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Polymer Network Formed in a Ferroelectric Liquid Crystal and Its Influences on the Molecular Packing Arrangement of the Liquid Crystal Host of the Liquid Crystal Host

在铁电液晶中形成的聚合体网络及其对液晶载体分子组合排列的影响

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Abstract Polymer networks have been produced in a variety of liquid crystal phases in cells without surface treatment. The liquid crystal/monomer mixtures are prepared using a ferroelectric liquid crystal and a diacrylate monomer. The polymerisation of the monomer is carried out by UV curing the mixture when it was kept in a specific phase which can be obtained by controlling the temperature of the ferroelectric liquid crystal. Both the monomer and the polymer network will depress phase transition temperatures. The effects of the polymer network on the packing arrangement of the ferroelectric liquid crystal molecules are examined by means of optical microscopy. The molecular packing arrangement of the ferroelectric liquid crystal in a specific mesogenic phase is frozen on the formation of a polymer network in the ferroelectric liquid crystal in that phase. The existence of the diacrylate based polymer network can improve the electrooptical switching of the ferroelectric liquid crystal.

Key words ferroelectric liquid crystal, polymer network, molecular packing arrangement, photopolymerisation

摘要: 在灌装于未经表面处理的样品盒内处于不同状态的液晶中制备聚合体网络。液晶/单体混合物由铁电液晶和双丙烯酸单体制成。单体的聚合通过维持该混合物处在一定的液晶态的条件下经紫外线固化来完成。不同的液晶态可通过控制铁电液晶的温度来获得。双丙烯酸单体或聚合体网络的存在会导致铁电液晶载体的相变温度降低。通过光学显微镜可观察聚合体网络对铁电液晶分子组合排列的影响。结果发现: 在某一液晶态中铁电液晶分子的组合排列可被在该液晶态中聚合而成的聚合体网络所稳定,双丙烯酸基聚合体网络的存在可改良铁电液晶的电光开关特性。

关键词: 铁电液晶　聚合体网络　液晶分子组合排列　光聚合
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1 Introduction

In situ polymerisation of a small amount, typically with a concentration of ≤ 5% by weight, of crosslinkable monomer in a non-reactive low-molar-mass liquid crystal will result in the formation of a polymer network in the liquid crystal. Such a material is referred to as polymer network stabilised liquid crystal (PNSLC)[1~3]. PNSLCs have attracted considerable attention for both their potential applications in information displays and academic interests[3~14]. Over the years, PNSLCs have been intensively studied and found to have uses in many

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types of electrooptic devices[1,7~9]. With respect to fundamental research, the formation of a polymer network in a liquid crystal can promote many interesting features. For example, the morphology of the polymer network is strongly affected by the molecular ordering of the liquid crystal[11,12]. Many physical properties, such as phase behaviour and electrooptics, of the liquid crystal host can be modified by the polymer network[13,14].

One of the most interesting aspects of PNSLCs is the effect of polymer network on the orientation of the liquid crystal host. In a common liquid crystal display, the liquid crystal is sandwiched between two substrates. The orientation of the liquid crystal is determined by the surface-generated forces which result from physicochemical processes such as Van der Waal's and/or dipolar interactions, hydrogen bonding, and mechanical interactions between the liquid crystal and the walls of the substrates. The formation of polymer networks in a liquid crystal creates new inter-surfaces in the liquid crystal. NMR studies of the liquid crystals confined in low concentration polymer networks have revealed that there is strong surface interaction between the liquid crystal and the networks, and the liquid crystal molecules are oriented by the networks[15,16].

In most previous studies, the monomer was polymerised while the mixture was kept in a preferred alignment by using substrates coated with an alignment layer. The polymer networks formed acted together with the surface alignment layer to enhance the alignment of the liquid crystal. In the present studies, the mixtures containing a diacrylate monomer are sandwiched between substrates without any surface treatment. It is believed that this will provide an environment in which the strength of the surface action of the substrate is reduced, and the effects of the polymer networks are manifested. Using a ferroelectric liquid crystal as the host, polymer networks can be produced in a variety of liquid crystal phases. Here we report the influence of the polymer networks on the molecular packing arrangement of the liquid crystal host. The electrooptical performance of the PNSFLC is also presented.

2 Experimental

The polymer precursor used was a diacrylate-based mesogenic compound RM257 (Merck). The formula and the phase sequence of the monomer are shown in Fig. 1. The monomer was doped with 2 wt% of Irgacure 907 (Ciba Geigy), this provides free radicals when irradiated with UV light that induce polymerisation of the reactive monomer. The nonreactive liquid crystal used in the present studies was the ferroelectric liquid crystal Felix015/100 (Hoechst), which has the phase sequence:

$C(<0)\ S_C^*\ 73.6\ S_A\ 84.8\ N^*\ 87.5\ I.$

The liquid crystal/polymer composites were prepared by mixing the monomer into the nonreactive liquid crystal.

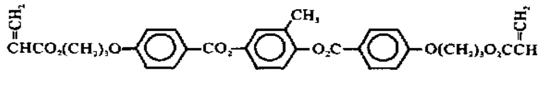


Fig. 1 The chemical structure of RM257

Samples were made by sandwiching the liquid crystal/monomer mixture between two glass plates which were separated using 5μm spacers. In the present studies, no surface treatment, such as cleaning and coating, has been carried out for the substrates. So there is not any preferential orientational direction for the liquid crystal in the cell.

The sample was heated to an elevated temperature so that the mixture was in the isotropic state, and then cooled down to a temperature at which the mixture was in a specific liquid crystal phase. While it was kept at the temperature, the polymerisation of the reactive diacrylates in the mixture was carried out. The polymerisation was initiated using 365nm wavelength UV radiation from a mercury lamp (Phillips 93136E). The UV intensity on the surface of the sample was 10 mW/cm^2. In the present studies, the UV dosage for the curing was fixed at 30J/cm^2. The temperature of the sample was controlled using a Linkam TMS93 temperature system.

The materials, both liquid crystal/monomer mixtures and PNSFLCs, were examined by means of optical microscopy, which was performed in an Olympus CH-2 polarising microscope. An Olympus OM-2 camera was used to take photomicrographs.

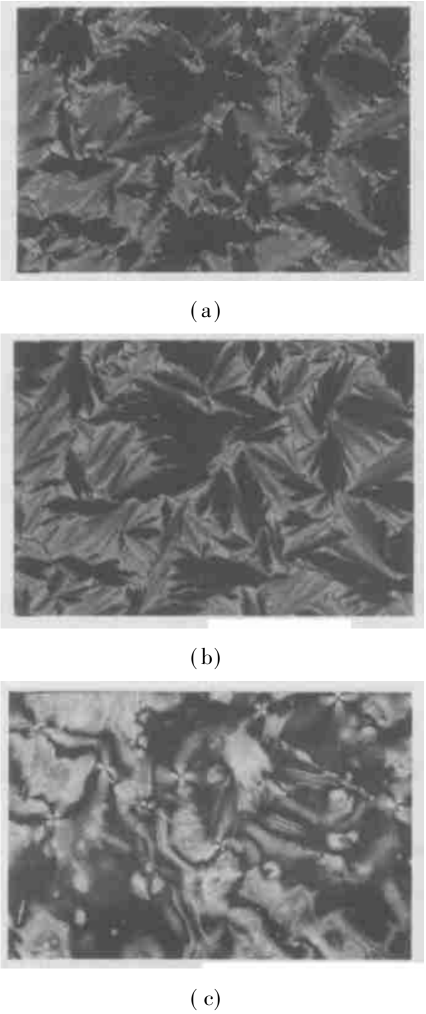
3 Results and Discussion

3.1 Phase Behaviour

The phase behaviour of the materials was first observed. The purpose of the observation of phase behaviour here is to determine the temperature range of a specific phase so that the phase in which the polymerisation is carried out can be identified. As PNSLCs studied containing a small amount of monomer/polymer, we focus on the examination of the phase transition temperatures for the composites with a concentration of monomer or polymer not greater than 5% by weight. On heating the liquid crystal/monomer mixture, the fan shape, schlieren textures, and the black view field corresponding to the S_C^*, S_A, N^* phases, and the isotropic phases, respectively, can be observed using the polarising microscope. Fig. 2 shows photomicrographs of optical textures corresponding to the mesophases that are inherent in the liquid crystal host for the mixture containing 1 wt% of RM257. The phase transition temperatures were determined by measuring the temperature at which the change in the optical texture of the mixtures occurred. The results are plotted in Fig. 3. The phase transition temperatures are lowered upon the addition of the monomer into the liquid crystal, and the increase in the amount of the monomer caused further decrease in the transition temperatures. It is noticed that the addition of monomer into the liquid crystal causes dramastical decrease in the S_C^*-S_A and S_A-N^* transition temperatures, whereas the change in the N^*-I transition temperature is relatively small. The N^*-I phase transition temperature decreases linearly with the increase in the amount of the monomer. The phase transitions are sharp, with biphasic regions smaller than 1K. After the UV curing, the phase transition temperatures of the network systems increase, but are still lower than those for the pure ferroelectric liquid crystal. The shift of the phase temperatures to a low temperature region is a typical phenomenon in two-component systems, and it has been reported before[13].

3.2 Effects of Polymer Network on Molecular Packing

Before the UV curing, heating or cooling the liquid crystal/monomer mixture causes phase transitions. The phase transitions were in association with changes in the optical texture. The optical texture of the mixture is determined by, and in turn reflects, the configurations of the packing arrangement, i.e. the locations and mass centres, of the molecules of the mixture. When the liquid crystal/monomer mixture is confined in a cell made using solid substrates, certain molecular packing arrangement will form. The features of the packing arrangement of the molecules of the mixture are determined by the boundary conditions


(a)

(b)

(c)

Fig. 2 Photomicrographs showing

(a) the broken fan shape texture of the S_C^* phase, (b) the focal-conic fan texture of the S_A phase, and (c) the schlieren texture of the N^* phase for a mixture containing 1 wt% RM257 in Felix015-100.

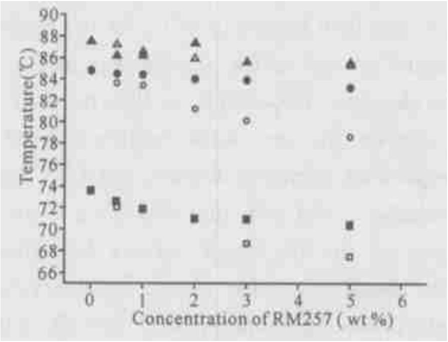


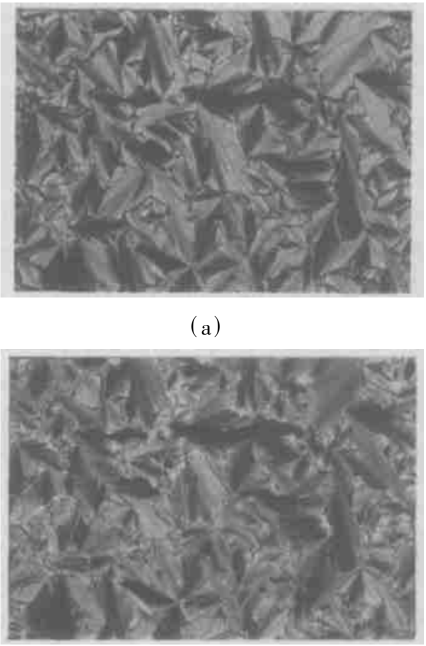
Fig. 3 Phase transition temperatures against concentration of RM257

□: S_C^* - S_A transition before UV curing; ○: S_A - N^* transition before UV curing; △: N^* - I transition before UV curing; ■: S_C^* - S_A transition after UV curing; ●: S_A - N^* transition after UV curing; ▲: N^* - I transition after UV curing.

between the molecules of the mixture and the surfaces of the substrates, and the thermodynamic states of the system. Due to the nature of the birefringence of the liquid crystal molecules, the mixture shows an optical texture corresponding to the molecular packing arrangement. A molecular packing arrangement of the liquid crystal/monomer mixture is stabilised by a balance of all interactions. Heating or cooling the sample will break the balance, and cause changes in molecular packing arrangement leading to changes in optical textures of the mixture.

Initially, the major forces to maintain the molecular packing arrangement of the mixture are imposed by the surface of the substrates. The fact that the texture varies with the change in the liquid crystal phase indicates that the forces imposed by the substrate surfaces are not strong enough to hold molecular packing within the whole liquid crystal phase range, i. e. the temperature range from the smectic phase up to the isotropic phases.

In order to investigate the influences of polymer networks on the molecular packing of the liquid crystal host, a sample was made by sandwiching a mixture consisted of 1 wt% RM257 between the untreated substrates, heated to 105℃, i. e. about 20℃ above the clearing temperature, and then cooled down to 80℃. The sample was in the S_A phase and showed the focal conic fan shape texture. While it was kept at 80℃, i. e. in the S_A phase, the sample was exposed to UV light for curing. Fig. 4a shows a photomicrograph of the sample after being UV cured. It can be seen that, the fan shape texture is retained. The UV cured sample was then heated to 95℃. At the temperature, the liquid crystal in the sample was in the nematic phase. However, the sample, as illustrated in Fig. 4b, still showed the fan shape texture instead of the corresponding schlieren texture. Carefully examining the sample, it was seen that there is a layer of liquid floating on the fan shape texture background. The floating liquid is a layer of the liquid crystal in the nematic phase. This suggests that the bulk of the liquid crystal in the cell is in the nematic phase, whereas the liquid crystal molecules in regions adjacent to the stems of the polymer network are anchored and have the same orientation as that in the S_A phase. The schlieren texture of the nematic phase is generated because of the existence of the singularities in the material. The disappearance of the schlieren texture in the nematic liquid crystal suggests that the singularities for the generating schlieren texture have been either removed or modified due to the existence of the polymer networks which are produced in the S_A phase. The appearance of the fan shape texture did not disappear even when the sample was well above the clearing temperature when the liquid crystal was in the isotropic phase. When the sample was cooled down to room temperature, there was no observable change in the structure of the fan shape texture.


(a)

(b)

Fig. 4 Optical textures of the sample containing 1 wt% RM257 polymerised in the S_A phase at 80℃, and 85℃ respectively.

(a) 80℃; (b) 85℃

Using the same mixture and following the same procedure as described above, the second sample was prepared. This time, the sample was polymerised at 90℃ when the mixture was in the nematic phase and the sample showed a schlieren texture. Fig. 5 shows photomicrographs of the sample before and after the UV curing. As illustrated, the initial schlieren texture was retained after the UV curing of the sample. The sample was cooled down after the UV curing. At room temperature, the liquid crystal is in the S_C phase. However, the expected fan shape texture does not appear, but is replaced by a sanded texture with a schlieren pattern that is coincident with the texture of the liquid crystal in the nematic phase (cf. Fig. 5b).

The results show that the in situ formation of a diacrylate based polymer network in a liquid crystal can freeze up the packing arrangement of the liquid crystal molecules in the phase, in which the polymerisation is carried out. The fact that the optical textures of the polymer network stabilised liquid crystals can stay unchanged when liquid crystal host changes its phase indicates that the polymer networks can provide very strong anchoring force, and can stabilise the orientation of the liquid crystal.

(a)

(b)

Fig. 5 Optical textures of the sample containing 1 wt% RM257 polymerised at in the N^* phase at 84℃, and 80℃ respectively.

(a) 84℃; (b) 80℃

3.3 Effects of Polymer Network on Electrooptic Performance

The effects of polymer networks on the electrooptic performance of PNSLCs were examined using the mixture with 1 wt% of RM257. The mixture was introduced into a cell with rubbed polymer alignment layers, and was planarly aligned. The electrooptical measurements were carried out when the sample was in room temperature, i.e. the liquid crystal was in the S_C^* phase. So the device is a ferroelectric liquid crystal shutter. The addition of the monomer causes the decrease in the response time, as illustrated in Fig. 6, This might result from the decrease in dipole density and the increase in disorder in the liquid crystal due to the addition of the monomer. After the UV curing, the response speed increases dramatically. It is interesting to notice that the response speed of the PNSLC is slightly higher than the pure ferroelectric liquid crystal, i.e. the existence of the polymer network will improve the electrooptic switch of the ferroelectric liquid crystal. The mechanism behind the phenomenon has yet to be elucidated. Fig. 7 shows the contrast ratio against driving electric field for pure liquid crystal, liquid crystal/monomer, and polymer network systems, respectively. As can be seen, the addition of the monomer causes the decrease in the contrast ratio. After the UV curing, the contrast ration is increased. However, the contrast ratio of the PNSLC is lower than that of the pure ferroelectric liquid crystal. The reduction in the contrast ratio may result from the light leakage from the device. However the mechanisms for the liquid crystal/monomer mixture and its polymer network system, respectively, are different.

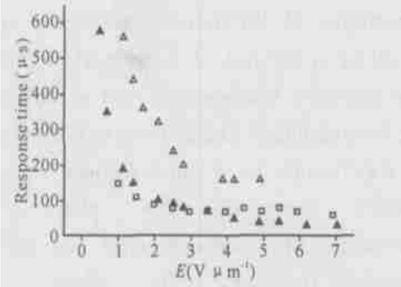


Fig. 6 Response time against electric field for the sample containing 1 wt% RM257 before and after polymerisation of the monomer.

□: Pure LC; △: LC/monomer; ▲: PNSLC

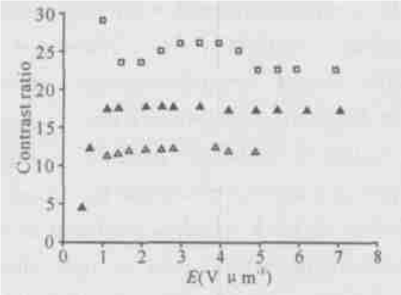


Fig. 7 Contrast ratio again electric field for sample containing 1 wt% RM257 before and after the polymerisation of the monomer.

□: Pure LC; △: LC/monomer; ▲: PNSLC

In the ferroelectric liquid crystal/monomer mixture, when an external electric field is applied, the coupling of dipoles with the field results in the ferroelectric liquid crystal molecules are driven to orient in a direction perpendicular the field, whereas the monomers are tending to align them parallel to the field. This inconsistency in motion between the ferroelectric liquid crystal molecules and monomers may cause local turbulences, and result in the light scattering from the cell leading to the reduction in the darkness of the sample in the black state. On the other hand, other interactions between the ferroelectric liquid crystal and monomer may cause incomplete switching of the ferroelectric liquid crystal molecules leading to a reduction in the brightness of the sample in light state. As a result, the contrast ratio of the sample decreases.

In the case of PNSLCs, the polymer networks will not be driven by the applied electric field. The decrease in the contrast ratio is mainly caused by the light leakage from the sample due to light scattering because of a mismatching in refractive indexes between the ferroelectric liquid crystal and the polymer networks.

4 Conclusions

It has been demonstrated that the phase transition temperatures of the ferroelectric liquid crystal are lowered upon addition of a diacrylate monomer. The phase transition temperatures tend to shift towards a more ordered phase. The increase in the amount of the monomer results in further decrease in the phase transition temperature. The phase transition temperatures are increased after the monomer is polymerised. However, the phase transition temperatures are depressed by the embedded polymer networks. The added monomer does not destroy the packing arrangement of the ferroelectric liquid crystal. In a cell constructed with substrates without any surface treatment, the molecules of the ferroelectric liquid crystal/monomer mixture are packed in different arrangements due to the existence of singularities. A molecular packing arrangement of the mixture in a specific mesogenic phase can be frozen by a polymer network which is produced in situ in the ferroelectric liquid crystal host in that phase. It has been found that the liquid crystal molecules are strongly anchored to the polymer network, and the molecular packing arrangement within the polymer network is very stable within a wide temperature range which covers whole mesogenic phase range of the ferroelectric liquid crystal. Both the added monomer and the embedded polymer networks cause decreases in the contrast ratio of the ferroelectric liquid crystal shutter. The decrease in the contrast ratio may result from the light leakage from the cell. However, the mechanisms are different. In a device made using a ferroelectric liquid crystal/monomer mixture, the light leakage may cause by the disturbance due to the difference in molecular motion between monomer and liquid crystal molecules in an applied electric field. In the case of PNSFLCs, the light leakage may be a result of the mismatching in refractive indexes between the ferroelectric liquid crystal and the polymer network. It is also found that the embedded polymer network may increase the response speed of the ferroelectric liquid crystal.

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