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

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Evolution of Network Structure in Polymer-Stabilised Liquid Crystals

Mark Brittin [a] & Geoffrey R. Mitchell [a]

[a] J.J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading, RG6 6AF, U.K.

Version of record first published: 24 Sep 2006

To cite this article: Mark Brittin & Geoffrey R. Mitchell (1999): Evolution of Network Structure in Polymer-Stabilised Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 329:1, 145-152

To link to this article: http://dx.doi.org/10.1080/10587259908025935

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 145-152
Reprints available directly from the publisher
Photocopying permitted by license only

Evolution of Network Structure in Polymer-Stabilised Liquid Crystals

MARK BRITTIN and GEOFFREY R. MITCHELL

J.J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading, RG6 6AF, U.K.

Experiments were performed to investigate the evolution of structure and morphology of the network in polymer-stabilised liquid crystals. In situ optical microscopy revealed that the morphology was significantly altered by extraction of the LC host, while scanning electron microscopy showed that the network morphology was also dependent on the polymerisation conditions and closely related to the depletion of monomer, as monitored by high performance liquid chromatography. Transmission electron microscopy allowed observation of internal structure, resolving microstructure on the order of 0. 1 μm.

Keywords: Polymer networks; in situ photopolymerisation; electron microscopy; morphology; high performance liquid chromatography

INTRODUCTION

The electro-optic properties of LCs have been shown to be significantly affected by dispersing a small amount of a polymer network within a LC host [1-3]. Such a system, commonly known as a polymer-stabilised liquid crystal (PSLC)[4,5] or anisotropic gel[6], is formed by dissolving a suitable monomer within a LC host and polymerising it photochemically. The monomer is typically a mesogenic diacrylate, and is polymerised using ultraviolet radiation in conjunction with a photoinitiator. Since this is an isothermal process, the reaction can take place in a desired mesophase by controlling the temperature

of the mixture during irradiation. The resulting network, which is thermally stable[7], reflects the anisotropic character of the medium in which it was formed, and exerts aligning forces on the free molecules[8], giving rise to novel electro-optic devices. In this work we explore the formation of such networks using scanning electron microscopy (SEM) in conjunction with high performance liquid chromatography (HPLC) to determine the extent of polymerisation and transmission electron microscopy (TEM) to evaluate the internal structure.

EXPERIMENTAL

The mesogenic diacrylate RM60 (K 73 °C N 80 °C I) was dissolved within BL087 (Merck R&D U.K.), a eutectic mixture with a nematic phase (T_{NI} = 89.5 °C). The diacrylate made up only 1% w/w of the system, which also included 0.2% w/w of Irgacure 651 (Ciba-Geigy) to photoinitiate the polymerisation. The mixture was contained inside glass sandwich cells with rubbed polyimide layers and Kapton spacers while being polymerised by UV radiation (365 nm, 10 mW cm^{-2}) at 35 °C (N phase) or 100 °C (I phase) for 0-4 minutes. Following polymerisation, the network was separated from the bulk LC using acetone or hexane over four days. On removal, the solvent was allowed to evaporate before the cells were carefully split apart and prepared for SEM observation. Thin films of the network for TEM studies were prepared using microtomy[9]. To improve contrast in the TEM, heavy atoms (Cl, Br) were incorporated into the network. This also allowed network areas to be identified by energy dispersive spectroscopy. The material removed by dissolution was analysed by HPLC. This made it possible to deduce the extent of polymerisation by detecting the proportion of monomer which does not react for a given set of conditions. Full details of the technique will be given elsewhere[10]. In order to

determine the influence of the dissolution procedures on the morphology of the extracted network, the process was monitored using *in situ* polarised light microscopy.

RESULTS AND DISCUSSION

Separation of network and host

The process of solvent extraction was observed using optical microscopy on a sample of 12.5 μm thickness which had been polymerised for 3 minutes at 35 °C. Initially, the network was barely visible due to poor contrast with the LC solvent. However, addition of acetone caused considerable changes. As acetone leached into the cell, boundaries between LC and isotropic areas were observed. At the same time, inside the LC, the network became much more visible, appearing as a very fine structure retracting in towards the centre of the cell (Fig. 1(a)). As the solvent boundaries moved further in, the fine network gradually disappeared, with the rest of the LC soon following. As the LC dissolved, a larger strand-like network appeared at various points along the solvent boundary (Fig. 1(b)). These strands are artefacts of the drying process, which causes agglomeration of the network rather than reflecting the initial morphology. This is consistent with the appearance of finer aggregates from thinner cells, in which the tendency of the network to collapse should be less. Addition of more BL087 does not cause separation of the aggregates. Experiments with hexane showed a variation in results, with a very fine network present as well as some larger aggregates. It is possible that this finer material is a better indicator of the network in its original form, but for both solvents, it is clear that the dissolution process has a considerable effect on the structure.

The HPLC results (Fig. 2) show that the depletion of monomer is a first order rate process, with the amount present decreasing exponentially over time. The reaction proceeded faster in the nematic phase compared to the isotropic phase, suggesting that the enhanced orientation of the LC medium assists the polymerisation in line with previous observations[11, 12]. The reaction was also faster for thinner cells, probably due to the energy of the UV beam being spread over a smaller volume, effectively causing an increase in power.

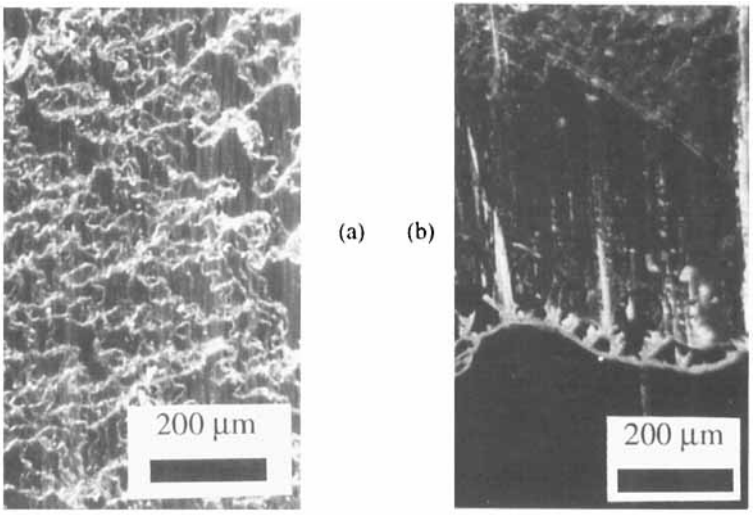

FIGURE 1 Polarising optical micrographs of a PSLC: (a) on addition of acetone; (b) after the acetone has dissolved most of the LC solvent
(See color plate V at the back of this issue)

Network Structure

SEM showed that the "dry" network morphology is highly dependent on the reaction conditions, with a variety of structures observed. Here, we concentrate on four morphologies (Fig. 3). For a sample of thickness 50 µm polymerised at

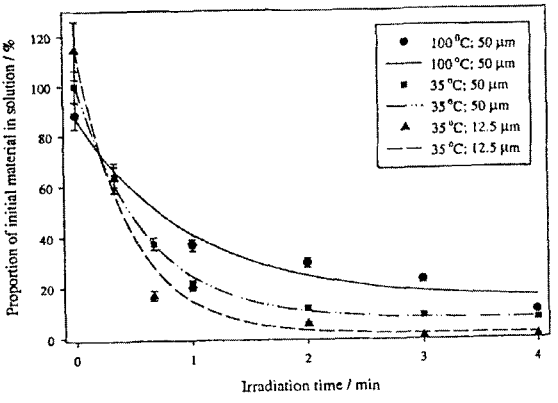

FIGURE 2 Plots of unreacted monomer proportion against irradiation time for a series of polymerisation conditions. The data sets are each fitted to exponential decay curves

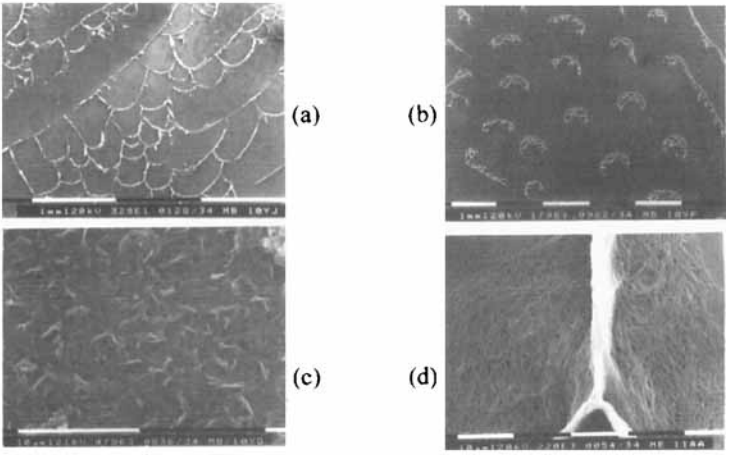

FIGURE 3 Network morphologies observed by SEM for the following monomers, polymerisation temperatures, irradiation times and cell thicknesses: (a) RM60, 35 °C, 3 min, 50 µm; (b) RM60, 35 °C, 40 s, 50 µm; (c) RM60, 100 °C, 3 min, 50 µm; (d) RM103, 35 °C, 5 min, 50 µm

35 °C for 3 minutes, a network of cross-linked strands was formed (Fig. 3(a)), while reducing the irradiation time to 40 s revealed more isolated semi-circular features, with a few strands starting to grow from them (Fig. 3(b)).

Changing the phase of the material by polymerising at 100 °C also had a marked effect on the morphology. The resulting network (Fig. 3(c)) was on a much smaller scale than in other samples, while appearing porous and amorphous due to the less ordered conditions in which the reaction took place.

As might be expected, the depletion of monomer is closely related to the network morphology. For low depletion, a relatively small amount of network is present, with isolated structures being formed on extraction of the LC host. As more monomer is used up, the resulting network is increasingly branched and cross-linked. Much of the detail of the branching structure can be related to the extraction process, with the moving solvent boundary resulting in uni-directional branching. Therefore, the key features in determining these morphologies are the washing-out process and the amount of network present, which is determined by the reaction conditions. In contrast to such aggregate structures, networks prepared using a different monomer (RM103) show a much finer texture in addition to some aggregates (Fig. 3(d)). This variation emphasises the dominating role of the extraction process and complications which may arise as a result of different monomer/host and network/solvent interactions. Clearly, there is a difficulty in deriving relationships between growth conditions and the resultant morphology within the LC host.

In order to observe internal network structure and potentially resolve fine material within the aggregates, TEM studies were performed. This proved difficult due to poor contrast between the RM60 networks and the usual embedding media for microtomy[9]; to improve this, such a network was stained with bromine. This acted as a marker, making the network visible as a dark band across the section (Fig. 4(a)), while energy dispersive spectroscopy

(EDS) was used to confirm that bromine was present. However, the thickness of the section, combined with too much contrast in the image, made the network appear blurry with no structural details apparent due to the superimposing of features in the section. Therefore, RM103, which contains chlorine, was used instead of RM60. The image obtained (Fig. 4(b)) was much clearer, with the network appearing as a horizontal band (for both samples, the original cell thickness was perpendicular to the plane of the photographs). Since the section was thinner and the contrast less when compared with the brominated sample, microstructure could be observed: dark areas of dimension ~0.1 μm were apparent, which corresponded with the very fine fibrils observed by SEM for this particular sample (Fig. 3(d)). In contrast to the SEM, the fibril boundaries are blurry, which we attribute to diffusion of the resin into a more porous component in the peripheral regions of the fibrils. This suggests that the fibrils in the LC host have a rather open structure.

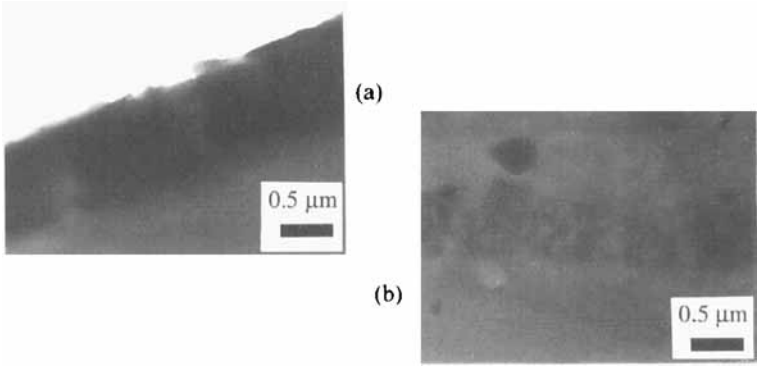

FIGURE 4 TEM micrographs of embedded networks. Network appears as (a) a diagonal band (brominated) and (b) a horizontal band (chlorinated)

CONCLUSION

We have shown that the structure of the network is modified by extraction of the LC host, causing partial-to-complete agglomeration of the original fine fibrils. The "dry" network morphology is also dependent on the polymerisation conditions and closely related to the depletion of monomer. TEM can provide a route to observing network microstructure, potentially resolving individual structures within the aggregates.

Acknowledgements
We thank Prof A Gilbert, Drs FJ Davis & AS Vaughan, University of Reading, Dr D Coates, Merck R&D UK, and Mr A Smith, Hichrom Ltd for valuable discussions. This work was supported by EPSRC and Merck R&D UK.

References

[1] R.A.M. Hikmet, *Mol. Cryst. Liq. Cryst.*, **213,** 117 (1992)
[2] R.A.M. Hikmet, B.H. Zwerver, *Liq. Crystals,* **12,** 319 (1992)
[3] D.-K. Yang, L.-C. Chien, J.W. Doane, *Appl. Phys. Lett.*, **60,** 3102 (1992)
[4] C.A. Guymon, E.N. Hoggan, D.M. Walba, N. A. Clark, C. N. Bowman, *Liq. Crystals,* **19,** 719 (1995)
[5] C.V. Rajaram, S.D. Hudson, L.-C. Chien, *Chem. Mater.*, **7,** 2300 (1995)
[6] R.A.M. Hikmet, *J. Appl. Phys.*, **68,** 4406 (1990)
[7] R.A.M. Hikmet, R. Howard, *Phys. Rev. E,* **48,** 2752 (1992)
[8] R.A.M. Hikmet, B.H. Zwerver, *Liq. Crystals,* **10,** 835 (1991)
[9] M. Brittin, G.R. Mitchell, A.S. Vaughan, to be submitted to *Liq. Crystals*
[10] M. Brittin, G.R. Mitchell, A. Gilbert, to be submitted to *J. Mat. Chem.*
[11] C.E. Hoyle, C.P. Chawla, A.C. Griffin, *Polymer,* **60,** 1909 (1989)
[12] C.A. Guymon, E.N. Hoggan, N.A. Clark, T.P. Rieker, D.M. Walba, C.N. Bowman, *Science,* **275,** 57 (1997)