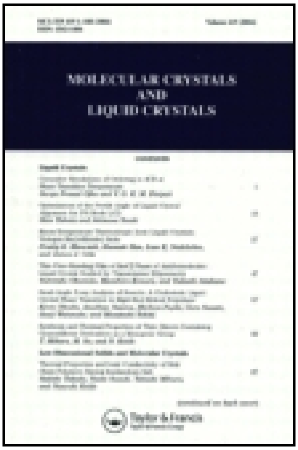

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NON-CONVENTIONAL ALIGNMENT SURFACES FOR ANTIFERROELECTRIC LIQUID CRYSTALS

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Antiferroelectric liquid crystals (AFLC) feature interesting properties for a number of photonic applications. However, alignment of planar structures of these materials using conventional alignment layers is not satisfactory.

One of the main problems dealing with these materials is the limited alignment obtained with standard manufacturing procedures, and the contrast decrease in multiplexed devices derived from the presence of pretransitional effect.

The influence of alignment layers on AFLC contrast and switching has been studied. Using different alignment materials or manufacturing processes, it is possible to obtain different threshold voltage, dynamic range, and time response for the same material.

We have studied the influence of alignment in two kinds of AFLC materials, namely regular tristate AFLCs and orthoconic AFLCs. Regular tristate materials feature long pitch and relative small cone angle. Contrast is not very good, but dynamic switching properties are excellent. Orthoconic materials are short pitch, wide cone angle (90°) materials. Contrast is excellent (200–300), but dynamic behavior is below regular materials.

Keywords: alignment layer; antiferroelectric liquid crystal; crosslinking; nylon; polyimide

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INTRODUCTION

Polyimides are customarily used as aligning layers for nematic liquid crystals. Polyimides give also good orienting layers in the case of ferroelectric liquid crystal mixtures showing the cooling phase transition sequence:

isotropic phase → *nematic* → *smectic A* → *chiral smectic C phase*.

Antiferroelectric liquid crystal mixtures usually lack the nematic phase within the phase sequence, which is reduced to:

isotropic phase → *smectic A* → *chiral smectic C* → *chiral smectic CA*.

Such mixtures are not efficiently oriented by standard rubbed polyimides used for nematics or ferroelectrics [1]. In the absence of a nematic phase in the sequence, formation of a bookshelf geometry maintained upon cooling down becomes marred [2]. This effect has been attributed to the misalignment of the smectic layer normal in the plane of the display [3] and to the presence of certain types of ions leading to interactions between the liquid crystal and the alignment layer [4]. The use of skew rather than parallel rubbed surfaces has been proposed to alleviate this problem [5], however the dynamic contrast on passive multiplexing driving is still reduced by light leakage in the dark state. The above notwithstanding, some special polyimides have been recently employed in AFLC alignment [6].

Polyamides such as Nylon 6 (polycaprolactame) are, according to our experience, the best alternative to polyimides for AFLC alignment. The aligning properties of nylons are well known for many years; indeed, they were used for nematic LCs before aligning polyimides were developed. Polyimides are currently preferred for several reasons related to solvent handling upon manufacturing, and long-term degradation of orienting properties of nylon. This degradation can be avoided by modifying the nylon surface through crosslinking, or trapping nylon chains in two dimensional networks formed by polydiacrylates. The network can be made a self-oriented layer using monomers which show a nematic LC phase. Alternatively, the nylon solution can be doped with a liquid crystal before preparing the surface. This liquid crystal can even be a component of the AFLC mixture that is to be aligned.

A study of the alignment properties of several modified nylons has been carried out. The results have been compared to AFLC alignments obtained with a number of experimental polyimides. The study has been extended to regular and orthoconic AFLCs. Alignment of orthoconics proved to be specially difficult for their short pitch.

EXPERIMENTAL

Several polyamides and polyimides with different chemical structures were used as the alignment layers in thin homogeneous cells. 1 cm^2 planar cells with ITO-coated glasses were prepared. The LC thickness was 1.5 μm, thin enough to achieve surface stabilization conditions. Cells were filled with two different AFLC materials, the orthoconic antiferroelectric material (AFLC45) mixture W-182, and a regular commercial AFLC material CS-4001 (Chisso).

Some nylons were tested in preliminary experiments: Nylon-6, Nylon-6,6, and Nylon-6,10. No relevant differences were found between them; therefore, only one (Nylon-6) was used. The solubility of Nylon-6 was investigated in different solvents. Two solvents have been used for the experiments: trifluoroethanol and trichloroethanol. Nylon 6 solubility in trifluoroethanol is excellent and the solution is significantly less viscous than trichloroethanol solution. 10 wt% solutions in trifluoroethanol were prepared by placing the Nylon 6 in the solvent during two days at room temperature. Polyimides were solved in DMF.

Alignment layers of both, polyimides and polyamides, were deposited by spin-coating, and homogenous alignment was induced by rubbing the surfaces unidirectionally.

NYLON MODIFICATIONS

Crosslinking of Nylon with Copper Acetate

Nylon in 1 wt% solution in trifluoroethanol or trichloroethanol were mixed in the same proportion with saturated $(CH_3COO)_2Cu$ solution. After spinning the samples were dried at 90°C and thermal cured 1 h at 150°C. Alternative methods of crosslinking nylon surface with copper, consisted on deposition of nylon layer from its 1 wt% solution. The glass covered with Nylon 6 layer was then kept for 24 h in 1% water solution of $(CH_3COO)_2Cu$ then watered and dried.

Crosslinking of Nylon with Diisocyanate

Hexane diisocyanate of the formula:

$$O{=}C{=}N-(CH2)6-N{=}C{=}O$$

was used as crosslinking agent. This compound is very reactive avoiding the use of the above mentioned solvents (CF_3CH_2OH, CCl_3CH_2OH).

No nylon solvent inert for diisocyanate was found. Therefore the nylon layer was spinned in the usual way and then the layer was treated with 1 wt% of tetrahydrofurane solution of diisocyanate by spinning. The solvent was evaporated at 60°C and glass covered with nylon and diisocyanate was heated 1 h at 150°C. Substrates treated at this way were difficult to manage for mounting process.

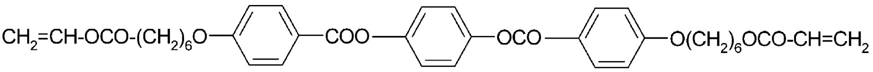
Crosslinking of Nylon with Diepoxides

An aryl diepoxide (bis(4-glycidyloxyphenyl)methane) and an aliphatic diepoxide (1,4-butandioldiglicidylether) were chosen as crosslinking agents. The mole ratio of epoxide to active Nylon-6 group was 1:9. The polymer layer was prepared in the following way:

First diepoxide (bis(4-glycidyloxyphenyl)methane) (0.02 g) was solved in 9 cm^3 CF_3CH_2OH and then mixed with 1 ml of 10 wt% nylon solution in CF_3CH_2OH. This solution was spinned on glass plates. Solvent was evaporated at 75°C during 1 h and crosslinking was done by heating 1 h at 150°C. A similar process was used for the second diepoxide.

Thermally Polymerized Diacrylate

Diacrylate of formula



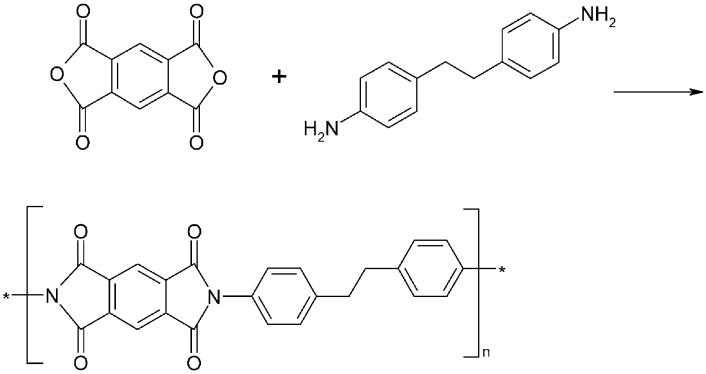
was prepared and tested as orienting layer in pure form and in the mixture with Nylon 6 or polyimide MP-9. This compound is a nematic liquid crystal having phase transitions: Cr 108.1–109.1 N 339–346 Iso. It polymerizes when heated above 100°C and forms a polymeric glass. The diacrylate was used to prepare three types of aligning layers:

a. Diester diacrylate was solved in DMF at 50°C in amount to obtain 1 wt% solution. The glass plates were covered by normal spinning procedure and then the plates were heated 0.5 h at 100°C and next for 0.5 h at 150°C.
b. Diacrylate was mixed with Nylon 6 in mole ratio 1:9. 0.053 g diacrylate was dissolved in 9 ml of CF_3CH_2OH at 50°C and then 1 ml of 10 wt% Nylon-6 was added. The layers were prepared on glass in the same way as in the case of nylon modification by diepoxide.
c. Diacrylate was mixed with Nylon 6 in mole ratio 9:1. 0.53 g diacrylate was dissolved in 9.9 ml of CF_3CH_2OH at 50°C and then 0.1 ml of 10 wt% Nylon 6 was added.

POLYIMIDES

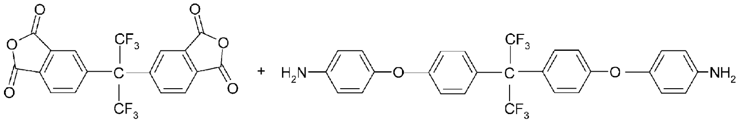
Several types of polyimide prepolymers of different chemical structures were prepared in cooperation with Technical University of Radom (Poland). Polyimides are obtained by reaction between dianhydrydes and diamines as follows:

MK 4

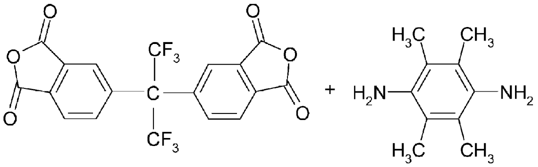


The following dianhydryde and diamines were used for preparation of other polyimides:

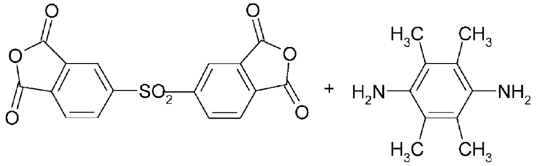
AW-16



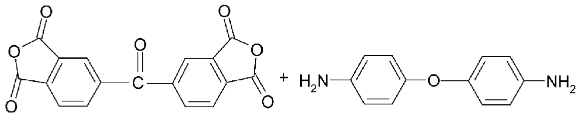
DWK-2



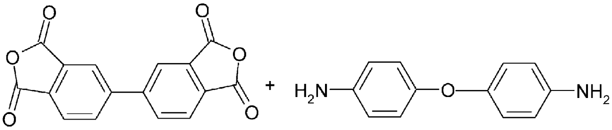
DWK-4



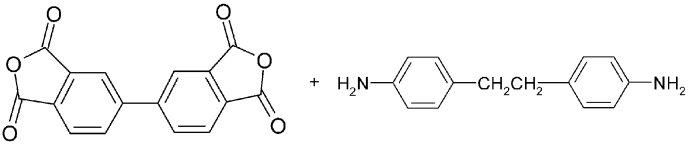
DWK-9



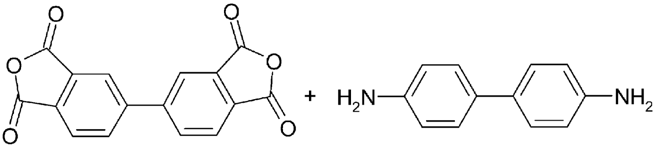
MP-2



MP-9



MW-1



AW-16 and DWK-2 contain CF_3 groups in polymer unit, DWK-4 and DWK-9 contain SO_2 or CO group in polymer unit between benzene rings and MP-2, MP-9, MW-1 are derivatives of biphenyldicarboxylic anhydride and 4-aminofenyloxyaniline or 4(4-aminophenylethyl)aniline or 4-(4-aminophenyl)aniline.

The prepared prepolymers were dissolved in DMF (0.7 wt%). The solution was used for spinning polymeric layers on glass and then the glass plates were heated 1 h at 145–150°C and 3 h at 180°C.

RESULTS

Contrast and Textures

Best alignment textures were obtained with Nylon-6 or fluorinated Nylon-6. The orthoconic material showed better contrast because of its 90° cone angle (sometimes higher than 200:1), but switching voltage ranges were

TABLE 1 Characterization of Alignment Surfaces with Two AFLCs

				Contrast ratio	Response time (µs)	Vth	Dynamic range (V)
Polyamides	Trifluoroethanol	W-182	Nylon	98	58	20	11.02
			Fluorinated Nylon	96	38	14	4.51
			Nylon + Cu	179	81	14	13.75
			Nylon + Aryl Epox.	100	24	21	16.59
		CS-4001	Nylon	31	11	15	12.63
			Fluorinated Nylon	27	20	10	3.70
			Nylon + Cu	40	22	14	8.48
			Nylon + Aryl Epox.	10	18	15.5	9.82
			Nylon + Aliphatic Epox.	13	20	17	17.55
	Trichloroethanol	W-182	Nylon	136	80	14	3.71
			Nylon + Cu	59	120	15	7.67
			Nylon + LC + Cu	75	52	15	4.27
		CS-4001	Nylon	76	17	9	3.32
			Nylon + Cu	22	19	13.6	6.42
Polyimides	DMF	W-182	DWK-9	45	24	13	2.27
			MP-2	134	44	13	5.85
		CS-4001	DWK-9	15	19	13	4.27
			MP-2	18	19	14	4.41
			MP-9	23	25.5	13.5	4.25
			MP-9 + Ester	9	36	13	5.90
			MK-4	15	27	13.5	4.44
			MW-1	8	25.5	13.5	4.25

wider and dynamic response was slower. Contrast in regular materials was lower but dynamic properties were acceptable in most cases.

Polyimides MP-9, MP-2 and MK-4 best aligned the regular AFLCs. MP-2 was best for orthoconic W-182. MP-9 modified with LC ester did not show any improvement. As a rule, contrast were higher in modified nylons.

Dynamic Response and Crosslinking

The response of orthoconic materials aligned either with polyimides or nylons was very slow. Additionally, most of them showed a memory effect by which the gray level obtained in a frame depends on the gray level of the previous frame. This effect was only removed when the frame rate was substantially reduced. Consequently, these orthoconic materials can only be used in applications where the refreshing rate is low. In these conditions, orthoconic AFLCs show excellent contrast ratio.

Copper cross-linking of Nylon improved contrast in some instances, but switching voltages and response times increased in most cases. Experiments with LC Ester produce focal-conic textures.

Cross-linking polyamides with diisocyanate produces very strong anchoring (high switching voltages); however, the manufacturing process became jeopardized by interaction of this material with the cell sealing gasket.

Cross-linking polyamides with aryl epoxide and aliphatic epoxide produces strong anchoring conditions.

A summary of results is presented in Table 1. Some alignment surfaces that did not give acceptable results have not been included.

CONCLUSIONS

The alignment properties of some modified surfaces on AFLCs have been studied to avoid long term degradation of nylon alignment layers. Crosslinking of nylon has been successfully obtained with copper acetate and diepoxides. The latter is useful for adjusting dynamic properties of the LC upon manufacturing. A number of polyimides have achieve AFLC orientation as well. Some of them show properties close to nylon surfaces. Polyimides, along with nylon crosslinkings, can therefore be an interesting alternative to nylon layers.

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