophenone or DEAP. The monomer system used is described in the example given above, such that it had a 1·5 ratio of SH/C=C groups. This was mixed 50 : 50 (by volume) with BDH-E7 and the various concentrations of added initiators as indicated in figure 2, which shows the clearing points of the resultant liquid crystal droplets in the polymer dispersed liquid crystal formed by ultraviolet exposure. The polymer dispersed liquid crystals made with the copolymerizable initiator showed clearing points from 57 to 58°C range over the entire range studied, while those made with the conventional initiators showed much lower clearing points which were in the 49–54°C range. This indicates that much less of **I** was contained in the liquid crystal droplets than was the case with benzophenone and DEAP.

Another series of similar experiments is shown in figure 3. These were all carried out with an overall initiator concentration of 1·5 per cent of **I**, benzophenone, or DEAP. The SH/C=C group ratio in the monomer system was varied (by varying the mixtures of TMPTMP with MVU), mixed 50:50 (by volume) with BDH-E7, and the initiator added. The clearing points of the polymer dispersed liquid crystals made with **I** were 3–6°C higher than for those made with the conventional initiators over the whole range of different monomer compositions. It is interesting to note that in the 0·9–1·5 range of SH/C=C ratios, the clearing points of the polymer dispersed liquid crystal made with **I** were in the 59–61°C range, which is essentially the same as for the pure E7 starting material. This indicates that for these compositions, the liquid crystal droplets formed with the copolymerizable initiator were probably only slightly contaminated with initiator, while initiator contamination of the liquid crystal droplets made with benzophenone and DEAP was probably the main cause of the lower clearing points when the SH/C=C ratio was in this same range. There is probably contamination of the liquid crystal droplets by the TMPTMP at higher SH/C=C ratios (above 1·6).



**I**

4-(2-acryloyloxyethoxy)phenyl 2-hydroxy-2-propyl ketone



**II**

4-(2-allyloxyethoxy)phenyl 2-hydroxy-2-propyl ketone

Figure 1. Copolymerizable photoinitiators used in the polymer dispersed liquid crystal studies.

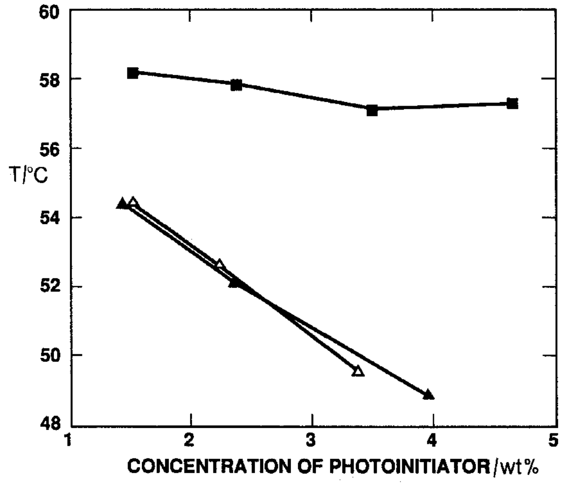


Figure 2. Effect of photoinitiator structure and concentration on the clearing point of polymer dispersed liquid crystals made from a 50 : 50 (by volume) mixture of monomer (HRL-URC with a SH/C=C ratio of 1·5) and BDH-E7. (■) is with copolymerizable initiator **I**, (△) is for benzophenone, and (▲) is for DEAP.

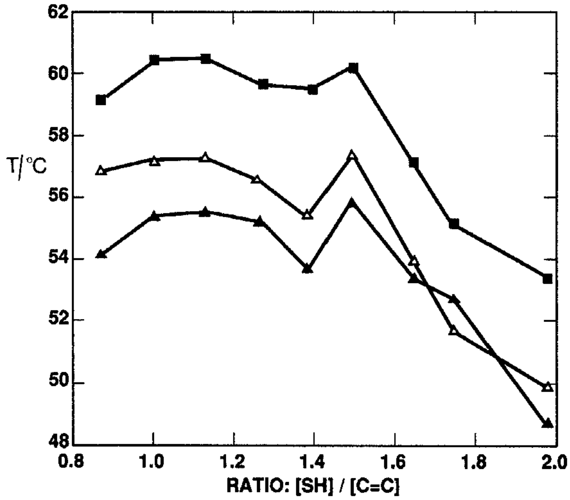


Figure 3. Effect of photoinitiator type and SH/C=C ratio in the monomer on the clearing point of polymer dispersed liquid crystals made from a 50 : 50 (by volume) mixture of monomer (HRL-URC) and BDH-E7, with 1·5 per cent initiator added to the overall solution. (■) is with copolymerizable initiator **I**, (△) is for benzophenone, and (▲) is for DEAP.

Results similar to those in figures 2 and 3 were obtained with polymer dispersed liquid crystals made from solutions of the liquid crystal HRL–PD50 (in volumes in the range of 35–50 per cent of liquid crystal) with the same HRL-URC monomer system having SH/C=C ratios in the 1·1–1·9 range. The clearing points of the liquid crystal droplets in the polymer dispersed liquid crystals made with **I** as the photoinitiator were close to those of the starting liquid crystal while those made with DEAP were 6–10°C lower than for HRL–PD50.

Photostability studies on another series of polymer dispersed liquid crystals made with HRL–PD50 are shown in the table. The samples used each had 35·5 per cent of HRL–PD50 mixed with 64·5 per cent of the HRL–URC monomer system at a SH/C=C ratio of 1·6, and the following initiator and accelerator additives:

Sample No. 1 had 1·8 per cent of copolymerizable initiator **I**,
Sample No. 2 had 1·8 per cent of **I** and 1·2 per cent QC accelerator,
Sample No. 3 had 2·3 per cent benzophenone and 1·5 per cent QC.

The results in the table show the total hours of intense exposure at 2 W cm$^{-2}$ in the 372–750 nm range and the resulting percentage change in resistivity (%$\Delta\rho$), percentage change in the voltage required to reach 90 per cent of the fully-on state (%$\Delta V_{(90)}$), and the percentage change in contrast ratio (%ΔCR) as compared to the polymer dispersed liquid crystal before exposure. The goal of these tests was to retain an operational polymer dispersed liquid crystal after 1000 h of exposure, while keeping the increase in $V_{(90)}$ to less than 50 per cent change, and to have less than a 10 per cent decrease in contrast ratio. Samples No. 1 and No. 2 (containing copolymerizable initiator) passed these tests and had good operational characteristics when the tests were stopped after 1029·2 h of exposure (about 2058 Wh cm$^{-2}$ of exposure). Sample No. 1, with **I** and without QC, was the most stable of the three samples, showing very little change in characteristics. Polymer dispersed liquid crystal sample No. 3 (made with a conventional photoinitiator) was inoperable after 542 h, and at this exposure showed percentage changes in characteristics that were larger than the goal limits.

We also tested the use of copolymerizable initiators **I** and **II** in the formation of many other polymer dispersed liquid crystals of various compositions and types, including other polymer dispersed liquid crystals formed with morphologies of the droplets (Swiss cheese) type [8], the network (polymer ball) type [8], and the gel type [9] with reverse electro-optical mode (i.e. clear off-state and scattering on-state). In all cases the copolymerizable photoinitiators gave polymer dispersed liquid crystals with improved characteristics such as clearing point, resistivity, and contrast ratio as compared to polymer dispersed liquid crystals of the same compositions made with conventional photoinitiators. Even polymer dispersed liquid crystal gels containing 96 per cent BDH-E7 showed clearing points 1–3°C higher (in the 59–60°C range) when made with 0·6 per cent photoinitiator **II**, as compared to polymer dispersed liquid crystals made with the same monomer compositions using 0·6 per cent DEAP as the photoinitiator (which resulted in clearing points in the 55–59°C range).

Effect of photoinitiator on photostability of polymer dispersed liquid crystals exposed with high intensity (2 W cm$^{-2}$) light at 43°C. Results are given in per cent change from the initial properties. Polymer dispersed liquid crystals were made from 64·5 : 35·5 (by volume) mixture of monomer (HRL-URC with a SH/C=C ratio of 1·6) and liquid crystal (HRL–PD50) with the following initiator and accelerator additives: No. 1 = 1·8 per cent of copolymerizable initiator **I**, No. 2 = 1·8 per cent of **I** and 1·2 per cent QC accelerator, No. 3 = 2·3 per cent benzophenone and 1·5 per cent QC.

| Sample | Total exposure/h | %$\Delta\rho$ | %$\Delta V_{(90)}$ |  | %ΔCR |  |
|---|---|---|---|---|---|---|
|  |  |  | 100 Hz | 500 Hz | 100 Hz | 500 Hz |
| 1 | 1029·2 | — | +19·2 | +18·6 | −2·5 | +2·2 |
| 2 | 1029·2 | −78·7 | +31·0 | +12·2 | −4·6 | +16·9 |
| 3 | 542·2 | −70·6 | −55·7 | −67·6 | −45·5 | −39·6 |

## 4. Conclusions

We have shown that contamination of the liquid crystal phase of polymer dispersed liquid crystals made with conventional photoinitiators is a problem in regard to the temperature range and operational stability of the polymer dispersed liquid crystals. This problem can be minimized by the use of copolymerizable photoinitiators which tend to be trapped in the polymer phase rather than in the liquid crystal phase of the polymer dispersed liquid crystals during their ultraviolet-induced formation. Two different copolymerizable photoinitiators were studied in a wide range of liquid crystal/monomer systems to form polymer dispersed liquid crystal films of various morphologies, including the liquid crystal–droplet type, network type, and gel type morphologies. In all cases the polymer dispersed liquid crystal films made with copolymerizable initiators were superior to those formed with conventional initiators, resulting in polymer dispersed liquid crystals with higher clearing points, higher resistivity, and better long term photostability to broad band exposures of intense light.

The authors are grateful to Dr J. Ohngemach of E. Merck for providing laboratory test samples of the copolymerizable photoinitiators used in these studies and for discussions of his pioneering work in this area.

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