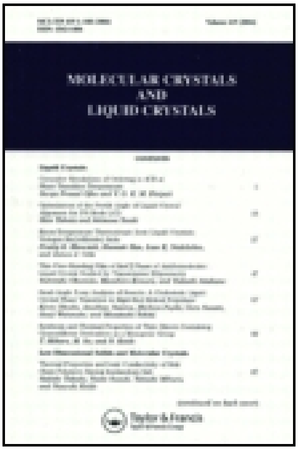

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New Coumarin Polymers as Non-Contact Alignment Layers for Liquid Crystals

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New Coumarin Polymers as Non-Contact Alignment Layers for Liquid Crystals

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The synthesis of polymethacrylate derivatives of 6- and 7-hydroxycoumarin is described and their use as photoinduced alignment layers for liquid crystals is discussed. Strong anchoring is found with azimuthal anchoring energies > 6.9×10^{-5} J m^{-2}. The liquid crystal alignment direction is parallel to the polarisation direction of the incident UV light when low fluences are incident. At a critical fluence threshold, a sharp change to perpendicular alignment is found. The incorporation of a flexible spacer into the coumarin sidechain results in stronger anchoring at low fluences. These results are discussed in terms of a molecular model.

Keywords: liquid crystals; alignment; photoinduced; hydroxycoumarin; polymer

INTRODUCTION

Many new liquid crystal devices require surface anchoring conditions which cannot be provided by the traditional rubbed polyimide alignment layer. For example, multi-domain displays with wide viewing angles need microscopic variations in director orientation[1], and the recent bistable nematic displays rely on either bistable surface anchoring[2] or two alignment layers with different anchoring strengths[3]. Rubbing of polyimide layers also generates dust and static electricity which lowers the yield of active matrix liquid crystal displays. The photoinduced anisotropic

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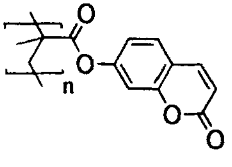
crosslinking of sidechain polymers is among the most promising of the various non-contact alignment technologies which are being explored to meet these demands. It was found that polyvinylcinnamate (PVC) films exposed to linearly polarised ultraviolet light gave liquid crystal alignment perpendicular to the polarisation direction of the light[4,5]. The alignment results from an anisotropic depletion of the cinnamate sidechains because of (2+2) cycloaddition although some authors suggest that cis-trans isomerisation is also involved at low fluences[6]. A low azimuthal surface anchoring energy of $\approx 4 \times 10^{-6}$ J m^{-2} is measured[7] but better alignment is found when PVC derivatives are used[6,8] Small liquid crystal pretilt angles ($\approx 0.3°$) have been generated in PVC by means of a double exposure of the alignment layer[9]. However the pretilt angle is more easily varied by exposure at non-normal incidence when the alignment direction is parallel to the polarisation direction of the UV light. These conditions have been reported with a coumarin side-chain polymer[1] and multi-domain devices are described using this material[10].

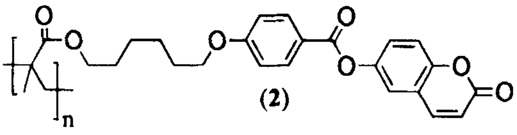
In this paper, we report on the synthesis of polymers containing coumarin moieties and their use as liquid crystal alignment layers. The relationship between molecular structure and the alignment properties of the polymers is discussed.

EXPERIMENTAL

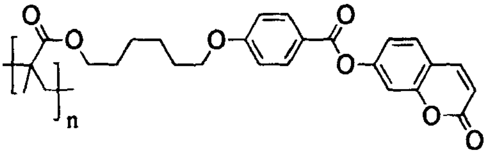
Polymethacrylate derivatives, **(1)**, **(2)** and **(3)** of 6- and 7-hydroxycoumarin were synthesised as detailed below.



(1)



(2)



(3)

Thin films were prepared by spin-casting a solution of the polymer in cyclopentanone. They were irradiated using linearly polarised light of wavelength 300 nm from an Argon Ion laser. An incident power of 2 mW cm^{-2} was used and the fluence was varied by changing the time for exposure. Twisted cells of thickness 17 μm filled with the nematic liquid crystal E7 (Merck) were constructed using one exposed alignment surface and one rubbed polyimide layer. The twist angle, ϕ, of the cell was measured using a polarising microscope. The rubbing direction of the polyimide surface was perpendicular to the polarisation direction of the incident UV light onto the exposed surface. The crystal rotation method[11] was used to determine the pretilt angle of antiparallel nematic cells constructed using two photo-aligned surfaces with equal UV exposure. The polymers (**1-3**) were modelled using $Cerius^2$ (version 3.5) from Molecular Simulations on Silicon Graphics Indy machines and minimised using the Universal 1.01^4 force field[12].

RESULTS AND DISCUSSION

Symmetry considerations dictate that the liquid crystal alignment direction at a photoinduced aligning substrate should be either parallel or perpendicular to the direction of the incident linearly polarised light. However, ϕ is normally less than 90° because of competition between the bulk twist energy and finite surface anchoring energy so that twist disclinations are observed in the twisted nematic cells. Assuming infinite anchoring at the rubbed polyimide surface, the azimuthal anchoring energy, W_ϕ, can be found from the equation:

$$W_\phi = \frac{2K_{22}\,\phi}{d\sin 2\phi} \qquad (1),$$

where K_{22} is the twist elastic constant and d the cell spacing measured before filling using a spectrophotometer. Figure one shows the twist-off angle, defined as the difference between ϕ and the polarisation direction of the incident beam, as a function of laser fluence for the samples.

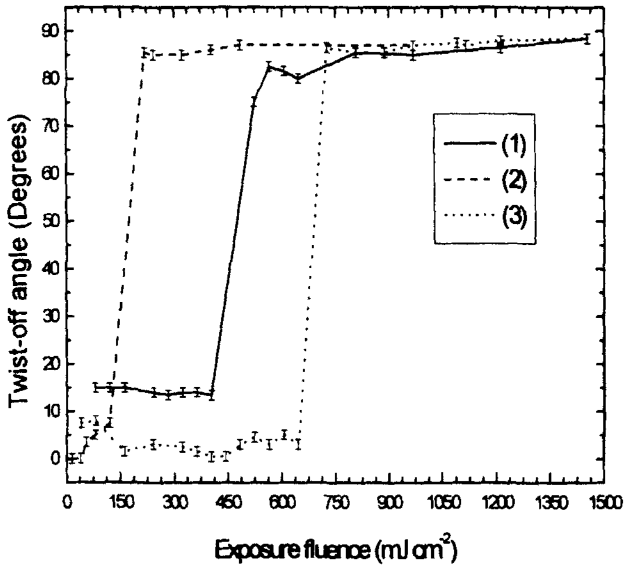


Figure one Variation of twist off angle with incident fluence for polymers (**1**), (**2**) and (**3**).

The results show, that for all three polymers, the alignment direction is parallel to the polarisation of the incident UV light on exposure with low fluences. Then, at a critical fluence threshold, a sharp transition to perpendicular alignment is found. Very low exposures give strong azimuthal anchoring to polymers (**2**) and (**3**): for the former, the 6-hydroxycoumarin derivative, a fluence of 16.2 mJ cm^{-2} gives a twist-off angle of < 0.5° which corresponds to an azimuthal anchoring energy > 6.9 × 10^{-5} J m^{-2}. The threshold of (**3**) is somewhat larger, 40 mJ cm^{-2}, and a similar large anchoring energy is achieved with a fluence of about 400 mJ cm^{-2}. Much higher twist-off angles are measured for the spacerless polymer (**1**) equivalent to anchoring energies of 2 × 10^{-6} J m^{-2}. However, a stronger anchoring energy, up to 2.3 × 10^{-5} J m^{-2}, is found for this polymer when the alignment has switched to perpendicular.

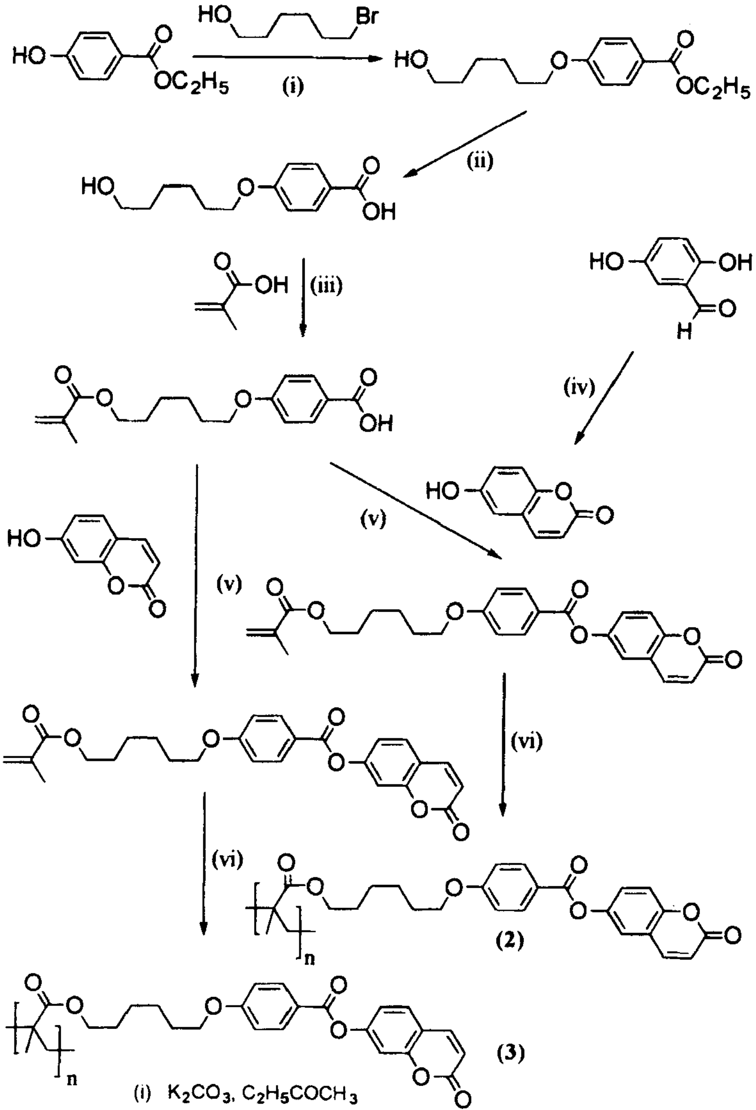
As discussed above, photoinduced liquid crystal alignment in cinnamate and coumarin containing polymers results from an anisotropic depletion of the sidechains because of (2+2) cycloaddition. An epitaxial type of alignment is assumed with the liquid crystal rods tending to align parallel to the polarisation axis of the sidechain. Exposure of PVC polymers generally gives liquid crystal alignment perpendicular to the incident polarisation. This has been explained in terms of the preferred cyclobutane-derived photoproduct having a trans- azimuthal configuration perpendicular to the incident UV polarisation axis. Then, the alignment direction resulting from the photoproducts is parallel to that from the unreacted sidechains: the maximum density of undepleted sidechains is also perpendicular to the polarisation direction. However, for the coumarin material, molecular modelling has shown that the alignment direction of photoproducts is parallel to the incident polarisation direction. On the other hand, the unreacted sidechains align perpendicular to it. The resultant liquid crystal alignment direction, which is observed to vary with fluence, depends on the difference between the azimuthal aligning strength of photoproducts and unreacted sidechains. It is surprising that initial exposure gives alignment from the photoproducts whilst later, alignment appears to be governed by the undepleted sidechains. This suggests that the anisotropy of the dimerised product is initially greater than that of the coumarin sidechain. The movement of flexible sidechains would give a more isotropic depletion than that dictated by the $\cos^2\theta$ dependence of the photochemical reaction: θ is the azimuthal angle between the polarisation vectors of the sidechain and the incident light. Once formed, the photoproduct has a greater anisotropy because of the steric rigidity imposed by the cyclobutane ring. As the crosslinking density increases, the sidechains become more inflexible so that their depletion becomes more anisotropic. This model also suggests that polymers (**2**) and (**3**), which incorporate flexible aliphatic spacers, would have a stronger initial anisotropy than polymer (**1**) where the coumarin group is attached directly to the polymer backbone. This agrees with the experimental results.

The molecular models of the polymers also clarify the experimental measurements. For polymer (**1**), the coumarin moiety, which is fixed directly to the polymethacrylate mainchain, enforces a helical arrangement of the backbone and an almost fixed distribution of the coumarin chromophores around it. However, the presence of the flexible spacer (containing six methylene units) in the polymers (**2** and **3**) decouples the aliphatic backbone from the aromatic side-chain of benzoate and coumarin moieties and allows a degree of internal phase separation. This permits coumarin chromophores of neighbouring polymers to overlap more easily in areas of high chromophore concentration. This generates more active reaction sites and results in smaller alignment thresholds than that observed for (**1**).

The threshold fluence for alignment of (**2**), the derivative of 6-hydroxycoumarin, is less than half that for (**3**), the 7-hydroxycoumarin derivative. This suggest a greater probability of photochemical reaction for the former especially since its absorption at 300 nm is less than of the latter. This can be explained by examining their molecular configurations: the more linear sidechain (**2**) would be more easily polarised than (**3**).

SYNTHESIS

The polymer derivative (**1**)[13] of 7-hydroxycoumarin without a spacer was prepared by esterification of commercially available 7-hydroxycoumarin with methacrylic acid (2-methyl acrylic acid) using DCC and DMAP[14] to yield the methacrylic acid 2-oxo-2H-1-benzopyran-7-yl ester, which was polymerised radically using ACCN to form the required polymer (poly[1-methyl-1-(2-oxo-2H-1-benzopyran-7-yloxycarbonyl)]ethene **1**). The polymer was purified by repeated precipitation into methanol from solution in *N,N*-dimethylformamide until no more monomer or oligomers could be observed by thin layer chromatography. The polymer derivatives of 6-hydroxycoumarin and 7-hydroxycoumarin (**2** and **3**) were prepared following the general synthetic pathway depicted in the reaction scheme. Firstly ethyl 4-hydroxybenzoate was alkylated with 6-bromohexanol in a Williamson ether synthesis reaction. Saponification of the ester with potassium hydroxide followed by acidification yielded the 4-(6-hydroxyhexyloxy)benzoic acid, which was esterified with methacrylic acid using PTS under azeotropic conditions to yield 4-(6-[2-methyl-acryloyloxy]hexyloxy)]benzoic acid. This was in turn esterified either with 6-hydroxycoumarin or 7-hydroxycoumarin using DCC and DMAP[14] to yield the desired monomers, which were polymerised and purified as above to yield the required polymers (poly[1-methyl-1-(6-[4-(2-oxo-2H-1-benzopyran-6-yloxycarbonyl)phenoxy]hexyloxycarbonyl)]ethene (**2**) and poly[1-methyl-1-(6-[4-(2-oxo-2H-1-benzopyran-7-yloxycarbonyl)phenoxy]hexyloxycarbonyl)]ethene (**3**)[13], respectively). The 6-hydroxycoumarin was prepared according to a literature method[15] from commercially available 2,5-dihydroxybenzaldehyde as shown in the reaction scheme. The purity and dispersity of the polymers was established using GPC and DSC.



(2)

(3)

(i) K_2CO_3, $C_2H_5COCH_3$
(ii) a) KOH, CH_3OH b) H^+
(iii) PTS, $CHCl_3$
(iv) $(C_6H_5)_3P{=}CHCO_2C_2H_5$, $(C_2H_5)_2NC_6H_5$
(v) DCC, DMAP, CH2Cl2
(vi) ACCN, DMF

CONCLUSIONS

Polymethacrylate derivatives of 6- and 7- hydroxycoumarin are studied as alignment layers for liquid crystals using linearly polarised light to induce an anisotropy. The azimuthal anchoring is strong and low alignment thresholds are found when flexible spacers are incorporated into the coumarin backbone. The liquid crystal azimuthal alignment direction changes sharply with exposure time from parallel to perpendicular with respect to the polarisation direction of the incident light. A model is presented to explain these changes in terms of the anisotropies of the unreacted and dimerised sidechains.

Acknowledgements

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