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THE RELATIONSHIP BETWEEN THE MONOMER CHAIN LENGTH AND THE ELECTRO-OPTICAL PROPERTIES OF POLYMER DISPERSED LIQUID CRYSTALS

Five polymers dispersed liquid crystalline (LC) films were fabricated using photo-polymerizable monomers with different lengths of carbon chains. These LC films have shown different electro-optical (EO) properties. Through their SEM pictures, the relationship between the linear electro-optical effect and the mesh size of the polymer network was explored. With the increase of number of photo-polymerizable monomers, the mesh size of the polymer network would become larger. So the liquid crystal molecules would be easily oriented in the electric field and therefore, the threshold voltage and saturation voltage would decrease. The open state response times were also reduced and the off state response times would be extended. The DFT simulations have shown principal role of the ground state dipole moments in the observed electro-optical efficiency.

Keywords: liquid crystal, electro-optical property, polymer dispersed, mesh size, response time.

1. Introduction

Polymer dispersed liquid crystals (PDLC) attract great attentions in the recent years [1-6] due to their potential applications in electrically switchable optical devices and the advantages of organic materials in processing and modification,. Though ultraviolet (UV) polymerization-induced phase separation (PIPS) as an effective method was widely used in the preparation of PDLC some complications which affect the electro-optical (EO) properties need to be studied. Among them - the length of carbon chain for the photo-polymerizable monomers, UV light intensity, photo-polymerization temperature and chiral dopants [7-12].

Mesh size of the polymer network in PDLC films was considered as the direct factor for optimizing the threshold voltage and saturation voltage of the PDLC [13-15]. The threshold voltage, saturation voltage and the rise time of the PDLC would be decreased, as the mesh size of the polymer network increasing. The length of carbon chain of the photo-polymerizable monomers was considered as one of the most important factor in adjusting the mesh size.

So in this letter, the relationship between the length of carbon chain of the photo-polymerizable monomers and the EO properties of PDLC is studied by preparing the PDLC films under the same curing temperature, UV light intensity and photoinitiator with the same amount.

2. Experimental

2.1. Materials

Nematic Liquid Crystal: SLC7011-100 and SCL1717 were purchased from Shijiazhuang Chengzhi Yonghua display materials Co., Ltd; photoinitiator: chivacure BDK was purchased from Foresight chemicals Co., Ltd; ethyleneglycol dimethacrylate (EDMA), 1,4-butanediol diacrylate (BDDA), 1,6-hexanediol diacrylate (HDDA), 1,6-hexanediol dimethacrylate (HDMA), 3,5,5-trimethylhexyl acrylate (TMHA), isobornyl methacrylate (IBMA), 2-hydroxypropol acylate (HPDA), polyethylene glycol (PEG400) and 3-(trimthoxysilyl)propyl acrylate (TPA) were purchased from Beijing Innochem Science & Technology Co., Ltd. The structures of these monomers were shown in Fig. 1. All chemicals were used as received.
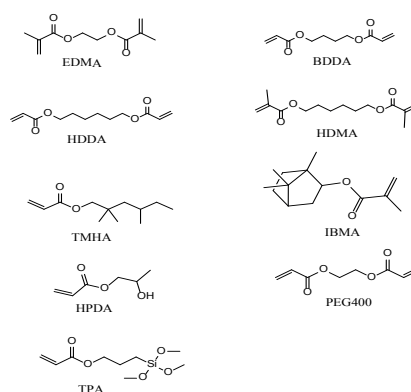

Fig. 1. Molecular structures of the monomers

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2.2. Preparations of PDLC films

Firstly, the IBMA, TMHA, HPDA, TPA monomers were mixed according to the ratio of 4.3, 1.5, 1.0 and 2.0. This mixture was called Ps. Then Ps was mixed with SCL7011-100, SCL 1717 and chivacure BDK according to the amount in Table 1. Then this mixture was mixed for the third time with EDMA, BDDA, HDDA, HDMA and PEG400 respectively also according to the amount in Table 1 affording us the final liquid crystal solutions. The liquid crystal was injected to the liquid crystal cell with the electrode space of 15 μm and the liquid crystal was solidified at 0°C by the UV irradiation affording us the samples.

TABLE 1.

The composition of the liquid crystal samples

Samples	Monomers [wt%]		LC [wt%]	
	25		75	
	5	20	40	35
1	EDMA	Ps	SLC7011-100	SCL1717
2	BDDA	Ps	SLC7011-100	SCL1717
3	HDDA	Ps	SLC7011-100	SCL1717
4	HDMA	Ps	SLC7011-100	SCL1717
5	PEG400	Ps	SLC7011-100	SCL1717
Ps -IBMA / TMHA/HPDA/TPA=4.3/1.5/1.0/2.0/				

3. Results and discussion

3.1. The EO properties of the liquid crystal films

There are many factors which could affect the threshold voltage and driving voltage: thickness of the film, the droplet size of the liquid crystal, the interaction between the liquid crystal and polymer, and so on. In this research, the liquid crystalline films were prepared by the same method and thickness. The principal factors affecting the EO efficiencies of the LC films were the size of the liquid crystal droplets and inter-molecular interaction between the liquid crystal molecules and the polymer network. By using the same curing temperature, UV light intensity and photoinitiator with the same amount, the only element affecting the size of the polymer network was limited to the length of the monomer chains.

The transmittance curves of samples 1, 2, 3, 4 and 5 versus the dc-voltage are shown in Fig.2. The saturation voltage for sample 1 is very high. Even the voltage was raised to 100 V, the transmittance was still increasing. Else, the open state transmittance of sample 1 was very low - it was just about 40%. So sample 1 is not a good LC film due to its ultra high saturation voltage, threshold voltage and ultra low open state transmittance. With the increase of the flexible chain length between the acrylic groups, the open state transmittances increases from 40% for sample 1 to 80 for sample 5. This result confirms that there exists relevance between the lengths of flexible chain between two acrylic groups and the open state transmittances of the studied LC films. The open state transmittance of sample 5 is very high, which could reach 80%. At the same time difference of the off state transmittances for the samples 1, 2, 3 and 4 is not very obvious. But the off state transmittance for the sample 5 is still very high (45%). This result might be decided by the so long flexible chain between the acrylic groups. The performed DFT simulations using B3LYP approach have shown a correlation between electro-optical efficiency and ground state dipole moments.
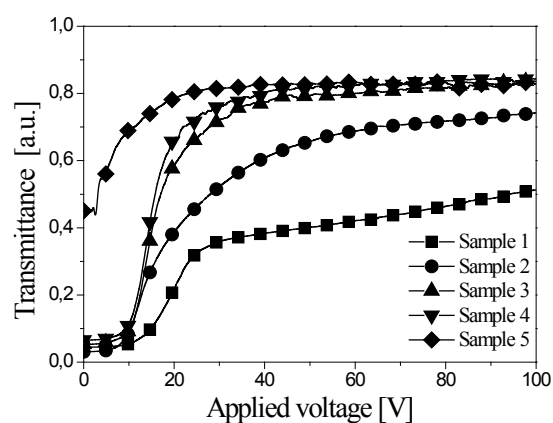

Fig. 2. DC-field voltage dependence of the transmittance for the studied samples

Most of the electronic optical properties of the LC films are given in Table 2, including the threshold voltages, driving voltages, open state response times, off state response times, contrast ratio and off state transmittances. The threshold voltages, driving voltages and open state response times were becoming lower from sample 1 to sample 5. The off state response times, transmittances and contrasts were becoming larger from sample 1 to sample 4. These results also indicate that there exists a strong correlation between the lengths of flexible chain between two acrylic groups and the electronic optical properties of the PDLC which is discussed below.

TABLE 2

Electronic optical properties of the liquid crystal films

Samples	Threshold voltage [V]	Driving voltage [V]	Ton [ms]	Toff [ms]	Contrast ratio	Off state transmittance
1	18	75	9	5	13	0.051
2	16	57	5	18	25	0.052
3	12	55	4	23	35	0.055
4	11	54	3	40	36	0.065
5	4	19	—	—	—	—

3.2. The structure properties of the liquid crystal films

The differences of the length and size among the monomers would make the differences of the polymer networks. To investigate the structures of the samples, scanning electron microscope (SEM) was used. After the LC molecules being eluted, the morphology of the polymer networks were studied by SEM and the pictures for sample 1 to 5 are shown in Fig. 3.

With increasing of monomers' length, the diameter size of polymer network holes were 2 μm, 3 μm, 4 μm and 5 μm respectively for the samples 1, 2, 3 and 4. For sample 5, it was very special. The morphology for the polymer networks couldn't be found and the liquid crystal droplet size reached approximately 50 μm. This result indicated that sample 5 had been out off the scope of polymer dispersed LC.

In order to clarify the role of the chromophore network diameters and the optical properties we have done quantum chemical evaluations of the ground state dipole moments originating from the borders of PMMA and chromophore using a method described in the ref. 16. We have found that with increasing of the diameter the effective ground state dipole moment magnitude increases also. For the diameter 2 μm the ground state dipole moment magnitude was equal to 5.6 D, for 3 μm – 6.1 D, for 4 μm – 7.4 D and for 5 μm – it was an exception – 6.3 D. It may be a consequence of a void on the border polymer-chromophore.
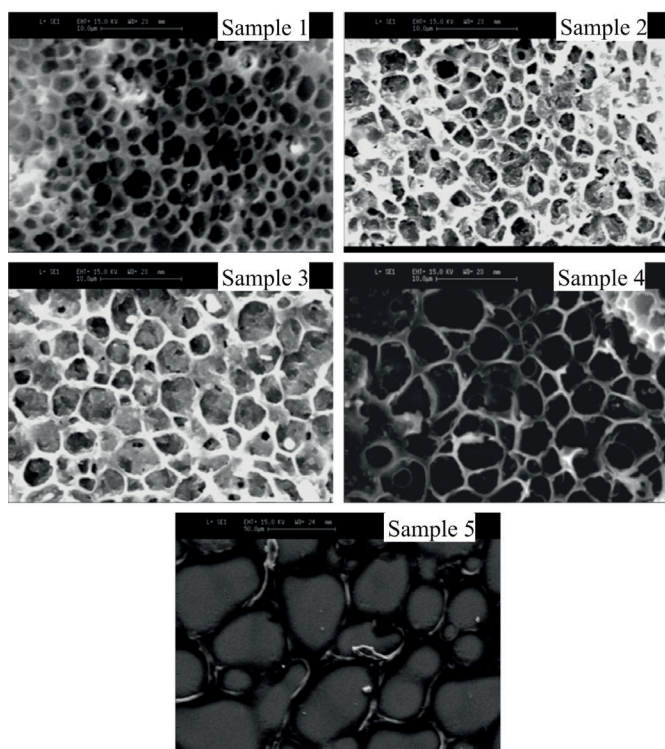

Fig. 3. The SEM images of five investigated samples

Such structures explain the electro optical properties for the samples very well. As the increasing of the diameter size of polymer network holes, the volumes of the liquid crystal droplets for the samples would become larger, and then the surface, anchoring ability for the liquid crystal droplets would be reduced. The LC molecules would be easily oriented in the dc-electric field and therefore, the threshold voltage

and saturation voltage would decrease. As the liquid crystal molecules' oriental ability increases the open state response times also decreases. The off state response times were decided by the recovery ability of the LC molecules. As the LC droplets becoming larger, the recovery ability of the LC molecules would become weaker, and the off state response times is extended.

As shown in Table 2, the off state transmittance is increased with the length of carbon chain of the photo-polymerizable monomers becomes longer. The reason for this phenomenon is that as the LC droplets become smaller, there were more scattering points, and the scattering would also become stronger. The diameter size of polymer network holes influences the light scattering intensity of the PDLC. As the diameter size becoming larger, the light scattering intensity became smaller. So, on the off state, the scattering intensity reduced and the transmittance is increased from sample 1 to sample 5. Else, the open state transmittance and the contrast also increased gradually.

4. Conclusions

By using photo-polymerizable monomers with different length of carbon chain, polymer dispersed liquid crystals with different mesh size were fabricated. We have established a strong correlation between the lengths of flexible chain between two acrylic groups and the electronic optical properties. As the mesh size becoming larger, these polymers dispersed liquid crystal films showed us different electro-optical properties. As the lengths of the photo-polymerizable monomers increasing, the threshold voltages, driving voltages, and open state response times reduced; the off state response times, contrast ration and off state transmittance increased. This phenomenon's were discussed in details and confirmed by the SEM pictures. The performed DFT simulations using B3LYP approach have shown a correlation between electro-optical efficiency and ground state dipole moments. We have found a correlation between the diameters and the dipole moment magnitudes.

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