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Reflectance properties of polymer-stabilised cholesteric liquid crystals cells with cholesteryl compounds of different functionality

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In this paper, we describe the synthesis of cholesteryl compounds of different functionality. A series of polymer-stabilised cholesteric liquid crystal (PSCLC) cells are prepared by photo-polymerisation of a cholesteric liquid crystal (Ch-LC) mixture containing a non-reactive liquid crystal, a nematic diacrylate and the above cholesteryl compounds. The effect of cholesteryl compound functionality on the morphology and the reflectance properties of PSCLC cells is evaluated, as are parameters such as the polymerisation temperature. The results indicate that the higher functional cholesteryl compound is more effective for broadening the reflection band of the Ch-LC composites, which is speculated to be a result of the pitch differences in the local network environment. Scanning electron microscopy is used to examine the morphologies of the polymer network of the PSCLC cells. We have found that the morphologies of the polymer network are determined by the functionality of the cholesteryl compounds as well as polymerisation temperature, which further influence the reflectance properties of the composites.

1. Introduction

Polymer–liquid crystal dispersions have attracted much attention in the past few years owing to their applicability to display devices and the fundamental insights they offer on liquid crystal/polymer composites [1]. Polymer stabilised liquid crystals (PSLCs) are composites with small amounts of polymer networks dispersed in liquid crystals (LCs). The general idea of PSLCs is the stabilisation of alignment of a low-molecular-mass LC by interactions between the polymer network and the LC [2, 3]. Therefore, it is necessary to investigate the morphology of the polymer networks formed in LCs, which is determined by the chemical structure of the monomer and the polymerisation conditions, and its connection to the control and optimisation of the optical properties of the composite system [4].

Owing to the unique helical supramolecular structure, a cholesteric liquid crystal (Ch-LC) can selectively reflect circularly polarised incident light with the same handedness as its helical axis. At normal incidence, the wavelength of the reflected light $\lambda = n \times P$, where $n = (n_o + n_e)/2$ is the average of the ordinary (n_o) and extraordinary (n_e) refractive indices of the locally uniaxial structure and P is the pitch length of the helical axis. The reflection bandwidth, $\Delta\lambda$, is given by $\Delta\lambda = \Delta n \times P$. Here $\Delta n = n_e - n_o$ is the birefringence of the LC. Within this reflection band, right-circularly polarised light is reflected by a right-handed helix, whereas left-circularly polarised light is transmitted. Outside the reflection band both polarisation states are transmitted [5–7]. In general, Δn is typically limited to 0.3; the reflection bandwidth $\Delta\lambda$ will be less than 100 nm in the visible spectrum. However, for some specific purposes, such as full-colour or black-and-white reflective displays, wide-band reflective polarisers are desired.

It is well known that introducing a pitch gradient (or forming a pitch difference) is an ideal method for increasing the reflection bandwidth of a Ch-LC [8, 9]. Some widely investigated examples can be found in previous reports [8–24]. Recently, it has been demonstrated that PSCLCs can be used to prepare wide-band reflective polarisers [10–14]. For example, Hikmet and Kemperman obtained a wide-band reflective polariser from the PSCLCs [10]. In this system, the reflection bandwidth can be increased in PSCLCs when compounds referred to as excited-state quenchers are added to the composites. Such quenchers can absorb ultraviolet (UV) light, causing an inhomogeneous intensity of UV light distribution.

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Furthermore, phase separation inducing an inhomogeneous distribution of the chiral component corresponding to different pitches within the system is expected. Relaix *et al.* showed that the broadening of the reflection band of PSCLCs can also be achieved without the intervention of a foreign UV light absorbing dye owing to the natural UV light absorbing properties of the LC constituent. It has been suggested that the existence of a polymer structure gradient is at the origin of the broadening phenomenon [13]. There have been studies on PSCLCs correlating the influence of the molecular structure of non-chiral liquid-crystalline diacrylate and chiral liquid-crystalline diacrylate on the reflection bandwidth. It has been revealed that the latter should be more suitable if the PSCLCs with broader bandwidth are expected [23]. In addition, the position and the stereochemical configuration of the chiral centres in chiral monoacrylates affecting the selective reflection characteristics have also been investigated [24].

In this paper, four cholesteryl compounds with different functionality are synthesised and PSCLCs cells are prepared by photo-polymerisation of a LC mixture containing a non-reactive LC, a nematic diacrylate and the above cholesteryl compounds. The influence of the functionality of the cholesteryl compound on the reflectance properties is investigated as well as parameters such as polymerisation temperature. In addition, we study the morphology of the polymer network of different systems in detail, in order to understand the relationship among the chemical structure of the monomer, the morphology of the polymer network and the reflectance properties.

2. Experiments

2.1. *Materials*

The nematic LC, SLC-1717 (Slichem Liquid Crystal Material Co., Ltd.), the chiral dopant, S811 (Merck Co., Ltd.), and the photo-initiator, 2,2-dimethopxy-1,2-diphenyl-ethanone (IRG651, TCI Co., Ltd) were used. The LC diacrylate monomer, C6M, was synthesised according to the method suggested by Broer *et al.* [25]. Scheme 1 shows the chemical structures of the above materials used.

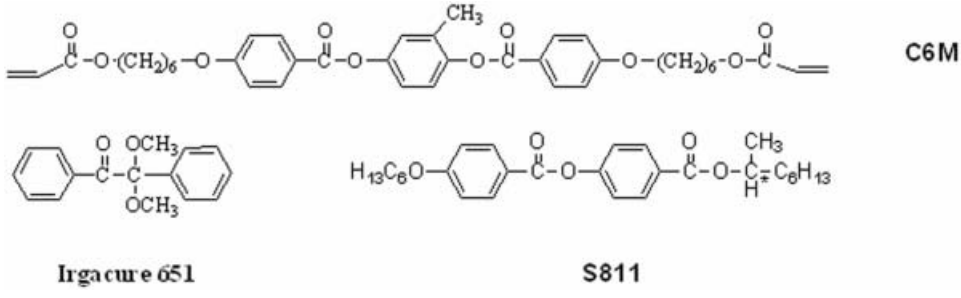
To prepare the expected compounds, tetrahydrofuran (THF) was heated under reflux over sodium and then distilled. Methylene chloride (CH_2Cl_2) was heated over calcium hydride and then distilled. Acryoyl chloride was distilled twice and stabilised with 2,6-bis (*t*-butyl)-*p*-cresol (BHT). All other chemicals were commercially available and used without further purification.

2.2. *Synthesis of cholesteryl compounds*

4-hexyloxybenzoic acid, 4-(6-acryloyloxyethyloxy) benzoic acid, 3,4-di-(2-acryloyloxyethoxy) benzoic acid and 3,4-di-(2-acryloyloxyhexyloxy) benzoic acid were synthesised according to the methods reported in [26–29], respectively.

2.2.1. Cholesteryl 4-hexyloxybenzoate (I). We dissolved 2.22 g (10.0 mmol) 4-hexyloxybenzoic acid and 3.86 g (10.0 mmol) cholesterol in 60 ml CH_2Cl_2 at room temperature. Then we dissolved 3.10 g (15.0 mmol) dicyclohexylcarbodiimide (DCC) and 0.12 g (1.0 mmol) 4-pyrrolidinopyridine (DMAP) in 40 ml CH_2Cl_2 and added this to the solution. The reaction mixture was stirred for 24 h at room temperature. It was then washed with water, dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane=1/6) and recrystallised twice from ethanol (EtOH). Yield: 3.89 g (60.2%). IR (KBr): 2932, 2852, 1699 (C=O), 1605, 1501 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.81–1.12 (m, 18H), 1.30–2.28 (m, 36H), 4.00 (d, 2H), 4.83 (s, 1H), 5.38 (s, 1H), 7.10–7.95 (d, 4H).

2.2.2. Cholesteryl 4-(6-acryloyloxyethyloxy) benzoate (II). A mixture of 2.36 g (0.01 mol) 4-(6-acryloyloxyethyloxy) benzoic acid, 3.86 g (0.01 mol) cholesterol, 2.06 g (0.01 mol) DCC and 0.148 g (0.001 mol) DMAP dissolved in 60 ml CH_2Cl_2 was



Scheme 1. The chemical structure of C6M, S811 and IRG651.

stirred at room temperature for 24 h. After filtration and removal of the solvent, it was then recrystallised from EtOH, further purification by column chromatography on silica gel with ethyl acetate/hexane (1/5) as the solvent. Yield: 4.1g (68.0%). IR (KBr): 2943, 2866, 1724, 1700 (C=O), 1636 (C=C), 1604, 1509, 1273, 1250, 1183, 1170, 1108, 1007, 775 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.68 (s, 3H), 0.8–2.1 (m, 42H), 2.45 (m, 2H), 4.25 (t, 2H), 4.5 (t, 2H), 4.82 (m, 1H), 5.40(m, 1H), 5.80 (dd, 1H), 6.16 (dd, 1H), 6.42 (dd, 1H), 6.92 (d, 2H), 8.00 (d, 2H).

2.2.3. Cholesteryl 3,4-di-(2-acryloyloxyethoxy) benzoate (III). According to the procedure described in [28], cholesteryl compound **III** can be achieved; here the last procedure for the preparation of cholesteryl compound **III** was improved. A mixture of 3.50 g (0.01 mol) 3,4-di-(2-acryloyloxyethoxy) benzoic acid, 3.86 g (0.01 mol) cholesterol, 2.06 g (0.01 mol) DCC and 0.148 g (0.001 mol) DMAP dissolved in 60 ml CH_2Cl_2 were stirred at room temperature for 24 h. After filtration and removal of the solvent, the residue was dissolved in 100 ml CH_2Cl_2 and washed twice with 40 ml 1N HCl and twice with 40 ml saturated sodium hydrogen carbonate solution. After removal of the solvent, the residue was recrystallised twice from 80 ml EtOH or purified by column chromatography on silica gel with ethyl acetate/hexane (1/5) as the solvent. Yield: 4.67g (65.0%). IR (KBr): 2951, 2870, 1716 (C=O), 1634 (C=C), 1620,1600, 1517, 1273, 1250, 1186, 1137, 878, 809 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.68 (s, 3H), 0.8–2.0 (m, 38H), 2.44 (d, 2H), 4.30 (m, 4H), 4.52 (m, 4H), 4.80 (m, 1H), 5.40(m, 2H), 5.84 (dd, 2H), 6.15 (2dd, 2H), 6.42 (dd, 2H), 6.90 (d, 1H), 7.60 (d, 1H), 7.67 (d, 1H).

2.2.4. Cholesteryl 3,4-di-(2-acryloyloxyhexyloxy) benzoate IV. A mixture of 4.62 g (0.01 mol) 3,4-di-(2-acryloyloxyhexyloxy) benzoic acid, 3.86 g (0.01 mol) cholesterol, 2.06 g (0.01 mol) DCC and 0.148 g (0.001 mol) DMAP dissolved in 60 ml CH_2Cl_2 were stirred at room temperature for 24 h. The purification process was identical to that of cholesteryl compound **III**. Yield: 5.09 g (60.0%). IR (KBr): 2950, 2870, 1716 (C=O), 1636 (C=C), 1619, 1600, 1517, 1274, 1250, 1184, 1137, 878, 810 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.68 (s, 3H), 0.8–2.1 (m, 54H), 2.45 (d, 2H), 4.02 (m, 4H), 4.18 (m, 4H), 4.82 (m, 1H), 5.38 (m, 2H), 5.80 (dd, 2H), 6.12 (2dd, 2H), 6.38 (dd, 2H), 6.85 (d, 1H), 7.52 (d, 1H), 7.62 (d, 1H).

2.3. *Characterisation of compounds*

The synthesised compounds were characterised by Fourier transform infrared (FT-IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectra. FT-IR spectra were recorded on a Nicolet-510P spectrometer at frequencies ranging from 400 to 4000 cm^{-1}. The ^{1}H-NMR experiments were performed at 400.1 MHz, on a Bruker DMX-300 spectrometer while $CDCl_3$ was used as the deuterated solvent for the compounds. The optical textures of samples were observed by polarising optical microscopy (POM; Olympus BX51) with a hot stage calibrated to an accuracy of ± 0.1 K (Linkam THMS-600). The differential scanning calorimetry (DSC) analysis was carried out using a Mettler DSC822e instrument with a heating and a cooling rate of 10°C min^{-1} under a dry nitrogen purge.

2.4. *Preparation of samples*

In order to induce a planar orientation of LC molecules, the inner surfaces of indium–tin–oxide (ITO) coated glass cells were coated with a 3.0 wt% polyvinyl alcohol (PVA) aqueous solution. The deposited film was dried at 80.0°C for 30.0 min and subsequently rubbed with a textile cloth under a pressure of 2.0 g cm^{-2} along one direction. Polyethylene terephthalate (PET) films of 25 µm thickness were used as the cell spacers. The samples were filled into the cells by capillary action.

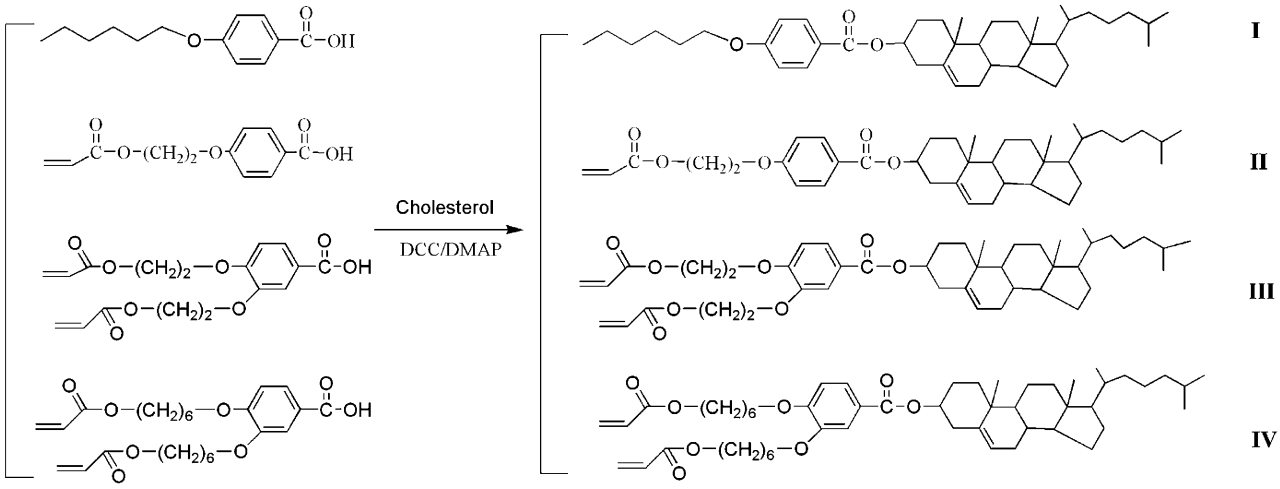
To induce photo-polymerisation, the cells containing samples were irradiated for 0.5 h with UV light (0.87 mW cm^{-2}, 365 nm). The compositions of the studied samples are listed in table 2.

2.5. *Measurements*

The transmission spectra were obtained with a UV/VIS/NIR spectrophotometer (JASCO V-570) in transmission mode at normal incidence, while the transmittance of a blank cell was normalised as 100%. As usually, λ_M and $\Delta\lambda$ are measured from the spectrum by considering the wavelength for the minimum of transmitted light inside the peak and the peak bandwidth at half-height, respectively. The morphology of the polymer network was observed by scanning electron microscopy (SEM; Cambridge S360). The samples for SEM studies were prepared according to the method described in [17].

3. Results and discussion

To investigate the effect of the cholesteryl compound functionality on the reflectance properties of the Ch-LC composites, a series of novel cholesteryl compounds without and with one and two acrylate groups were synthesised. Scheme 2 shows their typical synthetic routes. The synthesised compounds were identified using ^{1}H-NMR and FT-IR. As a representative sample, figure 1 shows the FT-IR spectrum of cholesteryl compound **II**. The specific



Scheme 2. The synthesis of the cholesteryl compounds with different functionality.

split absorptions around 1720 cm^{-1} might be a result of the existence of the two carbonyl groups. Double bond absorption also appeared around 1636 cm^{-1}. Figure 2 shows the ^{1}H-NMR spectrum of cholesteryl compound **II**. Peaks for the protons of the molecule were all identified and are shown in figure 2.

The phase transition behaviour was observed by POM, and the phase transition temperatures of the cholesteryl compounds measured by DSC are listed in table 1. As listed in table 1, all of the compounds exhibit a Ch phase. The compositions of SLC-1717/S811/Cholesteryl compound/C6M/IRG651 composites (samples A–D) are listed in table 2. The reason that the samples contain S811 is to adjust the reflection band of the samples in the visible region. After the samples were filled into cells, the cells were irradiated for 0.5 h with UV light (0.87 mW cm^{-2}, 365 nm). When observed by POM in transmittance mode, the cells exhibit a well-aligned planar Grandjean texture with a moderate presence of oily streaks.

Figures 3 (a)–(d) show the dependence of the spectra of samples A–D on temperature before polymerisation, respectively. From figure 3, it can be seen that the position of the reflection band changes little with temperature. This indicates that the pitch length for samples A–D changes little with temperature. It should be pointed out that the influence of polymerisation temperature on the reflectance properties is evaluated in the following discussion. Based on the above fact, that is, that the pitch of the Ch-LCs is almost independent of the temperature for all samples, other aspects induced by the temperature, such as the polymerisation condition, will considered as influencing the reflectance properties.

In our investigation, three different kinds of composite from four cholesteryl compounds were prepared. The reflectance properties of them are discussed in detail. Figure 4 shows the schematic representation of the distribution of the cholesteryl compounds in the different composites. Figure 5 displays the transmission dependence of samples A–D before polymerisation and after being polymerised by UV irradiation at various temperatures and wavelengths. In sample A, as shown in figure 4 (a), the polymer network was formed from the photo-polymerisation of the molecules of the C6M and cholesteryl compound **I** in the non-reactive LCs. As is well known, the function of the nematic diacrylate molecules, C6M in the PSCLCs, is as follows: (i) they can form crosslinks; (ii) they preserve the polymer structure and its distribution within the system [10, 11]. Cholesteryl compound **I** is incorporated as a free molecule as shown in figure 4 (a), that is, it does not participate in the formation of the network because cholesteryl compound **I** contains no acrylate groups. It can be observed from figure 5 (a) that the values of $\Delta\lambda$ of sample A being polymerised at 25°C and 55°C are 112 and 134 nm, respectively, while the value $\Delta\lambda$ of sample A before polymerisation is 95 nm. This should be attributed to the fact that only 3 wt% C6M was added to the composites: while cholesteryl compound **I** did not participate in the formation of the polymer network, the difference in the pitch length anywhere in the composites is very small; even if the polymer network formed after polymerisation, the increase in the value of $\Delta\lambda$ was very small. Meanwhile, the polymerisation temperature does not have significant influence on the reflectance properties of the composites.

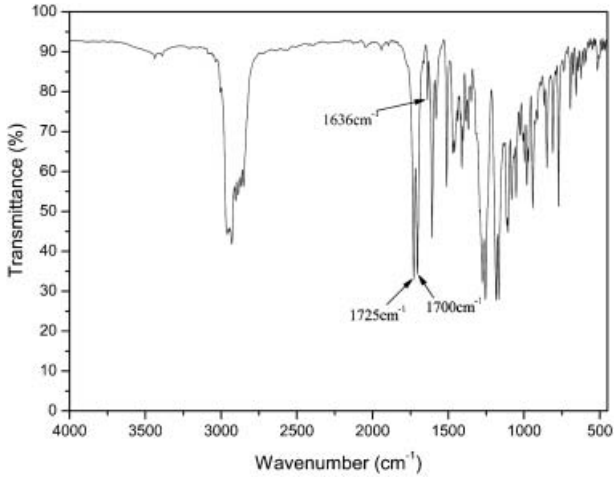


Figure 1. The FT-IR spectra of the cholesteryl compound **II**.

For sample B, as shown in figure 4 (b), the polymer network was formed from the polymerisation of the molecules of C6M and chiral monoacrylate **II** in the non-reactive LCs. In contrast to sample A, in which the chiral cholesteryl moiety as a free molecule was not incorporated into the network, here one end of cholesteryl monoacrylate **II** was attached to the polymer network and formed the side-chain polymer end-capped with cholesteryl moieties that are cross-linked by 3 wt% diacrylates after polymerisation. It can be observed in figure 5 (b) that the $\Delta\lambda$ value is 95 nm before polymerisation, while the $\Delta\lambda$ values are about 142 and 180 nm for sample B polymerised at 25°C and 55°C, respectively. Comparing figure 5 (a) with figure 5 (b), it is obvious that, when polymerised at the same temperature, the difference in $\Delta\lambda$ values of sample B before and after polymerisation is larger than that of sample A before and after polymerisa-

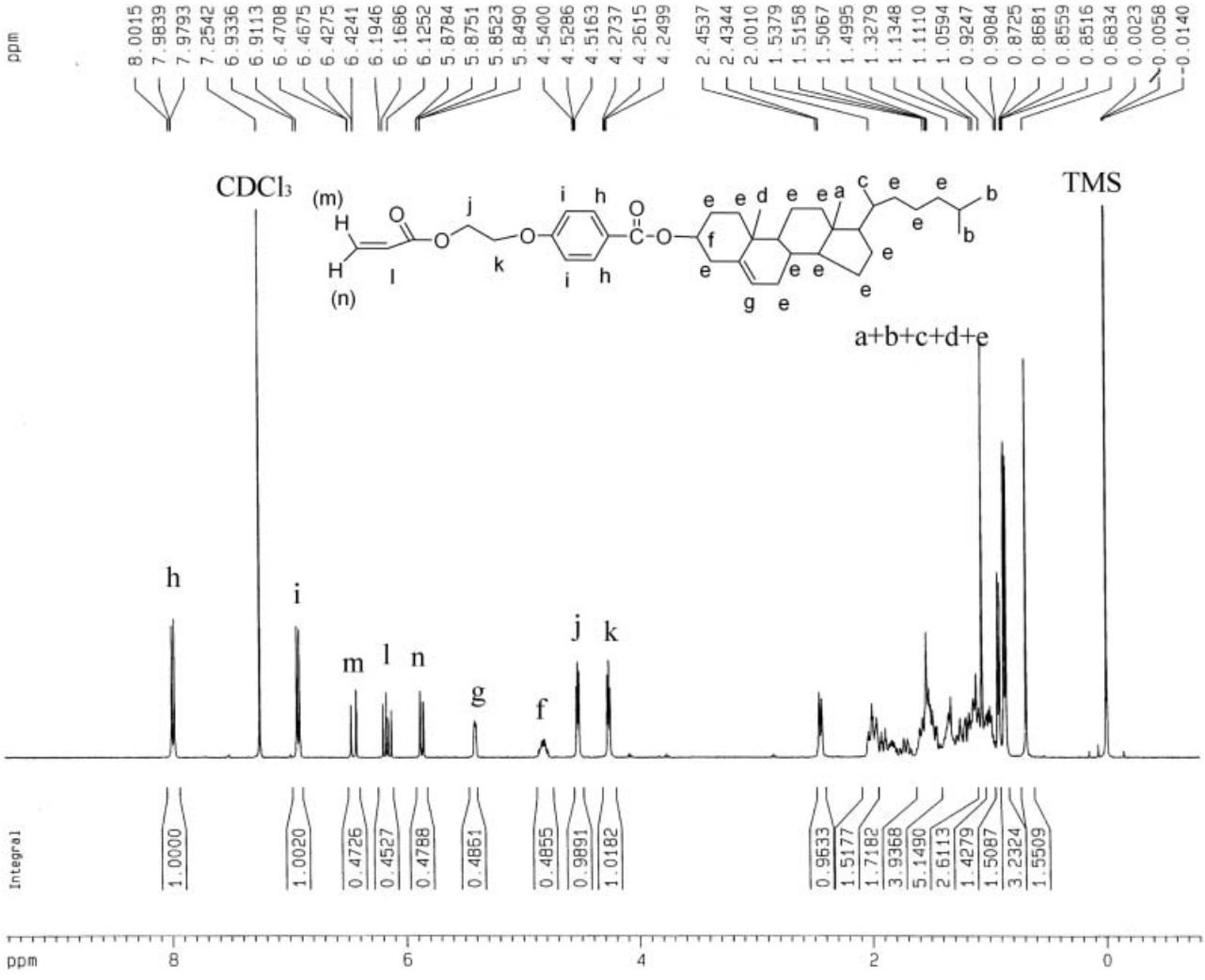


Figure 2. The ^{1}H-NMR spectra of the cholesteryl compound **II**.

Table 1. Phase transition temperatures of the cholesteryl compounds measured by DSC (first heating, 10°C min^{-1}): Cr, crystalline; Ch, cholesteric; I, isotropic.

Cholesteryl compound	Transition temperature (°C)
I	Cr 117 Ch 145 I
II	Cr 98 Ch 176 I
III	Cr 76 Ch 114 I
IV	Cr 57 Ch 89 I

Table 2. Compositions of SLC-1717/S811/cholesteryl compound/C6M/IRG651 composites (samples A–D). T_{Ch-I} is the clearing temperature from the cholesteric to the isotropic phase.

Sample	Cholesteryl compound	Weight ratio	T_{Ch-I} (°C)
A	**I**	71.94/15.0/10.0/3.0/0.06	71
B	**II**	70.94/15.0/10.0/3.0/0.16	66
C	**III**	69.94/15.0/10.0/3.0/0.26	61
D	**IV**	69.94/15.0/10.0/3.0/0.26	65

tion. Here, a conceivable explanation is given. In sample A, cholesteryl compound **I** as free molecules was dissolved in non-reactive LCs and the chiral centres dispersed in the LC domains uniformly. However, in sample B, as mentioned above, a chiral cholesteryl moiety should be located at the side chain of the polymer backbone after polymerisation which will influence the pitch of the bulk LCs, so the density of the chiral centres in the small local regions closer to the polymer network was larger than that in the small local regions farther from the network. Then, the pitch lengths of Ch-LCs in different regions were different in sample B, which resulted in sample B having a broader $\Delta\lambda$ than sample A when the polymerisation temperature was the same. In addition, in this system, the polymerisation temperature plays an important role in influencing the reflection bandwidth: from the results of previous investigations it can be assumed that increasing the polymerisation temperature affects predominantly the diffusion rate of the monomers and therefore leads to broader reflection bands [8, 9].

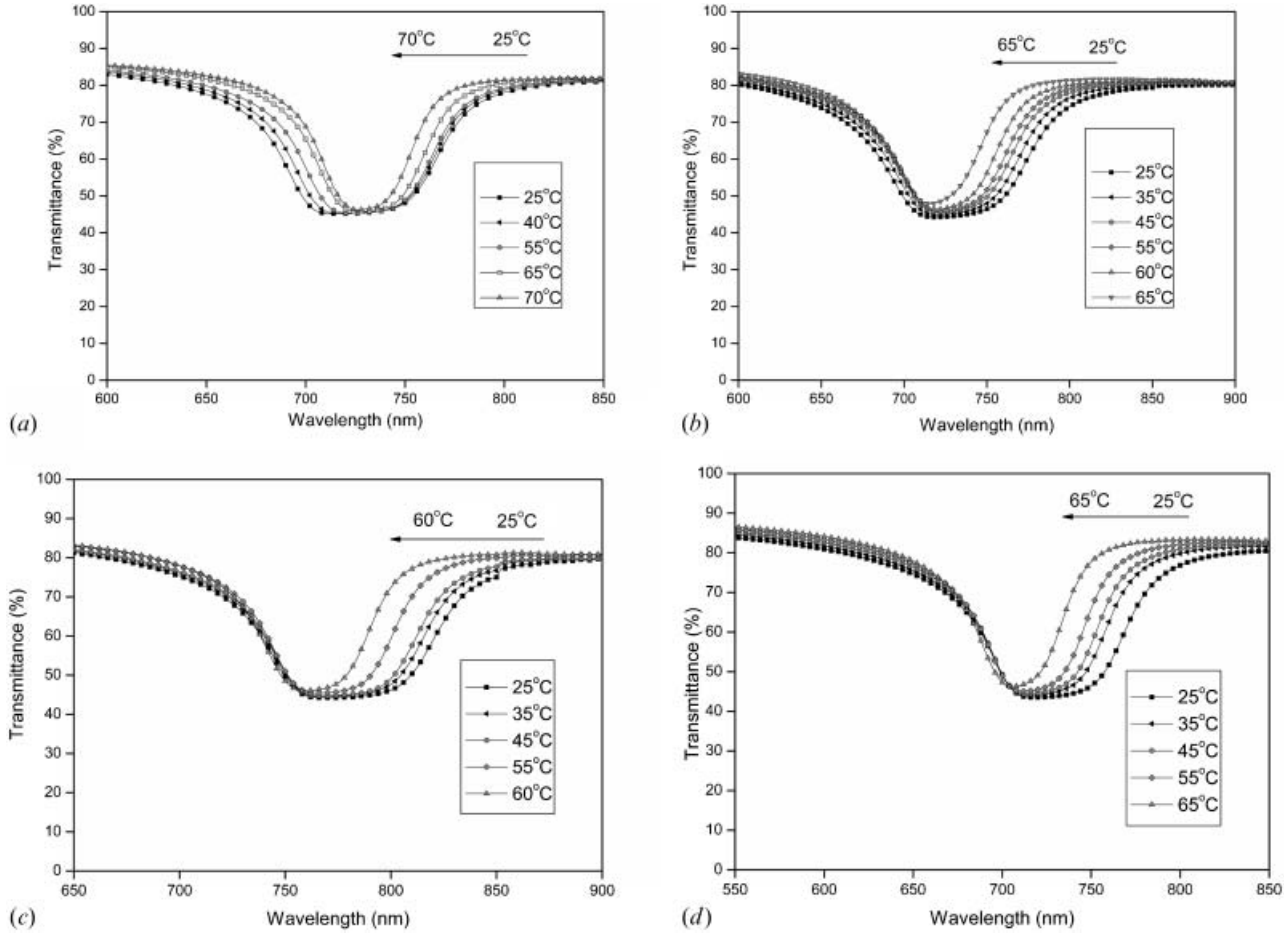


Figure 3. Temperature dependence of the reflection band for (a) sample A, (b) sample B, (c) sample C and (d) sample D before polymerisation.

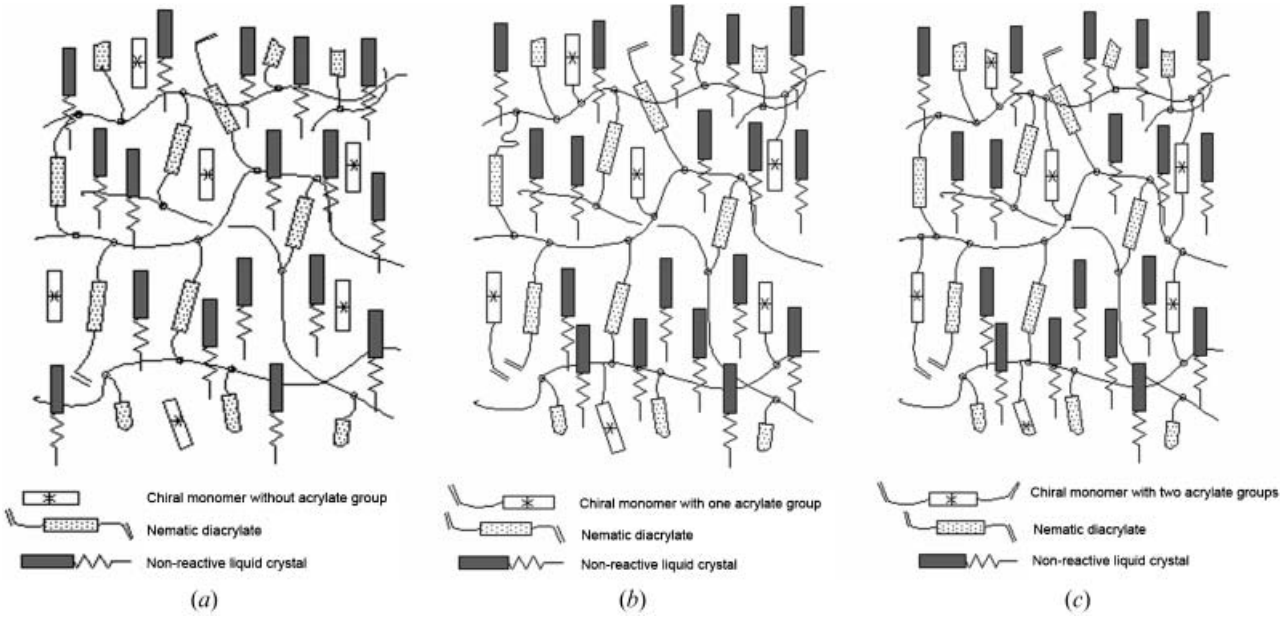


Figure 4. Modes of the network from cholesteryl compounds and C6M in nematic LCs: (a) mode 1, (b) mode 2 and (c) mode 3.

In order to further investigate the influence of the functionality of the cholesteryl compound on the polymer network and the reflectance properties, two chiral monomers with two reactive acrylate groups, cholesteryl compounds **III** and **IV**, were synthesised as shown in scheme 2. A model of such a system after polymerisation is indicated in figure 4 (c); in contrast to the polymer network described before, both ends of the cholesteryl diacrylates **III** and **IV** were attached to the polymer network in samples C and D, respectively. It can be observed that the value of $\Delta\lambda$ is about 280 nm for sample C polymerised at 55°C, which was obviously broadened, while the value of $\Delta\lambda$ is about 148 nm when polymerisation is at 25°C, as shown in figure 5 (c). As for sample D, cholesteryl compound **IV**, which has longer flexible spacer chains, was used. As can be seen in figure 5 (d), the values of $\Delta\lambda$ are 130 and 248 nm for sample D polymerised at 25°C and 55°C, respectively.

From the above discussion, it can be stated that the polymer network formed from the cholesteryl compounds with different functionality has an inherent influence on the value of $\Delta\lambda$. Phase separation induced by polymerisation leads to concentration fluctuations of chiral centres while the pitch lengths in different regions are different. The higher functional cholesteryl compounds **III** and **IV** are more effective for increasing the value of $\Delta\lambda$ than the cholesteryl compounds **II**. This result can be explained by the 'monomer diffusion' mechanism. It is well known that the chiral di-functional monomers are converted into polymers faster than the chiral mono- functional monomers during polymerisation [8, 9]. Diffusion during polymerisation is the key mechanism for the formation of a pitch gradient for samples C and D. As mentioned above, cholesteryl compounds **III** and **IV** participate in the crosslinking reaction, which leads to the creation of a higher monomer consumption gradient and therefore to a higher diffusion gradient. As a result, an inhomogeneous polymer network is created across the sample leading to the existence of a pitch gradient. On the other hand, the small local regions, a result of both ends of the cholesteryl compounds **III** and **IV** being attached to the polymer network, caused the chiral centres in samples C and D to be located closer to the polymer backbone, so that the difference in pitch length between local regions near the polymer backbone and those farther from the backbone was larger. We can therefore conclude that both of these factors can be attributed to the broadening the reflection bandwidth for samples C and D.

In the case of the polymerised samples, figures 6 (a) and (b) show the temperature dependence of the reflection band and reflection bandwidth for sample D polymerised at 25°C and 55°C, respectively. It can be seen that the λ_M of the reflection band has only a slight temperature dependence. While $\Delta\lambda$ becomes narrower with increasing temperature in figures 6 (a) and (b), the decrease in $\Delta\lambda$ is a result of a decrease in birefringence [11], whereas the temperature independence of the position λ_M indicates that the cholesteric pitch becomes frozen-in upon polymerisation and does not change with temperature. That is to say, this

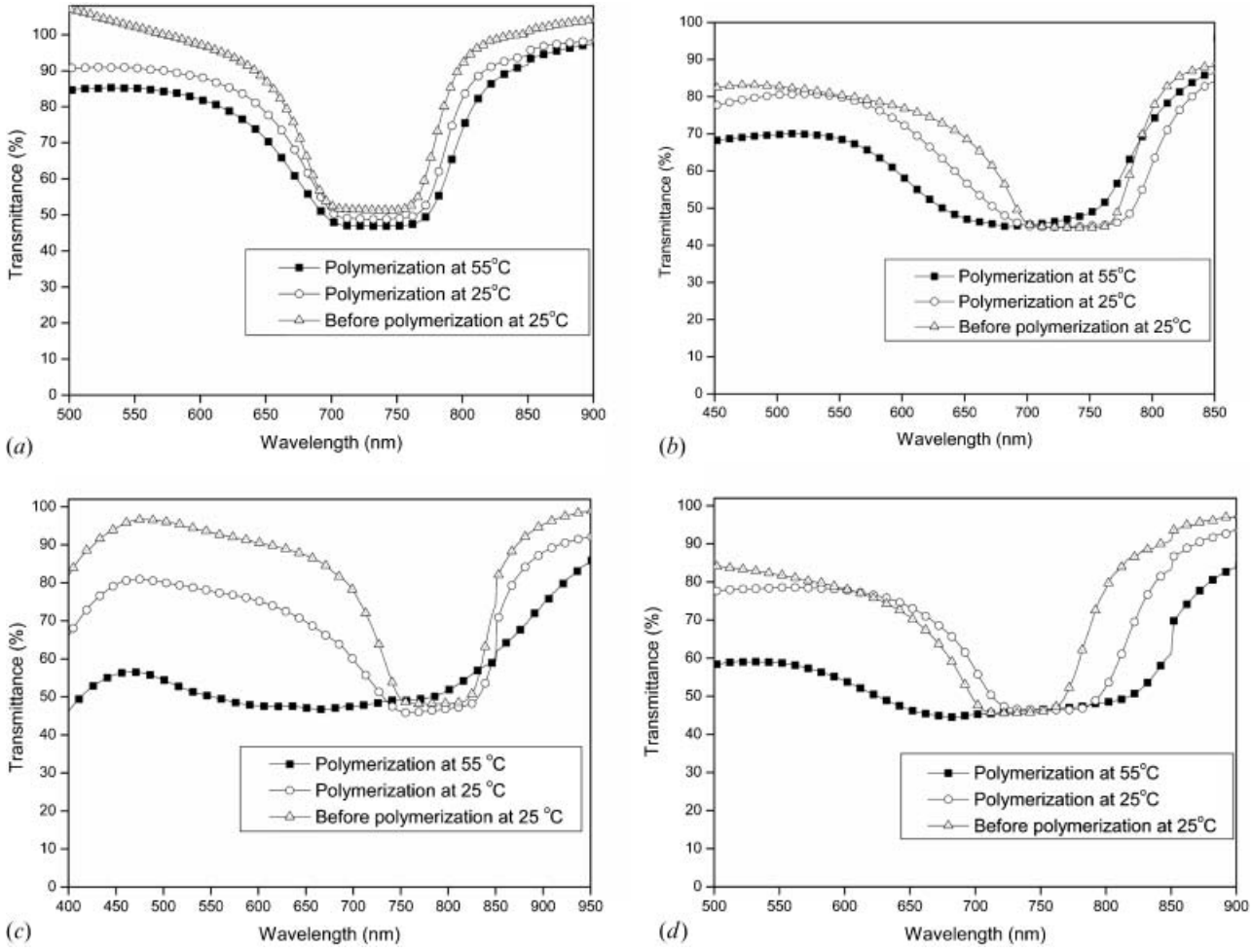


Figure 5. The transmission dependence of samples A–D before polymerisation and after being polymerised by UV irradiation at different temperatures and wavelengths: (a) sample A, (b) sample B, (c) sample C and (d) sample D.

behaviour is the result of polymer network formation, which freezes-in the cholesteric structure and hence the cholesteric pitch [30].

Figure 7 shows the SEM photographs of the polymer network in samples A–D polymerised at 55°C. A smooth polymer network can be observed

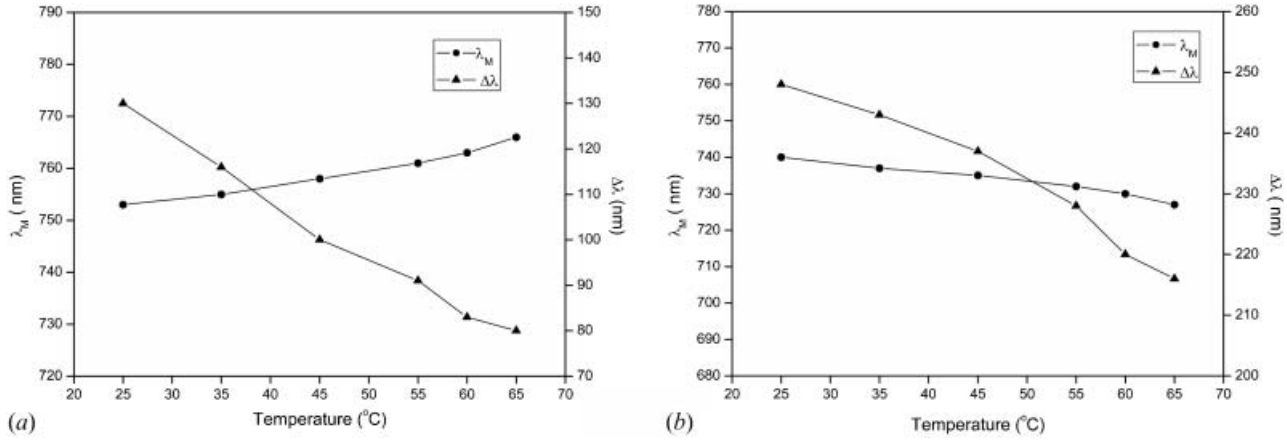


Figure 6. Temperature dependence of the reflection band and bandwidth for sample D after polymerisation at (a) 25°C and (b) 55°C.

for all of the photographs in figure 7. This indicates good solubility of the components within the LCs. It can be confirmed that if a monomer is highly soluble in LCs, it undergoes a radical chain polymerisation, leading to smooth networks [2, 3, 31]. For sample A, as shown in figure 7 (a), only 3 wt% diacrylate C6M formed the polymer network; therefore, such a low monomer concentration produced thick polymer strands, which is very similar to other reports [31–35]. As regards samples B–D, as well as 3 wt% C6M, 10 wt% cholesteryl compounds **II**, **III** and **IV** also took part in the formation of the polymer network, so this higher monomer concentration results in a much denser network as indicated in figures 7 (b)–(d). In general, increasing monomer concentration leads to denser polymer networks with fewer voids [2]. As mentioned above, 10 wt% chiral cholesteryl compounds attached themselves to the polymer network after polymerisation, so a greater non-uniform pitch distribution was produced in these composites. As a consequence, the broadband reflection can be obtained in these systems.

In order to evaluate the chemical structure of cholesteryl compounds influencing the polymer network, figures 8 (a) and (b) show SEM photographs of the polymer network in samples B and D polymerised at 55°C at a higher resolution. There is much experimental evidence that intramolecular crosslinking during chain crosslinking polymerisation leads to inhomogeneous network structures [2, 3, 31]. Here, we find that small structural changes in the cholesteryl compound, such as the number of acrylate groups and the length of flexible spacers, dramatically alter the network structure. It can be observed that, in the void of the polymer network, the LC droplets have a transition from spherical to non-spherical in figures 8 (a) and (b). This is because that cholesteryl compound **II** has one polymerisable acrylate group and does not participate in the crosslinking reaction, so that sample B has a lower crosslinked density. In contrast, sample D is more densely crosslinked owing to the cholesteryl compound **IV**, which participates in the crosslinking reaction. In a lower density crosslinked composite,

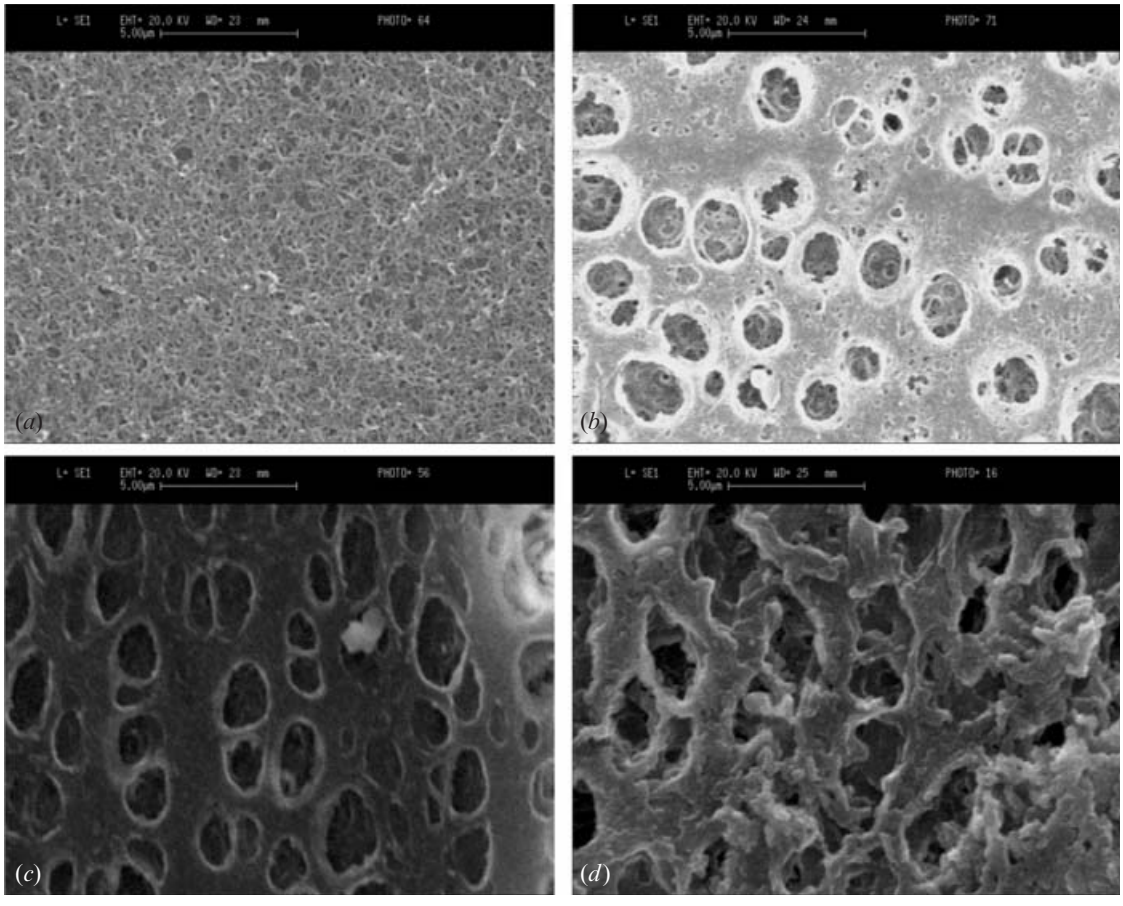


Figure 7. SEM micrograph of the polymer network for (a) sample A, (b) sample B, (c) sample C and (d) sample D polymerised at 55°C.

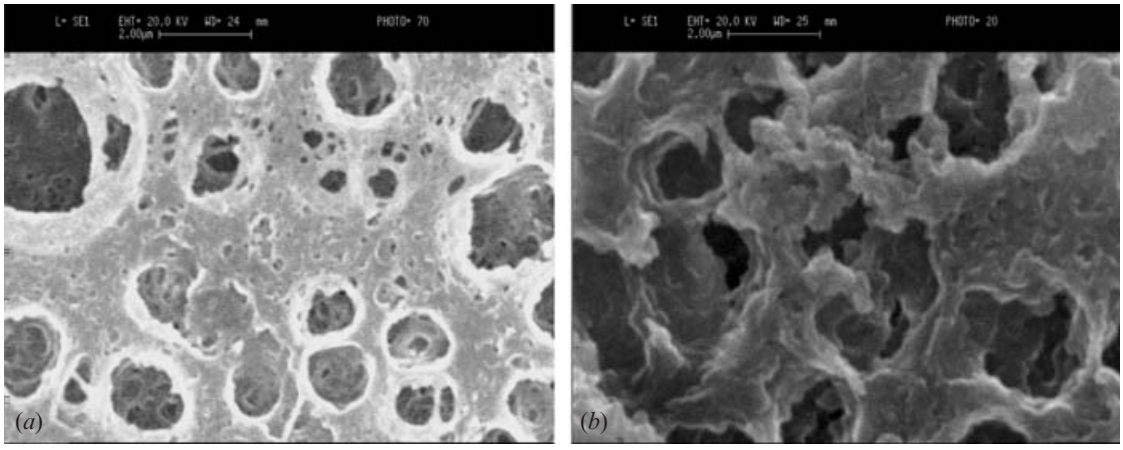


Figure 8. SEM micrograph of the polymer network for (a) sample B and (b) sample D polymerised at 55°C at a higher resolution.

the elasticity is so low that the droplets can easily assume their ideal spherical shape to minimise surface interactions. In a more densely crosslinked composite the higher elasticity not only opposes the growth of the droplets, leading to a larger number of smaller droplets, but also modifies the shape [36].

It is well known that the temperature at which the polymerisation takes place is another factor affecting the polymer network [4, 32, 34]. As a representative example, SEM photographs of sample D polymerised at 25°C and 55°C are shown in figures 9 (a) and (b), respectively. From these two images it is clear that the mean void size within these networks does increase with polymerisation temperature. That is, figure 9 (b) reveals much larger voids than figure 9 (a). This is because at higher polymerisation temperatures, as mentioned above, the diffusion of the monomers is faster, and in the phase separation, more polymer fibrils can get together to form larger strands. On the other hand, less LC is trapped in the polymer bundles on this condition, that is, many bulk LC molecules congregate together to form larger droplets. The network void sizes become larger after removal of the LC using solvent to expose the polymer network after polymerisation [4]. Based on the above discussion, there seems to be a significant relationship between the polymer temperature and the morphology of polymer networks. Considering the broadband reflection results, it has been suggested that the chiral polymer network, which could be well separated from the bulk LCs at higher temperatures, will induce a greater pitch difference in the different regions of the composites and produce the broader reflection band in the LC composites.

4. Conclusions

A series of novel cholesteryl compounds with different functionality have been synthesised and an investigation of the effects of varying functionality has been

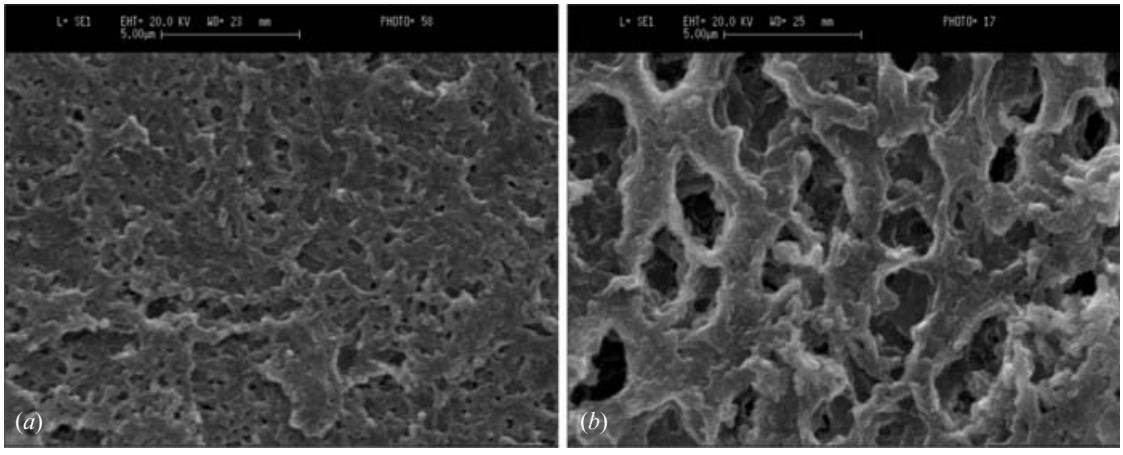


Figure 9. SEM micrograph of the polymer network for sample D polymerised at (a) 25°C and (b) 55°C.

conducted in the PSCLC cells from the above cholesteryl compounds. The results have shown that the PSCLC cells formed from the higher functional cholesteryl compounds exhibit a better broadband reflective effect, which we have speculated is a result of the pitch differences in the local network environment. In addition, the higher the polymerisation temperature, the broader the reflection band. Such conditions lead to the creation of a higher monomer diffusion, which generally results in a larger average void size within a polymer network, as has been shown with SEM images, and therefore to a larger pitch difference of the Ch-LC system. An increase in the cholesteryl compounds functionality leads to a much denser polymer network, as has also been indicated by SEM analysis, which further influences the reflectance properties of the composites.

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