Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 23 Sep 2006.

To cite this article: Ingrid Heynderickx & Dirk J. Broer (1995): Thermo-Optical Properties of a Polymer Dispersed Liquid Crystalline Polymer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 263:1, 415-427

To link to this article: http://dx.doi.org/10.1080/10587259508033601

Mol. Cryst. Liq. Cryst. 1995, Vol. 263, pp. 415–427
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THERMO-OPTICAL PROPERTIES OF A POLYMER DISPERSED LIQUID CRYSTALLINE POLYMER

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Abstract A side-chain liquid crystalline polymer dispersed into an amorphous polymer matrix can be used as a thermo-optical device that exhibits scattering at low temperatures and becomes transparent when heated above the clearing temperature of the liquid crystalline polymer. The blend of the side-chain liquid crystalline polymer and the UV-polymerizable monomer is yet two-phasic before polymerization and exhibits some additional phase separation during polymerization. Especially the thermal stability, but also the mechanical stability, of the thermo-optical device is considerably improved when dispersing a liquid crystalline polymer instead of a low molar mass liquid crystal into a polymer matrix.

INTRODUCTION

During the last decade polymer dispersed liquid crystals (PDLCs) have gained a lot of interest because of their application in electro-optical or thermo-optical devices.[1,2] In the case of an electro-optical device,[1] one has many possibilities of designing the system, most of them resulting in a scattering of the incident light when no voltage is applied, while the incident light becomes transmitted in an electric field. In the field-off state the liquid crystalline (LC) material is only locally aligned in the droplets, but not macroscopically aligned. The incident light is now scattered because it experiences a difference in the refractive index between neighbouring droplets and between the droplets and the polymer matrix. In the field-on state an LC material with a positive dielectric anisotropy becomes macroscopically aligned along the electric field lines. When the polymer matrix is chosen such that its refractive index equals the ordinary refractive index of the LC material, the incident light sees a composite with one single refractive index and is no longer scattered.

The design of a thermo-optical device[2] differs for two main reasons from that of an electro-optical device: (i) it is switched from a locally aligned state to an unaligned (isotropic) state instead of a macroscopically aligned state, and, (ii) the refractive index of the polymer matrix equals the mean refractive index instead of the ordinary refractive index of the LC material. At low temperatures the PDLC layer is scattering the incident

light in a similar way as in the field-off state of a PDLC electro-optical device. When heating the PDLC layer above the clearing temperature of the LC material, incident light sees an isotropic fluid dispersed in an isotropic polymer matrix. As the refractive indices of the polymer matrix and the isotropic LC material are chosen to match the incident light is transmitted without scattering.

The problem when using a PDLC as a thermo-optical device, however, is its limited thermal stability. This is illustrated in Fig. 1 for a PDLC made from a mixture of 50 wt% of the low molar mass LC material E7 (Merck Ltd, UK) in 50 wt% of a photosetting diacrylate. The transmission of the incident light at 550 nm increases by more than a factor of 5 after storing the sample for 1 hour at 145°C, and after less than one day storage at the same temperature the sample looks transparent at room temperature (RT).

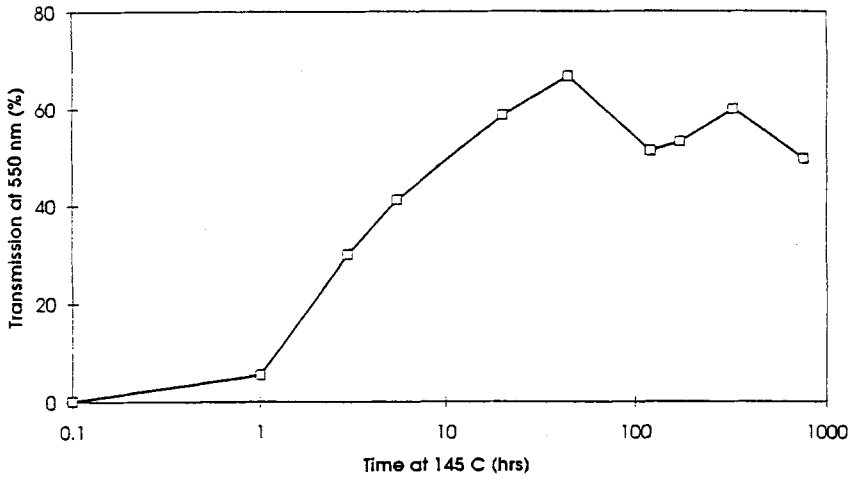

FIGURE 1 Thermal stability of a PDLC thermo-optical device at RT for storage at 145°

Since this loss in scattering is mainly due to evaporation of the LC material out of the isotropic polymer matrix, it is expected to be firmly suppressed by increasing the molecular weight of the LC. We will demonstrate in this paper that the thermal stability of a PDLC thermo-optical device can be considerably improved by dispersing a side-chain liquid crystalline polymer (SCLCP) into an amorphous polymer matrix. The polymer dispersed liquid crystalline polymer (PDLCP) functions as a thermo-optical device in exactly the same way as a PDLC: it is scattering at low temperatures where the SCLCP is only locally ordered, but not macroscopically aligned, and it becomes transparent when heated above the clearing temperature of the SCLCP. Processing of the PDLCP prior to polymerization of the isotropic matrix in the liquid state proceeds comparable to PDLC systems. During polymerization the dimensions and properties becomes fixed by the photo-crosslinking of the monomer. The influence of the polymerization reaction on the morphology of the PDLCP and its resulting scattering will be discussed.

EXPERIMENTAL

The SCLCP used to evaluate the characteristics of a PDLCP is the LCP93 (Merck Ltd. UK), the structure of which is given in Fig. 2a. It is based on a copolymer with a siloxane backbone and cyanobiphenyl sidegroups, which are also the basic compounds in the low-molar-mass E7 material. The degree of polymerization is about 40. It has a glass transition temperature of -4°C and exhibits a Sm_A phase at RT. The clearing temperature is given by Merck to be 79°C. For the photosetting material the ethoxylated Bisphenol A diacrylate SR349 (Sartomer) is used, the structure of which is given in Fig. 2b. It is chosen for its refractive index that should match the mean refractive index of the LCP93, which is 1.545 at 80°C. To the mixture of LCP93 and SR349 2 wt% of the photoinitiator Irgacure 651 (Ciba Geigy) is added.

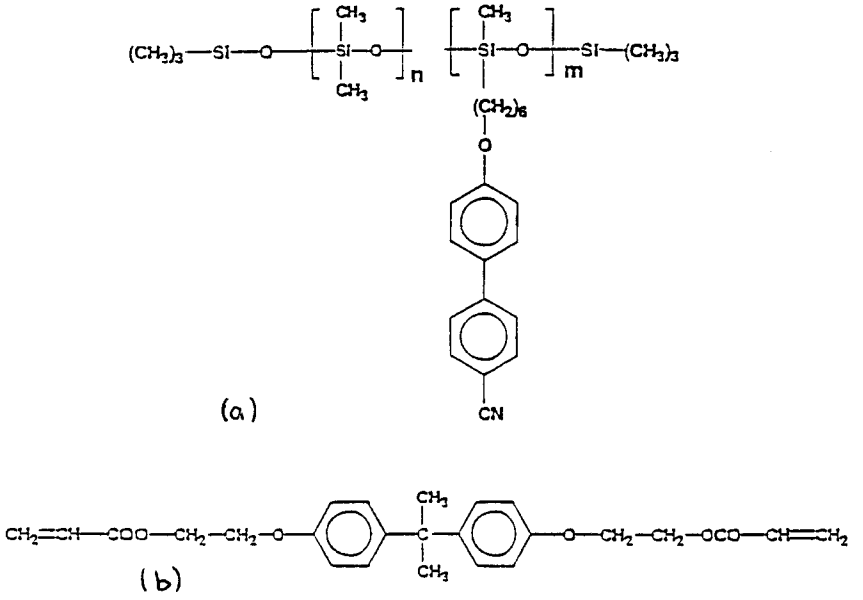

FIGURE 2 Molecular structure of the LCP93 (a) and the SR349 (b) used to make a PDLCP thermo-optical device

The materials were blended at elevated temperatures, well above the clearing temperature of the SCLCP, and the blend was then poured between two glass plates separated at a well-defined distance. After cooling down the samples to the polymerization temperature, they were illuminated with a standard intensity UV-source having an output of 5.8×10^{-4} W/cm^2 at 365 nm. To check the influence of the light intensity on the polymerization reaction, and the related scattering, some samples were cured with a less intense source having an output of 1.7×10^{-4} W/cm^2 at 365 nm or with a more intense source with an output of 1.4×10^{-3} W/cm^2 at 365 nm.

To optimize the scattering as a function of composition and polymerization temperature films of a thickness of 20 μm were used. The transmitted light was

measured in a UV-VIS spectrophotometer (Unicam 8700) with the smallest diaphragm in front of the sample holder, being placed at a fixed position as close to the detector as possible. This yields an angle of acceptance for the scattered light of about 10° in the forward direction. To study the morphology of the PDLCP thinner samples were made and the structure of the amorphous polymer matrix was visualized by SEM after dissolving the LCP93 in ethylacetate. The thermal stability of the thermo-optical devices was tested by measuring their transmission at RT in open configurations of samples with a thickness of 100 μm.

RESULTS AND DISCUSSION

Biphasic behaviour of the PDLCP

Using a polarizing microscope the transition from the Sm_A to the isotropic phase is found for the pure LCP93 of the batch used at 74.5°C. For a 1:1 mixture of the LCP93 with the SR349 monomeric diacrylate the transition from an anisotropic to the isotropic phase is observed at 47°C. At temperatures below this transition temperature the blend is opaque. In this blend the smectic character of the liquid crystalline phase is no longer clearly observed. But, the fact that we still observe a clearing transition in the blend indicates the existence of a liquid crystalline phase, which, however, is diluted by the

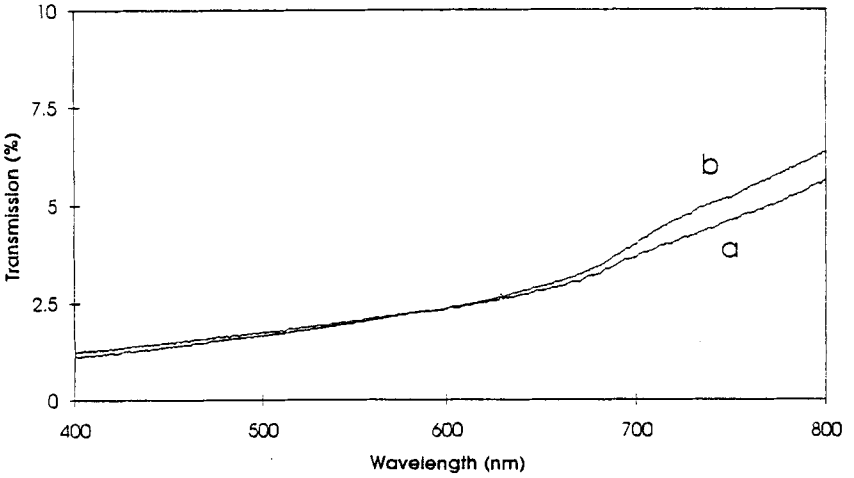

FIGURE 3 Influence of the UV-polymerization on the scattering of a PDLCP: (a) before polymerization at RT, (b) after polymerization at RT.

diacrylate explaining the drastic decrease of the clearing temperature compared to that of the pure LCP. Moreover, observation of the blend of the two, in principle, immiscible fluids shows that there is no complete mixing on a molecular scale of the LCP93 in the monomeric diacrylate. So, even before polymerization the blend is at least biphasic with a diluted LCP phase and a probably impure diacrylate phase. This is a clear difference with PDLC devices, in which, in general, the LC material is dissolved on a molecular

level into the UV-curable monomer, yielding before polymerization an isotropic transparent film.[1]

Upon UV-polymerization of the blend at RT the transition from anisotropic to isotropic shifts from 47°C to 72°C. This suggests that some phase separation occurs during polymerization, yielding a polymeric liquid crystalline phase with a higher degree of purity. As illustrated in Fig. 3, showing the transmission as a function of wavelength for 20 μm thick samples of the 1:1 mixture of LCP93 and SR349 before and after polymerization, this additional phase separation has almost no influence on the scattering of the thermo-optical device. This suggests that despite of the relatively high loading of diacrylate, the scattering originates intrinsically in the SCLCP rather than from the existence of the two phases with a different refractive index. This consideration will be further discussed in the next sections.

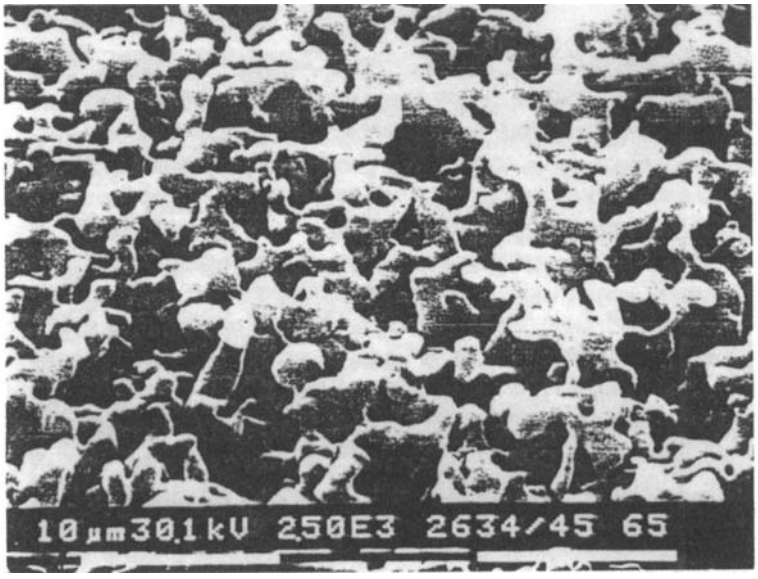

FIGURE 4 Morphology of the polymer matrix of a PDLCP as visualised by SEM. The blend of 65 wt% LCP93 + 35 wt% SR349 was UV-cured at RT.

Morphology of the PDLCP

The morphology of the amorphous polymer matrix, remaining after dissolving the SCLCP in ethylacetate, has been visualized by SEM. Fig. 4 shows an example of a sample composed of 65 wt% LCP93 dispersed into 35 wt% SR349 and polymerized at RT. It exhibits a sponge-like structure with irregular holes having largely varying sizes. The LCP "droplets" may be as small as 1 μm, but can also be as large as 7 μm. It is clear that the largest droplets have dimensions being too large to effectively scatter the incident light at the interfaces.[3] Therefore, we rather expect the domain formation of the

SCLCP within the largest droplets to be the cause for the scattering of the incident light.

Within the concentration range from 35 wt% to 65 wt% LCP93 we did not see much difference in the morphology of the isotropic polymer matrix. For any of the concentrations the sponge-like structure of the polymer matrix was very irregular. For higher concentrations of LCP93 the morphology of the matrix could not be visualized because the remaining film was too fragile after being washed out, while for lower concentrations of LCP93 we had difficulties in successfully dissolving the LCP in the ethylacetate.

There is a clear influence of the polymerization temperature on the morphology of the PDLCP. This is illustrated in Fig. 5, in which the polymer matrix of a PDLCP composed of 50 wt% LCP93 with 50 wt% SR349, but now polymerized at 100°C, is shown. Again the sponge-like structure exhibits irregularly shaped holes, but now with dimensions in the submicron range. Some droplets are as small as 100 nm and do no longer scatter the visible light effectively.

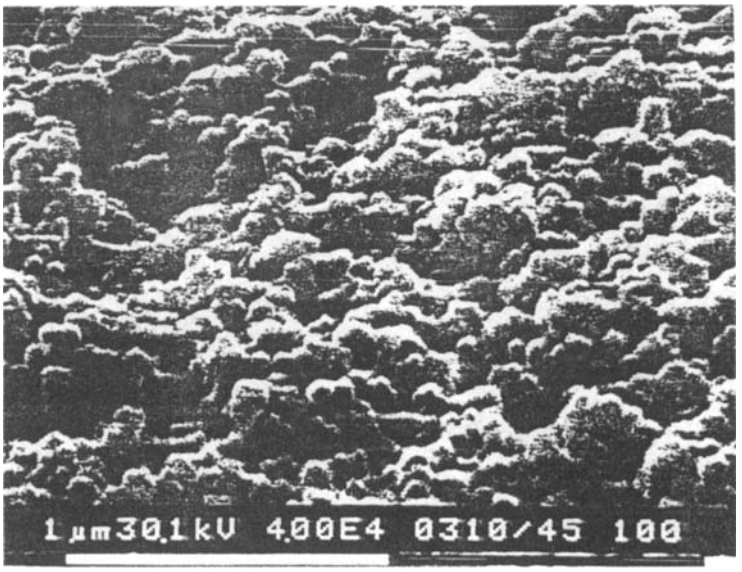

FIGURE 5 Morphology of the polymer matrix of a PDLCP as visualised by SEM. The blend of 50 wt% LCP93 + 50 wt% SR349 was UV-cured at 100°C.

Thermo-optical behaviour of the PDLCP

The thermo-optical characteristics of a PDLCP are shown in Fig. 6 for a sample composed of a 1:1 mixture of LCP93 and SR349 and polymerized at RT. The transmission measured at a wavelength of 550 nm is plotted against the temperature for both a heating and a cooling scan. It clearly demonstrates the sharp transition (within 1°C) from the scattering to the transparent state, and vice versa. One also observes only a small hysteresis of about 2 or 3°C between the heating and the cooling scan. Because

of the reflection losses at the interfaces we expect a maximum transmission in the transparent state of about 92%. For this sample, however, the maximum transmission approaches the value of 85% at a temperature of 74°C. The difference is explained by a small mismatch of the refractive index of the polymer matrix with the mean refractive index of the SCLCP. Moreover, upon further heating of the PDLCP the transmission decreases. In other words, due to the difference in temperature dependence of the refractive index of the glassy polymer matrix with that of the mean refractive index of the rubbery SCLCP, the latter being steeper than the former, the mismatch between both refractive indices becomes stronger. So, in order to improve even further on the transmission of the transparent state one should adapt the refractive index of the polymer matrix better to that of the SCLCP for a temperature well above the transition temperature of the thermo-optical device.

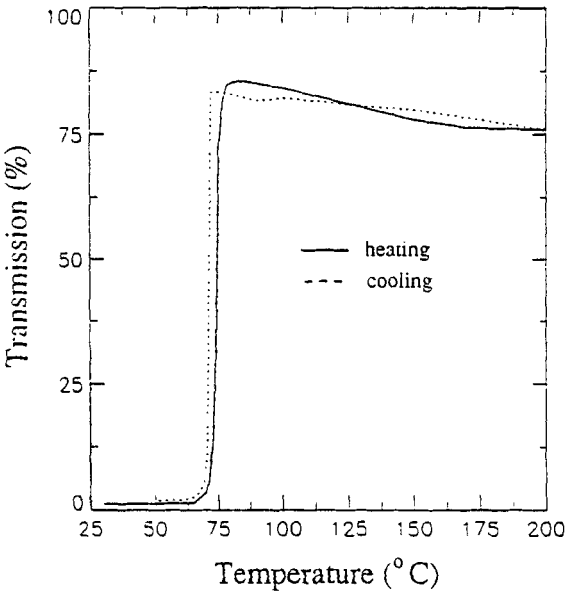

FIGURE 6 Thermo-optical characteristics of a PDLCP as measured in both a heating scan and a cooling scan.

Optimization of the scattering of the PDLCP

From the evaluation of the biphasic behaviour in the PDLCP and from the visualisation of the morphology we already know that the domain formation in the SCLCP largely contributes to the scattering in the low-temperature state of the thermo-optical device. This suggests that the presence of the polymer matrix has a negative effect on the scattering only. However, because of its improvement of the mechanical properties of the device and because of its firm reduction in the cost price, the addition of a polymer matrix may be preferred for some applications. Therefore, the influence of some polymer related parameters, like its concentration, the polymerization temperature and the light intensity of the UV-curing source, on the scattering is evaluated. One should

remark, however, that due to the initial morphology of the emulsion the amount of mechanical work performed to blend the diacrylate with the SCLCP may have a strong influence on the transmission measured. Especially for the thinnest samples using a small amount of material, a reproducibility of better than 25% may not be expected.

Influence of the composition

To study the influence of the concentration LCP93 on the scattering efficiency of the PDLCP, samples with a thickness of 20 μm were UV-polymerized at RT with the standard intensity UV-source. The spectra of the transmission as a function of the wavelength are given in Fig. 7 for some discrete values of the concentration LCP93.

The lowest transmission over the whole wavelength range is found for the pure LCP93 material. This again confirms that there is an important contribution to the scattering coming from the domain formation in the SCLCP, a conclusion that has already been deduced from the results of the previous sections. Increasing the amount of monomeric diacrylate in the blend yields an increase in the transmission merely for the longer wavelengths. This means that in fact the dimension of the scattering entities

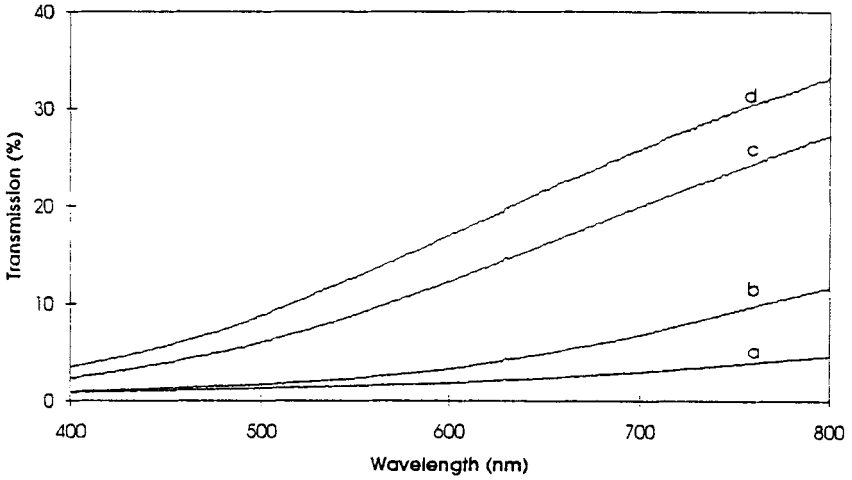

FIGURE 7 Influence of the amount of LCP93 in the blend on the scattering of the PDLCP: (a) 100%, (b) 50%, (c) 40%, (d) 20%.

is changed by incorporating an amorphous polymer matrix into a scattering SCLCP, a phenomenon which is also observed in traditional PDLC systems.[3-5] How the formation of the polymer matrix affects the domain formation in a scattering SCLCP is an interesting question that has not yet been answered. When further decreasing the LCP93 concentration to less than 50 wt%, the transmission increases for the shorter wavelengths in a similar way as for the longer ones. This implies that merely the number of the scattering entities is changed at these concentrations. So, now the polymer matrix just dilutes the scattering SCLCP.

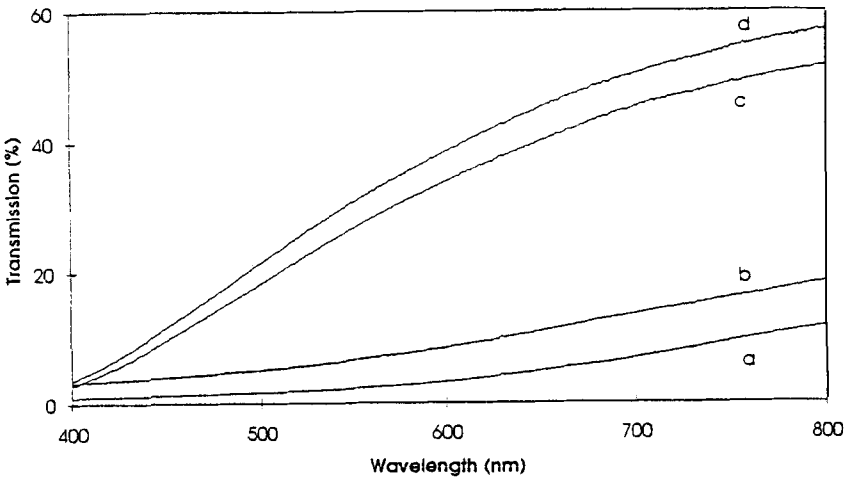

FIGURE 8 Influence of the polymerization temperature on the scattering of the PDLCP: (a) RT, (b) 50°C, (c) 70°C, (d) 100°C.

Influence of the polymerization temperature

The effect of the polymerization temperature T_p on the amount of scattering in the PDLCP has been evaluated by measuring the transmission spectra at RT for samples with a thickness of about 20 μm and composed of 50 wt% LCP93 + 50 wt% SR349. The samples were polymerized with the standard intensity UV-source at different temperatures ranging from RT to 100°C. It should be mentioned that the latter polymerization is performed with the SCLCP being isotropic. The corresponding spectra are given in Fig. 8.

Increasing T_p from RT to 50°C yields an increase in transmission for both the short and the long wavelengths, which suggests that the incident light experiences a smaller number of scatterers at a higher T_p. Increasing T_p further towards 70°C or 100°C results in a larger transmission increase for the longer than for the shorter wavelengths, which means that now the dimension of the scatterers is changed too. This was also concluded from the evaluation of the morphology of the polymer matrix as a function of T_p. The dimension of the SCLCP droplets was found in the submicron range with some scatterers being as small as 100 nm.

These observed tendencies may be explained in terms of an improved solubility of the monomeric diacrylate into the SCLCP at higher polymerization temperatures. Due to this improved solubility one expects also after the phase separation during polymerization smaller SCLCP and polymer matrix particles at higher T_p. Apparently, this leads at first instance to a reduction of the number of domains in the SCLCP. In a later stage the SCLCP "droplets" become smaller than the size of a domain. Now, the light will be scattered rather by the refractive index difference between polymer matrix and SCLCP and no longer by the domains in the SCLCP. Finally, the droplets become too small to effectively contribute to the scattering of the incident light.[3-5]

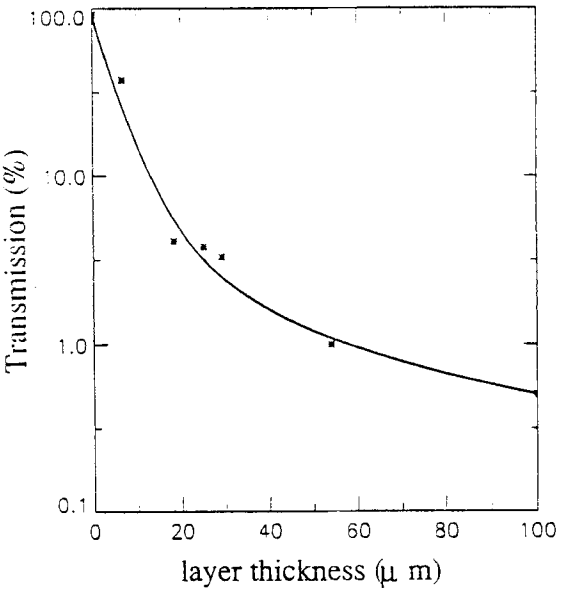

FIGURE 9 Influence of the layer thickness on the scattering of the PDLCP

Influence of the sample thickness

To find the optimal layer thickness for the PDLCP thermo-optical devices samples of 50 wt% LCP93 + 50 wt% SR349 were polymerized at RT with the standard intensity UV-source. Fig. 9 gives the corresponding transmission at 550 nm as a function of sample thickness. It shows a rapid decrease in transmission for the thinnest samples and a more steady decrease for the samples thicker than about 20 μm. It also illustrates that in this experimental set-up a contrast ratio larger than 50:1 is already obtained for samples as thin as 50 μm.

Influence of the light intensity during polymerization

The difference in transition temperature of the PDLCP before and after polymerization already suggested that some additional phase separation takes place during UV-curing. So, because of its influence on the time for molecular diffusion one would expect some effect of the light intensity used for curing. Moreover, one would expect that at those polymerization temperatures where we found an improved solubility of the diacrylate in the SCLCP, the process of phase separation would be influenced by the light intensity too. To check these expectations 20 μm thick samples of 50 wt% LCP93 + 50 wt% SR349 were polymerized with three different UV sources at RT as well as at 100°C.

For a T_p of 100°C no significant influence of the light intensity on the amount of scattering has been observed. For any of the intensities used to cure the blend the molecular diffusion is insufficient to enlarge the LCP "droplets" to sizes larger than those observed from the morphology study.

And also at RT we did not found a predominant effect of the light intensity on the amount of scattering for the curing conditions chosen. So, as was concluded from the evaluation of the biphasic behaviour too, the phase separation during polymerization hardly influences the observed scattering.

Thermal stability of the PDLCP

In the introduction it has already been demonstrated that the thermal stability of a PDLC when used as a thermo-optical device, is limited. For a sample of 50 wt% E7 dispersed into an UV-cured diacrylate matrix the transmission increased by a factor of 5 after 1 hour of storage at 145°C. In a similar experiment the thermal stability of a PDLCP composed of a 1:1 mixture of LCP93 and SR349 and UV-cured with the standard intensity source at RT has been tested. The resulting transmission at 550 nm is plotted in Fig. 10 as a function of the storage time of a free standing film in air at 145°C. It is clear that in contrast to the PDLC, the transmission of the PDLCP remains as low as 1%

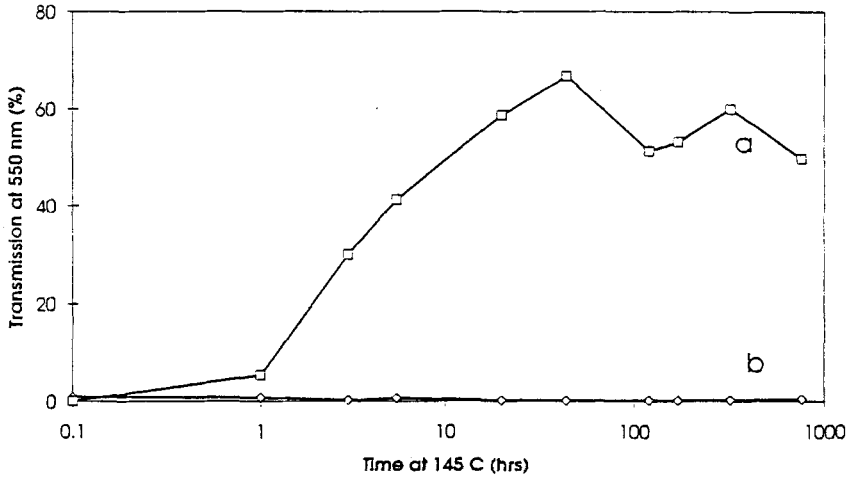

FIGURE 10 Thermal stability of a PDLCP (b) compared to that of a PDLC (a). The transmission at 550 nm is measured as a function of time for storing the sample at 145°C.

even after more than 800 hours of storage at 145°C. A point of concern is that the thermal degradation might affect the transition temperature of the device. Since, however, after 760 hours of storage the transition temperature of this same film decreased from 72 to 70°C, we can conclude that the change in switching temperature during aging at 145°C is only marginal.

The thermal stability as a function of temperature has also been tested for a similar PDLCP device by measuring the transmission at 550 nm at RT after storing the sample during 1 hour at continuously increasing temperatures. The results are given in Fig. 11 and illustrate that the PDLCP thermo-optical device has still a lifetime of 1 hour at temperatures as high as 270°C. However, above 210°C the contrast of the device starts

to decrease because of a yellowing of the isotropic matrix, that lowers the transmission in the open state. Above 250°C the degradation becomes so severe that also the scattering in the closed state decreases.

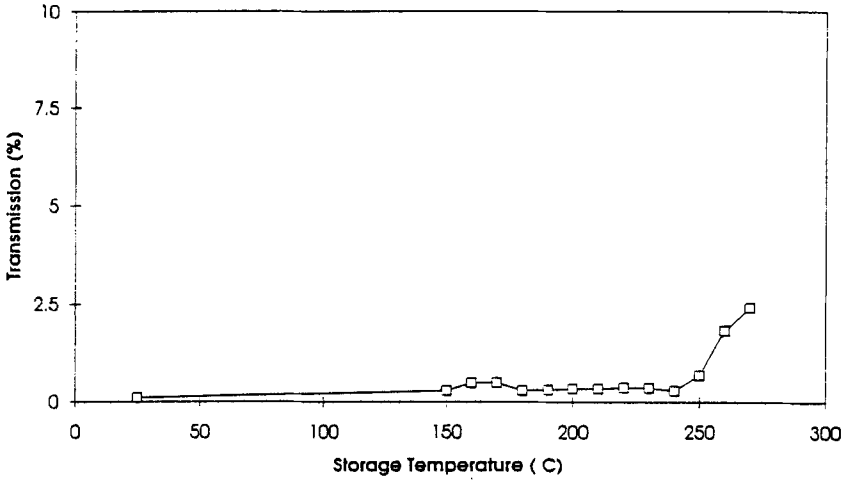

FIGURE 11 Thermal stability of a PDLCP for storing the sample during 1 hour at continuously increasing temperatures.

CONCLUSIONS

A PDLCP based on a SCLCP dispersed into an UV-cured diacrylate matrix can be used as a thermo-optical device exhibiting an improved thermal stability at elevated temperatures as compared to a PDLC. The drastic increase in molecular weight, realised by binding the cyanobiphenyls to a polymer backbone, considerably suppresses the evaporation of the LC material out of the isotropic polymer matrix. From the morphological point of view there are two main differences between a PDLCP and a PDLC. First of all, in the case of a PDLCP there is no complete mixing on a molecular scale when blending the SCLCP with the monomeric diacrylate. In other words, the phase separation during polymerization plays no dominant role in determining the amount of scattering of the incident light. And secondly, the scattering is rather due to the domain formation in the SCLCP than to the existence of a biphasic system of SCLCP dispersed into an amorphous polymer matrix. The addition of the amorphous polymer matrix has mainly a dilution effect on the scattering. But, from a practical point of view its presence may be preferred, since it largely improves the mechanical properties and firmly reduces the price of the thermo-optical device.

ACKNOWLEDGMENTS

We gratefully thank G.P. Melis and C.M.R. de Witz for their practical support, and Dr. C.J.E. Seppen for fruitful discussions.

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