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Improvements in morphological and electro-optical properties of polymer-dispersed liquid crystal grating using a highly fluorine-substituted acrylate monomer

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To improve the morphological and electro-optical properties of a polymer-dispersed liquid crystal (PDLC) grating, a type of highly fluorine-substituted acrylate monomer was added to the prepolymer mixture. The morphologies of the PDLC gratings were investigated using atom force microscopy and scanning electron microscopy. The grating had a very clear polymer/LC interface after addition of 3.9 wt% of fluorine-substituted monomer. The LC droplets in this case were much larger than the sample without fluorinated monomer. This phenomenon indicated that an almost complete phase separation had occurred. However, as the content of fluorine-substituted monomer increased, the morphologies of gratings became less defined and the volumes of LC droplets were smaller. The diffraction efficiency (DE) decreased with increasing of fluoride content and the V_{90} increased simultaneously, which may be ascribed to the blurry interface and the small LC droplets. The highest DE (90%) and lowest V_{90} (70 V) were obtained simultaneously under the condition of 3.9 wt% fluoride added in the prepolymer. In addition, it was also found that the fluorine-substituted monomer may disorder the alignment of LCs in the grating.

Keywords: polymer-dispersed liquid crystal; grating; fluorine-substituted acrylate monomer

1. Introduction

Since the electrically-tuneable grating based on a polymer-dispersed liquid crystal (PDLC) was first proposed by Sutherland *et al.* (*1*), the PDLC grating has been studied by several researchers. This type of grating has many advantages, such as simple fabrication, electrical tuneability, high-speed response, small volume, ease of integration, etc. (*2–5*). However, to date, PDLC gratings have not yet been applied in practice. The main reasons are their low diffraction efficiency [about 50–70% (*6–8*)] and high drive voltage [usually 10 V μm^{-1} (*2, 3, 9–11*)].

Some researchers considered the reasons were mainly caused by the incomplete phase separation during the photo-initiated polymerisation-induced phase separation (PIPS) process and higher surface free energy on the LC/polymer interface (*12, 13*). To deal with these problems, some researchers have used materials with long alkane chain as a surfactant to decrease the free energy of the interface, such as octanoic acid (*14, 15*) or stearyl methacrylaye (*16*). Others have added different types of fluorine-substituted monomers into the prepolymer mixture to promote phase separation and decrease the free energy of the interface, such as 2,2,2-trifluoroethyl (TFEA) and 1,1,1,3,3,3-hexafluoroisopropyl (HFIPA) acrylates (*17–19*). These studies have been very valuable and helpful for the development of PDLC gratings, and some of results are exciting. However, some shortcomings of these additive materials should be considered. First, octanoic acid is not a photosensitive molecule, so it can not polymerise with other monomers; thus, residual octanoic acid may lead to some light scattering loss and decrease the diffraction efficiency. Second, although TFEA and HFIPA can polymerise in PIPS, the fluorine content of the TFEA molecule is not very high, only 37% (calculated from the chemical structure), so the fluorination effects are very weak when adding a small amount of TFEA to the prepolymer. If the content of TFEA is increased to enhance the fluorination effects, the average functionality of the prepolymer system is changed significantly [the suitable average functionality to prepare the PDLC grating should be in the range of 2–4 (*20–22*)], which may result in some negative effects on grating morphologies. For HFIPA, this kind of monomer has a larger fluorine content, about 51%, however its refractive index is too low (n=1.319 at 20°C), which may influence the index-matching [the ordinary refractive index (n_o) of the LC should be approximately equal to the refractive index of polymer (n_p)] and decrease the diffraction efficiency of the grating.

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Aiming at the abovementioned shortcomings, in this work we adopted a new fluorine-substituted acrylate monomer (dodecafluoroheptyl methacrylate, n=1.549 at 20°C; hereafter called Actyflon), which has a very high fluorine content (57%) and is very suitable for index-matching. In addition, such a mono-functionality monomer can polymerise during PIPS. The contact angles of LCs on the fluorinated polymers were investigated to explore the influence of Actyflon on surface free energy and phase separation. The morphologies of the gratings were observed using atom force microscopy (AFM) and scanning electron microscopy (SEM) to evaluate the phase separation effect caused by Actyflon. The refractive index of fluorinated polymers was measured using an Abbe refractometer. Finally, the electro-optical properties of the PDLC gratings were examined.

2. Experiments

Materials

The monomers used to fabricate the PDLC gratings were pentafunctional dipentaerythritol hydroxyl pentaacrylate (DPHPA, n=1.49 at 20°C) and difunctional neopentyl glycol diacrylate (NPGDA, n=1.54 at 20°C). They were mixed together with a weight ratio of 1:1 to modulate the average functionality of monomers in the range 2–4. For photopolymerisation of monomers under a YAG laser (central wavelength 532 nm), a small amount of photo-initiator Rose Bengal [0.5 wt%; with a peak molar extinction coefficient in the range of 488–550 nm (*23, 24*)] and the co-initiator *N*-phenylglycine (NPG, 2 wt%) were also added to the mixture (all materials were supplied by Aldrich). The mixture was stirred at 65°C for about 12 h. After that, some nematic LC, TEB30A (Δn=0.1703, n_e=1.6925, T_{NI}=61.2°C; supplied by Slichem Co, Ltd, Shi Jia Chuang, China), was added to the monomer mixture with a weight ratio of 3:7 (LC/monomers) and stirred at 65°C for about 12 h.

In order to investigate the effect of Actyflon on the morphological and electro-optical properties of the grating, five mixtures with different Actyflon (supplied by XEOGIA Fluorine-Silicon Chem. Co, Ltd, Harbin, China; n=1.549 at 20°C) contents were prepared. The compositions of the mixtures and their average functionalities are shown in Table 1. All mixtures were re-stirred at 65°C for about 6 h. The chemical structures of DPHPA, NPGDA and Actyflon are shown in Figure 1.

Fabrication of gratings

The five mixtures listed in Table 1 were injected into ITO glass cells. The cell gap was maintained by 12 μm thick transparent spacers. After that, the cells were laid statically in a dark box for several minutes and then exposed by two coherent laser-beams (YAG dual-frequency laser, central wavelength 532 nm) for about 15 min; the intensity of the single beam was 3.6 mW cm^{-2}. To stabilise the structure of the gratings, the cells were radiated by a UV lamp for about 3–5 min after exposure. The UV intensity was 2 mW cm^{-2} and its central wavelength 365 nm.

Table 1. Compositions of the mixtures and their average functionalities.

Sample	Content of Actyflon /wt%	Average functionality[a]
A	0	2.86
B	3.9	2.78
C	7.4	2.71
D	10.8	2.64
E	13.9	2.58

[a] Calculated from the molar fraction of each component.

Property testing

The contact angle of the nematic LC TEB30A on the fluorinated polymer surfaces was tested using a contact angle analyser (SEO Phoenix-300, Korea). A drop of 10 μl LC was generated by a micro-thruster fixed upon the sample and contacted with the fluorinated polymer surface very slowly. The contact angle was analysed automatically with the software after 2 min to make sure that the droplet was static on the sample.

The morphologies of gratings fabricated from mixtures A–E (see Table 1) were observed using AFM (Nanoscope Dimension 3100, USA) and SEM (Hitachi S-4800, Japan). The samples were immersed in alcohol for about 24 h to extract residual LC from the gratings, fixed on a slick conductive substrate and blow-dried with high-purity nitrogen. All samples were observed by AFM using the tapping mode. For SEM observation, a very thin gold film was sputtering-coated on the surface of the samples. Simultaneously, the contents of fluorine contained in the samples were detected from their energy-dispersive X-ray spectra (Genesis 2000 XMS 60S, EDAX Inc).

In addition, to explain the influence of Actyflon on the LC alignment in the grating, the angular transmittance intensity of the grating was examined using a polarising optical microscope (Olympus BX-51, Japan). Figure 2 shows the principle of this testing. The polarised directions of the two polarisers are adjusted to be orthogonal with each other and the gratings inserted between the two polarisers. Initially, the angle between the grating vector direction and the polarised direction was adjusted to 90° (i.e. the

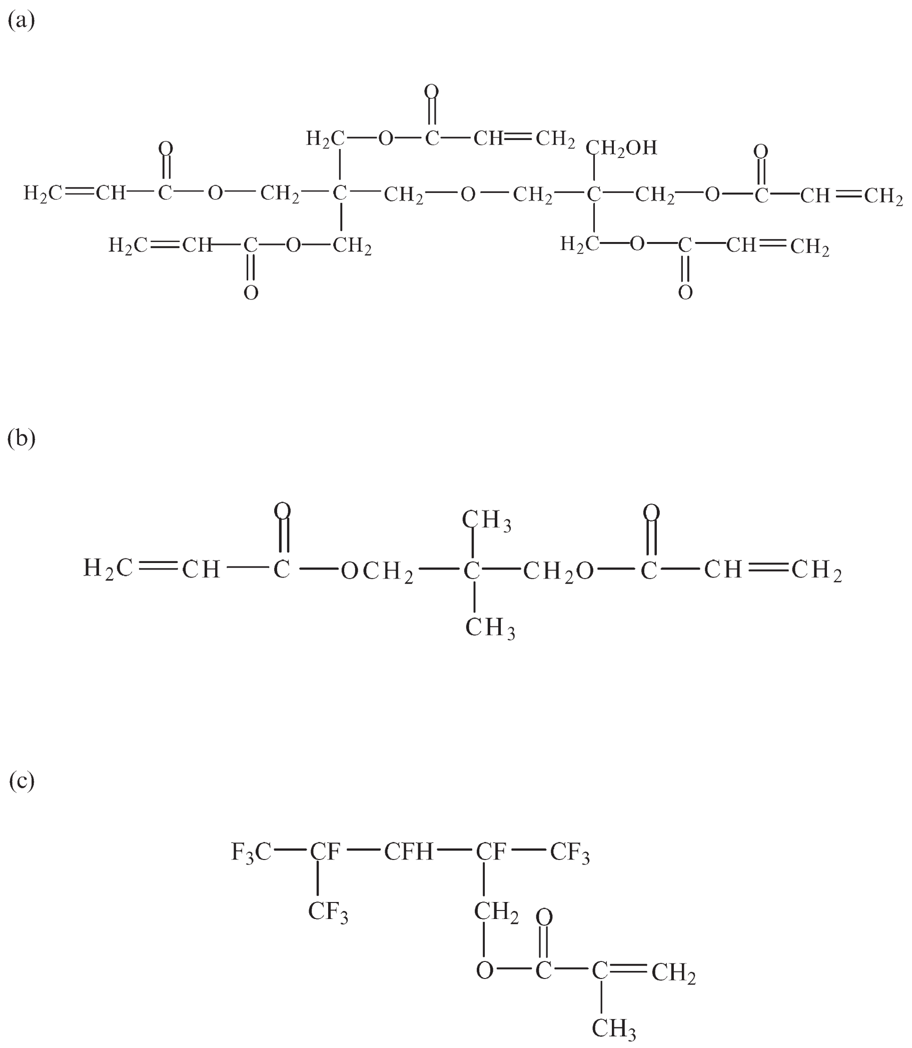

Figure 1. Chemical structures of (a) DPHPA, (b) NPGDA and (c) Actyflon.

transmittance at this position is the lowest). The grating vector is labelled as a black arrow in Figure 2. A fibre was connected with the spectrometer to detect the transmittance. The grating rotated by 5° and the transmittance intensity recorded; thus, the angular transmittance of the grating was obtained. This testing is usually used to estimate the alignment of LC in the grating. Details of such tests have been reported previously (*25*).

Refractive indices of the fluorinated polymers were measured using an Abbe refractometer (Zoushan Optical Instrument, 2WAJ, Shanghai, China). Five monomer mixtures without LC were prepared (their Actyflon contents corresponded to the mixtures in Table 1) and spin-coated on a clean and transparent glass, before being cured using a UV lamp to form polymer films. Thus, the refractive index of the resulting polymer was determined.

The electro-optical properties of the gratings were tested using a p-polarized He–Ne laser and a signal

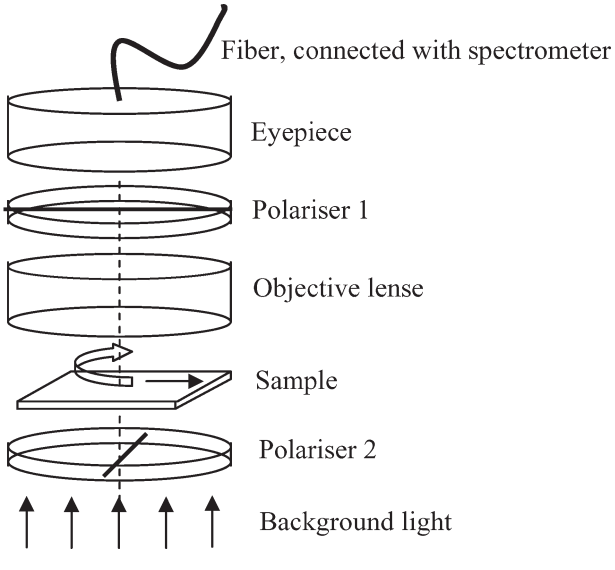

Figure 2. Schematic diagram of the angular-transmittance testing setup.

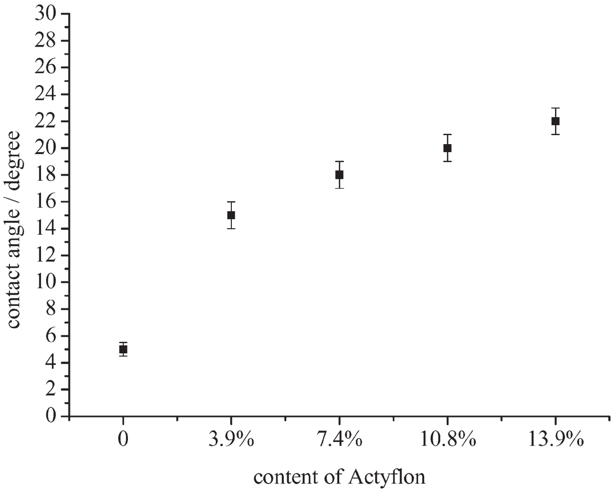

Figure 3. Contact angles of the LC droplet on the polymer surface.

generator. The drive voltages (V_{90}) were determined using a sinusoidal wave signal with a frequency of 50 Hz. To ensure the electro-optical properties were reasonably stable at the time of testing, all samples were saved in a dark box for 10 days prior to testing.

3. Results and discussion

Contact angle

Contact angles of LC on the polymer surface, measured as a function of Actyflon content, are shown in Figure 3. It can be seen that the contact angle increases with increasing Actyflon content in the prepolymer. The main reason for this is the additional fluorine atoms, which reduce the free energy of the surface, so that the surface tension is reduced gradually and the contact angle increases. The other reason is related to the differences of solubility parameter ($\Delta\delta$) between polymer and LC. Previous investigations indicated that fluorination can increase the $\Delta\delta$ between polymer and LC (*26*), and that the contact angle is proportional to $\Delta\delta$ (*27*). So the contact angle increases in the experiment. These results show that increasing the content of Actyflon may lower the surface free energy and surface tension of the polymer, which is of benefit for phase separation of LCs.

Morphologies of PDLC gratings

The morphologies of gratings fabricated with the five mixtures listed in Table 1 were observed using SEM and AFM. Figure 4 shows the SEM photographs of the gratings. It can be seen that the structures of the gratings are very clear in the cases of 3.9 wt% (Figure 4(b)) and 7.4 wt% (Figure 4(c)) Actyflon content. However, with increasing Actyflon content, the structure becomes very indistinct (Figures 4(d) and 4(e)), more so than for grating produced without added Actyflon (Figure 4(a)). In the case of 3.9 wt% Actyflon, the volumes of LC droplets (the black holes in the figures) in the PDLC grating were the largest and the width of LC-rich zone is broader than other samples, which indicates a more complete phase

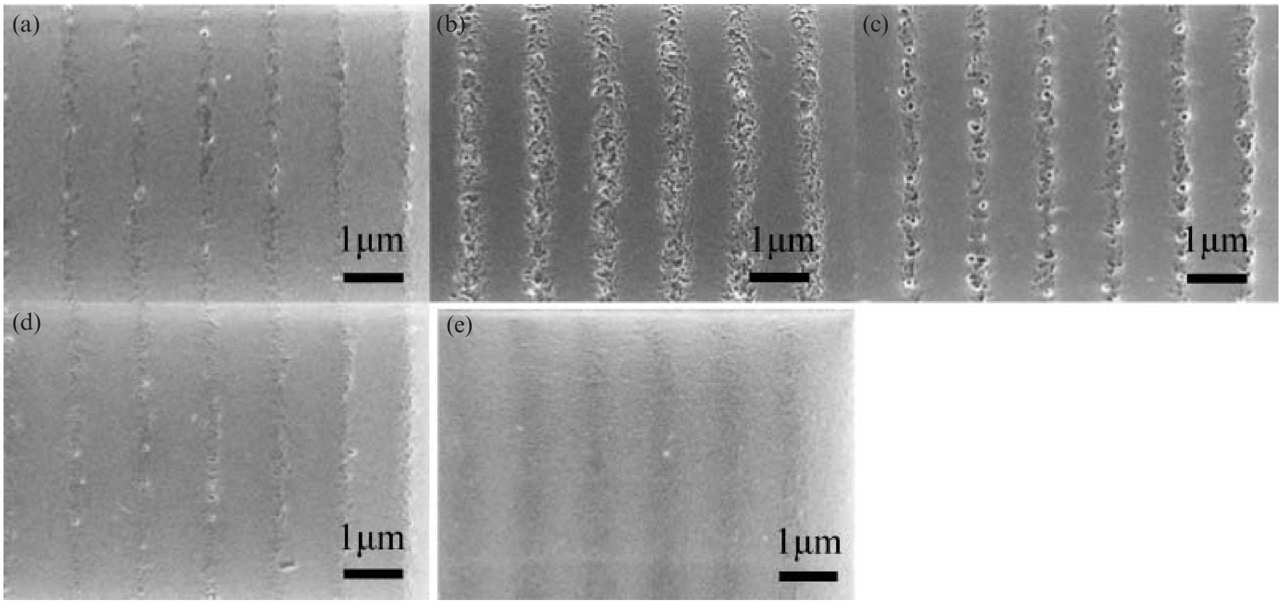

Figure 4. SEM photographs of the PDLC grating fabricated with different mixtures: (a) 0 wt%; (b) 3.9 wt%; (c) 7.4 wt%; (d) 10.8 wt%; (e) 13.9 wt% Actyflon.

separation in this case. The droplet volumes in the grating with 7.4 wt% Actyflon content are smaller than the former, and the volume becomes smaller with the increasing Actyflon content (as shown in Figures 4(c)–4(e)).

The AFM photographs of these PDLC gratings are shown in Figure 5. It was found that the average depth of grooves in the grating fabricated by the mixture with 3.9 wt% Actyflon (Figure 5(b)) was the deepest (about 120 nm), whereas the groove depth of the grating fabricated using the mixture with 7.4 wt% Actyflon (Figure 5(c)) was about 60 nm, which is only the half of the former. The groove depth decreases step by step as the Actyflon content is increased. The depth of the grating fabricated by the mixture with 10.8 wt% Actyflon (Figure 5(d)) is only 30–40 nm, which is the same as that for the grating without Actyflon (Figure 5(a)). When the Actyflon content reaches 13.9 wt% (Figure 5(e)), it is hard to distinguish the grooves. The average depth in that case is less than 10 nm. From the AFM photographs, it is also found that the LC/polymer interfaces are smoother on comparing the fluorinated gratings with the normal grating.

The AFM observations are in accordance with the results obtained by SEM. The deepest groove depth, the

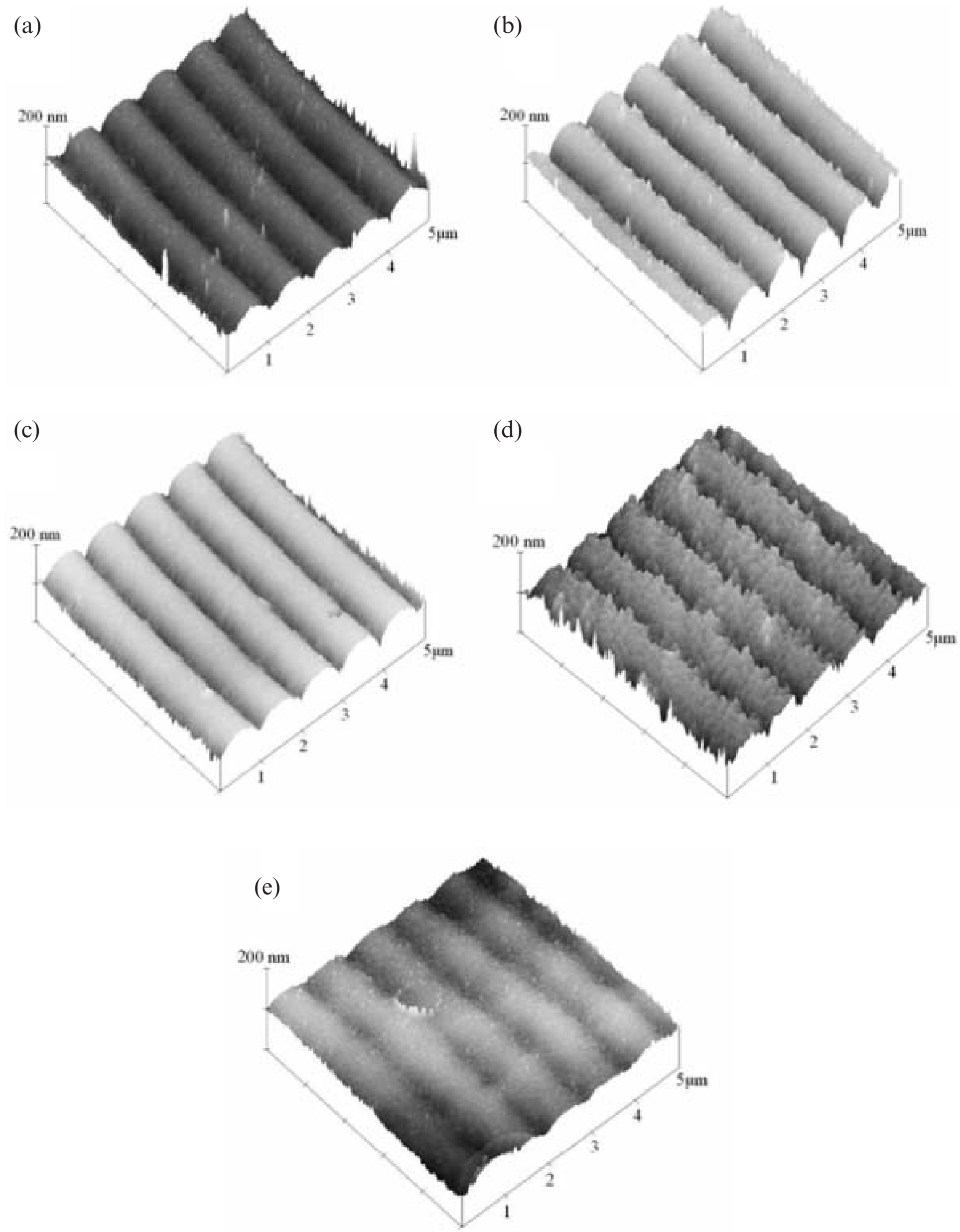

Figure 5. AFM photographs of PDLC gratings fabricated with different mixtures: (a) 0 wt%; (b) 3.9 wt%; (c) 7.4 wt%; (d) 10.8 wt%; (e) 13.9 wt% Actyflon.

widest LC zone and the largest LC droplets of the grating prepared with the mixture contain 3.9 wt% Actyflon indicate a better phase separation between LC and the fluorinated polymer host. The enhanced phase separation can be interpreted by the reduced solubility between the fluorinated polymer and LC. However, according to our SEM and AFM observations, fluorination is not always of benefit for phase separation. When the content of Actyflon exceeds a limit (about 3.9 wt% in our experiments), fluorination does not result in a clear grating structure. Excess Actyflon always leads to incomplete phase separation and poor grating structure, as shown in Figures 4e and 5e.

Three factors that may induce incomplete phase separation need to be considered. The first one is that poor phase separation is always associated with lower average functionality of the monomers. To examine this, the average functionality of the mixtures from A to E were calculated and shown in Table 1. The results indicate there is no significant difference in average functionality on adding Actyflon (2.86–2.58), so it is believed that functionality is not the main reason for the incomplete phase separation. Consider the second factor. In photopolymerisation, Actyflon is converted to a monoradical because of its mono-functionality (i.e. only one radical centre), so the concentration of monoradicals in the reaction system is increased as the Actyflon content is increased. According to the results obtained by Zhu and Hamielec (*28*) and Joshi and Rodriquez (*29*), an increase of monoradicals will enhance the termination rate, which will decrease the crosslinking density and lead to so called dead-end polymerisation (*30*). In that case the monomers are hardly likely to react with others and convert to the polymer. In our experiments, it is found that excessive Actyflon leads to incomplete phase separation, low groove depth and an indistinct LC/polymer interface. We propose that the reason may lie in the dead-end polymerisation brought about by excessively adding mono-functional Actyflon. To clarify whether dead-end polymerisation greatly affects grating formation, the energy dispersive X-ray spectrum was used to detect the fluorine content of the polymer medium in the gratings (the LC and some residual monomers were extracted using alcohol before testing). In the tests, we use the fluorine content to reflect the polymerisation of the system. The test results are shown in Table 2. As shown in the table, the fluorine contents of the polymer medium increases linearly (from 1.9 wt% to 7.6 wt%). It can also be seen that the photoreaction rate of Actyflon lies in the range 55–65%, and that this rate is approximately equal to the ene conversion rate that has been reported previously (*31, 32*). That is, Actyflon monomers are converted to the polymer and dead-end polymerisation has been generated during the PIPS process, no matter what content it is. Considering the better diffusion dynamic characteristic of Actyflon (*26*), the addition of it can promote the diffusion of monomers in reaction system and delay dead-end polymerisation in the system. So it can be conjectured that the dead-end effects may be overwhelmed by the better dynamic characteristic of reaction system. In addition, for the high functionality (near 3) of the monomers, the reaction capability of the system is stronger, which is related to the cross-linking polymerisation of the monomers. Thus, the effects of dead-end polymerisation on the phase separation and the grating formation are not evident. The fluorine contents in the monomers mixture, which are shown in Table 2, can be calculated using the following:

Table 2. Fluorine content of the polymer medium in the grating.

Sample[a]	Content of fluorine tested by EDS /wt%	Total fluorine content in monomers mixture /wt%[b]
B	1.9	3.2
C	3.6	6.1
D	5.7	8.6
E	7.6	11.0

[a] Samples B–E are the same as those listed in Table 1. [b]This content is not the Actyflon content in the syrup; it is the content in monomers mixture, which do not contain LCs, calculated using Equation (1).

$$[\mathrm{F}]\ \mathrm{wt}\ \% = \frac{0.57 m_{\mathrm{A}}}{m_{\mathrm{A}} + m_{\mathrm{D}} + m_{\mathrm{N}}} \times 100\%, \qquad (1)$$

where m_{A}, m_{D} and m_{N} are the amounts of Actyflon, DPHPA and NPGDA, respectively, in the monomers mixture. The constant 0.57 is the fluorine content of the Actyflon molecule. The photoreaction rate of Actyflon mentioned above is defined as the ratio between the tested values (the second column in Table 2) and the total values (the third column in Table 2).

The main factor that leads to poor grating structure is considered to be as follows. An excess of Actyflon monomers may lead to them being dispersed in the LC medium due to the effect of Fick diffusion. During PIPS, the Actyflon molecules in the LC medium would polymerise rapidly, thus blocking the diffusion of LC. Many small LC droplets would be trapped by the polymer network, so phase separation would be incomplete and the structure of the grating is very indistinct. This explanation has been proved by previous molecular dynamics calculations (*26*). Klosterman *et al.* reported the contamination of LC in the presence of surfactant molecules and proved this experimentally when studying the interfacial influence on

PDLC gratings caused by octanoic acid (*14*). A similar problem has been noted by White *et al.* when studying the influence of NVP on PIPS (*31*). Actyflon has similar dynamic characteristics and molecular weight to both octanoic acid and NVP, so the dispersion of it in LC should be possible and thus provides a more reasonable explanation.

Alignment of LCs in gratings

It has been reported that there is an alignment of LC in the PDLC grating (*25*), the alignment uniformity being closely related with the free energy on the interface. LC alignments of four gratings fabricated using mixtures containing 3.9 wt%, 7.4 wt%, 10.8 wt% and 13.9 wt% Actyflon were examined using a polarising optical microscope. The angular transmittance intensities of the four gratings are shown in Figure 6. For the grating fabricated with the mixture containing 3.9 wt% Actyflon, the transmittance ratio between peak value and vale value is about 70. For the grating fabricated using the mixture containing 7.4 wt% Actyflon the ratio is 25, and for the grating fabricated with the mixture with 10.8 wt% Actyflon the ratio decreases to only 5. When the Actyflon content in the mixture reaches 13.9 wt%, the angular transmittance is almost a horizontal line, so there is no uniform alignment of LC. These results indicate two aspects; on the one hand, the higher ratio corresponds to a good phase separation of LC. For the samples with a poor phase separation, the distribution of LC director in the grating is random, which leads to a lower peak-to-vale ratio. On the other hand, the changes may be relates to a decrease of the interfacial free energy. As the Actyflon content is increased, the interfacial free energy decreases; this affects the uniform alignment of the LC. In previous molecular dynamics studies, this phenomenon has been proved by calculating the LC order parameter near the interface (*26*). In addition, Sarkar *et al.* reported the same phenomenon when they studied the effects of TFEA and HFIPA on PDLC gratings (*19*).

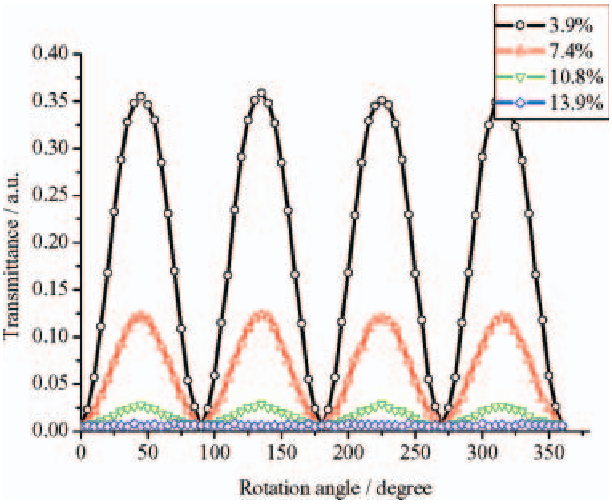

Figure 6. Angular transmittance intensity of PDLC gratings.

Electro-optical properties of the gratings

The first-order diffraction efficiencies and the drive voltages of the gratings were measured. In the test, the first-order diffraction efficiency is defined as $\eta = I_1/(I_0+I_1)$, where I_0 and I_1 are the intensities of the zero-order beam and the first-order beam, respectively. Figure 7 shows the test results for diffraction efficiencies. It can be seen clearly that the highest diffraction efficiency (about 90%) is obtained when the Actyflon content is 3.9 wt% and that it then declines very quickly to about 16% when the Actyflon content is 13.9 wt%.

The drive voltages are also determined. As can be seen in Figure 8, the drive voltage decreases to its lowest value (only 70 V) for 3.9 wt% Actyflon content, but it increases rapidly as the Actyflon content is increased further. When the content increases to 13.9 wt%, the drive voltage is as high as 135 V.

In the case of 3.9 wt% Actyflon content, a grating with higher diffraction efficiency and lower drive voltage can be fabricated. Remembering the morphological analysis, it is concluded that a better phase separation and a clear grating structure is of benefit for the improvement of electro-optical properties. According to results obtained by Wu *et al.* (*33*), the

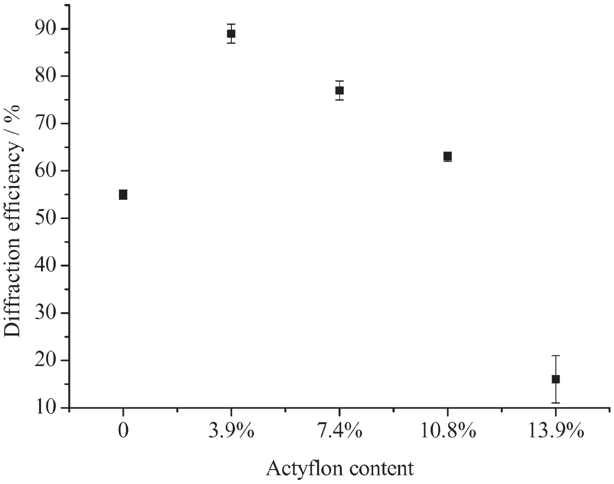

Figure 7. Diffraction efficiency of the gratings fabricated with mixtures of different Actyflon content.

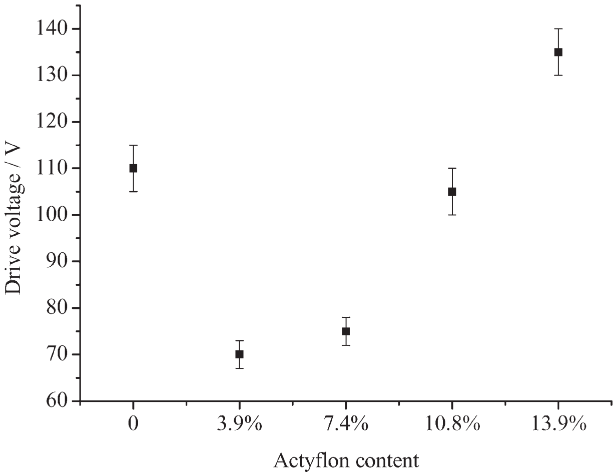

Figure 8. Drive voltages of the gratings fabricated with mixtures of different Actyflon content.

drive voltage is inversely proportional to the volume of LC droplets. So the lowest drive voltage of the grating corresponds to the largest LC droplet volume (Figure 4b).In contrast, the highest drive voltage corresponds to the smallest droplet (Figure 4e). In addition, as some fluorine atoms distribute on the LC/polymer interface, which weakens the interaction between polymer and LC, addition of a certain amount of Actyflon in prepolymer mixture can lead to a lower drive voltage.

The diffraction efficiency of a PDLC grating usually depends on two aspects. One is the depth of grooves. For the grating fabricated using the mixture with 3.9 wt% Actyflon content, the highest diffraction efficiency (90%) corresponds to the deepest grooves (120 nm). For the grating fabricated with the mixture containing 13.9 wt% Actyflon, the depth of grooves is very small, which leads to the lowest diffraction efficiency (only about 16%). The other is the refractive index modulation (Δn) between LC-rich zone and polymer-rich zone. The refractive index of polymer with different Actyflon content was tested; the results are shown in Table 3. The refractive index of polymer formed with the sample with 3.9 wt% Actyflon content is 1.521, which is almost equal to the ordinary refractive index of TEB30A, $n_o = 1.522$. So the index matches very well in that case and the grating has the largest Δn; thus, the largest diffraction efficiency was obtained consequently. For the other gratings, on the one hand their index-matching is not better than the former and, on the other hand, the incomplete phase separation leads to some LC droplets being trapped in polymer networks or some polymer networks distributed in the LC medium; thus the Δn of the grating is decreased.

Table 3. The refractive index of the polymers with different content of Actyflon.

Content /wt%	0	3.9	7.4	10.8	13.9
n_P	1.508	1.521	1.540	1.553	1.561

4. Conclusions

A type of highly fluorine-substituted acrylate monomer, Actyflon, was added to the prepolymer to improve the morphological and electro-optical properties of a PDLC grating. The morphologies of the gratings fabricated with mixtures of different Actyflon content were studied by SEM and AFM. Their diffraction efficiencies and drive voltages were tested and analysed combined with the morphological study. From these analyses, some meaningful conclusions are obtained:

(a) Actyflon monomer is very useful for decreasing interfacial interaction and interfacial free energy of a PDLC grating, which consequently can lead to a lower drive voltage.
(b) As a result of lower free energy on the LC/polymer interface, phase separation during PIPS is promoted by adding a small amount of Actyflon.
(c) Adding a certain amount of Actyflon to the prepolymer can modulate the refractive index of the polymer to provide a highly index-matching state.
(d) Adding excessive Actyflon to the prepolymer may lead to a dispersion of Actyflon in the LC medium and block the normal diffusion of LC during PIPS. Thus the phase separation is very incomplete and the refractive index modulation of the grating is low. So it is believed that adding Actyflon excessively into prepolymer is not of benefit for phase separation, although the additive has many advantages. In a word, the content of Actyflon should lie in a certain range (0–3.9 wt% in our experiments). If it exceeds this limit, there is no improvement in morphological and electro-optical properties.

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