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"IN-SITU PHOTOPOLYMERIZATION" OF DISCOTIC LIQUID CRYSTALLINE ACRYLATES IN THE DISCOTIC NEMATIC PHASE

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Abstract In order to stabilize the anisotropic properties of films made from discotic liquid crystals (DLCs), we applied the "in-situ photopolymerization" process to reactive DLCs. We synthesized triphenylene benzoate derivatives with 1 to 6 acrylate end groups and studied the influence of the number of acrylates on their discotic nematic (N_D) phase and on their photo-initiated polymerization behavior. The discotic acrylates align spontaneously between substrates in the N_D phase, leading to thin films with a negative birefringence. We used the Haller extrapolation method to evaluate the order parameter of these materials. Oriented thin films of monomer were then "frozen in" using photo-initiated polymerization. We studied the optical properties of the resulting polymer films and in particular the dependence of the birefringence on the polymerization temperature. X-ray diffraction analyses of polymer films made from the diacrylate show a decrease of order with higher polymerization temperatures.

INTRODUCTION

Discotic liquid crystals (DLCs) exhibiting the discotic nematic phase (N_D) are good candidates to make optical compensation layers to improve the viewing angle of twisted nematic liquid crystal displays.[1] However, the extent of the N_D phase often confines these anisotropic properties to a range of temperature not suitable for applications. We used the photo-initiated polymerization of discotic acrylates oriented in the nematic phase to obtain thermally stable films. The synthesis of mono-, di-, and tri-acrylates (called **1**, **2**, and **3**) is described elsewhere[2] (figure 1 shows one isomer of **2**). The hexa-acrylate (**6**), based on the same central core, was made in a similar way, and the reference discotic without acrylate group (hexa-((2-methyl-4-n-decyloxy)benzoate of triphenylene, **0**) was synthesized according to literature.[3]

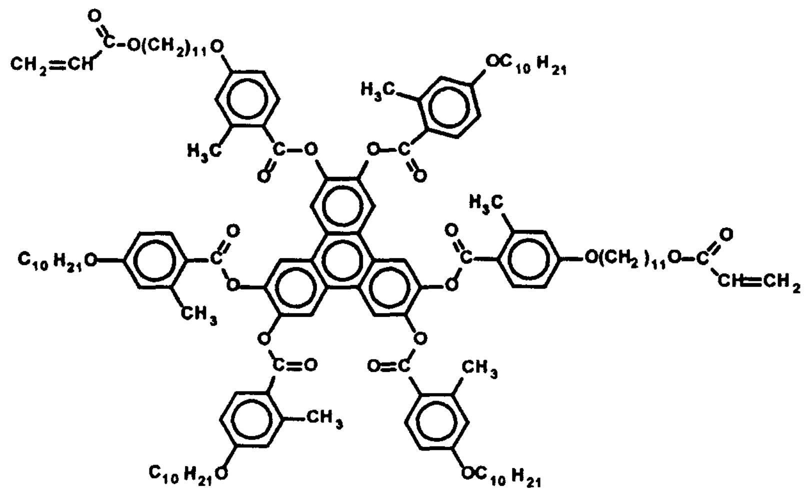

FIGURE 1 Chemical structure of one of the diacrylate isomers.

LIQUID CRYSTALLINE PROPERTIES

Figure 2 gives the DSC runs of compounds **0**, **1**, **2**, **3**, and **6**.

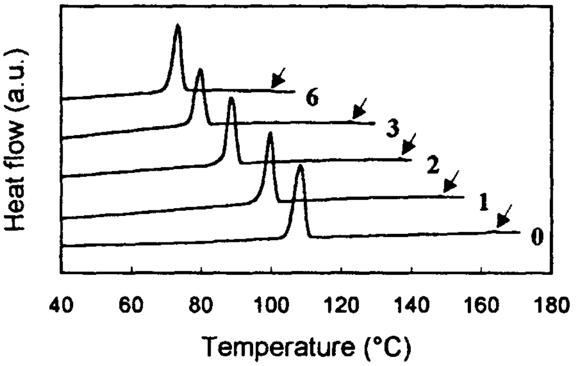

FIGURE 2 DSC runs of **0**, **1**, **2**, **3**, and **6**. The large endotherm indicates the crystalline-nematic transition, the smaller endotherm (arrows) marks the nematic-isotropic transition.

The monomers are crystalline at room temperature. In the case of **2** and **3**, X-ray diffraction patterns also show that parts of the materials remain amorphous even after annealing for 1 hour at 60°C. The presence of acrylate groups causes the melting temperatures (T_m) to decrease from 101°C for **1** to 73°C for **6**. A large super-cooled effect of the N_D phase allows polymerization in this phase down to at least 60°C for all monomers.

ORDER PARAMETER OF THE ALIGNED MONOMERS

We measured the ordinary (n_o) and extraordinary (n_e) refractive indices of all monomers with an Abbe refractometer (λ= 589 nm).[2] From those data, we evaluated the order parameter S of the aligned mono- and di-acrylate using the expression of Vuks[4] (below), and the extrapolation method of Haller[5,6,7] to determine the polarizability ratio $r = \bar{a}/(a_{\parallel}-a_{\perp})$, assumed constant with the temperature.

$$S=\left(\frac{\bar{a}}{a_{\parallel}-a_{\perp}}\right)\frac{n_e^2-n_o^2}{\bar{n}^2-1} \quad \text{with} \quad \bar{n}^2=\frac{1}{3}\left(n_e^2+2n_o^2\right) \quad \text{and} \quad \bar{a}=\frac{1}{3}\left(a_{\parallel}+2a_{\perp}\right)$$

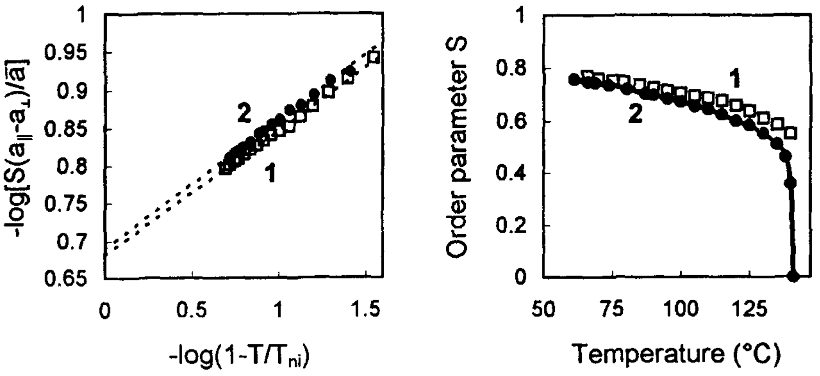

FIGURE 3 a) Haller plot for **1** and **2** (left); b) Order parameter as a function of the temperature for **1** and **2** (right)

Figure 3a gives the Haller plot for **1** and **2**. By extrapolation to T = 0K, where S = 1, we found $r_1 = -4.80$ and $r_2 = -4.90$. These values are very close because **1** and **2** differ only by one acrylate group. They are higher in absolute value compared to a previously investigated mixture of **0** (45 wt%) with triphenylene hexa-*n*-heptanoate, HET7, (r = -3.70).[7] In fact, **0**, **1** or **2** have a higher molecular polarizability $\bar{a}$ than HET7 due to their 6 peripheral phenyl rings. The polarizability anisotropy $a_{\parallel}-a_{\perp}$ also increases with more phenyl rings but not as much as $\bar{a}$ because those rings tend to form an angle of 30 to 40° with the triphenylene core according to modelling studies.[8]

The order parameters obtained for **1** and **2** (figure 3b) are high, indicating a good alignment of the monomers.

PHOTO-INITIATED POLYMERIZATION

We added 1% photoinitiator, 2,2-dimethoxy 2-phenyl acetophenone, and 200 ppm inhibitor, *p*-methoxyphenol, to all monomers. A detailed analysis of the photo-initiated polymerization of the mono-, di-, and triacrylate is presented elsewhere.[2] The conversions obtained for these monomers in the stable discotic nematic phase (above T_m) upon 15 min UV irradiation are 98, 88, and 80 %, respectively.[2] The hexa-acrylate leads to lower conversions (66 %) because of the hindered mobility at an earlier stage of the polymerization reaction due to the high density of cross-links. This conversion value is nevertheless relatively high because it indicates that an average of 4 acrylates per molecule reacted (compared to 2.4 for **3**, and 1.8 for **2**). In fact, monomers attached by 2 contiguous side-chains to the polymer back-bone probably have comparable mobilities to those of monomers attached by only one, which delays the freezing of the network to higher conversions.

After polymerization, the samples show no transition from room temperature to at least 200°C according to DSC, except for the side-chain polymer made from **1**, poly(**1**), which becomes isotropic at 156°C.

OPTICAL AND STRUCTURAL PROPERTIES OF THE POLYMERS

We focused on the polymer network made from **2**, poly(**2**), because of its higher thermal stability compared to poly(**1**), and because of the higher birefringence of **2** compared to **6** (too small quantities of **3** were available for further studies).

The preparation of oriented thin polymer films (between 4 and 15 μm) is reported elsewhere.[2] The birefringence of the polymer films made from the diacrylate can be tuned from -0.028 to -0.06 by varying the polymerization temperature (T_p) between 120°C and 60°C (figure 4a). The higher the T_p, the more the growing polymer chain interferes with the liquid crystalline ordering. This possibility to tune the birefringence with T_p was already observed with rod-like diacrylates.[9]

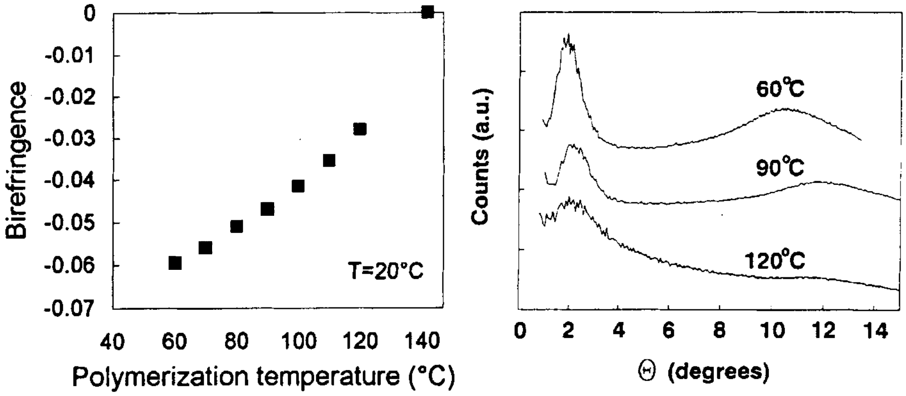

FIGURE 4 a) Birefringence of the polymers made from **2** as a function of the polymerization temperature (left). b) X-ray diffraction patterns of oriented films of **2** polymerized at 60°C, 90°C, and 120°C (right)

To characterize the ordering of the polymer films, we carried out X-ray diffraction experiments with a Siemens Hi-Star Area Detector (CuK_α radiation, X-ray beam parallel to the film surface). Figure 4b gives the profile obtained for poly(**2**) polymerized at 60°C, 90°C, and 120°C (by integration of the 2D X-ray diffraction patterns). The small angle reflection (60°C: 24 Å) is related to the molecular diameter, and the wide angle reflection to the core-core and tail-tail distances (60°C: 4.2 Å). The variation of the sharpness of the peaks clearly shows that lower polymerization temperatures lead to a higher order in the final polymer. In addition, the 2D pattern of poly(**2**) polymerized at 60°C shows a local arrangement of the disks in tilted columns oriented at 45° to the surface of the film.[10] This structure could be the result of a local crystallization in the super-cooled N_D phase during polymerization. However, the diffraction pattern of monomer **2** polymerized at 90°C in the stable N_D phase also show this local ordering. As a consequence, the local columnar structure obtained in the final polymer is most likely due to the existence of a pretransitional order[10,11] in the monomer near and below (on cooling) the melting point.

CONCLUSION

The photo-initiated polymerization of oriented reactive discotic liquid crystals is a convenient technique to obtain thermally stable thin films with a negative birefringence. We also show that the birefringence can be tuned by varying the polymerization temperature to values within a range useful for applications like optical compensation layers.

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