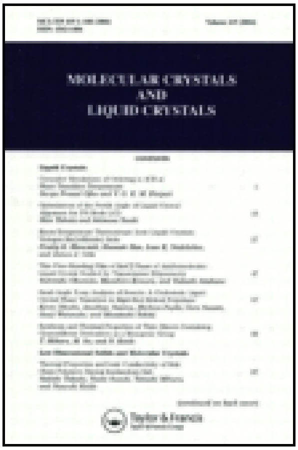

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Influence of Chain Stiffness and Preparation Methods on the Efficiency of Polyimide Alignment Layers for Liquid Crystal Orientation

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Influence of Chain Stiffness and Preparation Methods on the Efficiency of Polyimide Alignment Layers for Liquid Crystal Orientation

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In this work the influences of chain stiffness, solution concentration, and preparation methods on the formation and efficiency of highly oriented polyimide alignment layers are investigated. To quantify the performance of the alignment layers in liquid-crystalline (LC) cells, the orientation of a calamitic bis-azo dye in a low-molecular-weight nematic LC guest–host mixture was employed. The degree of orientation was quantified by measuring the dichroic ratio (DR_{UV}) of the dye with polarized UV spectroscopy. Alignment layers were prepared from precursors of polyimide polymers with different chain stiffnesses. Additionally, the effect of polymer solution concentration, denoted as low (approx. 2 wt%) and high (50 wt%), and orientation techniques (casting and shearing) were systematically investigated. Cells assembled with buffed polyimide alignment layers originating from 1.5 wt% solutions in N-methyl-2-pyrrolidone (NMP) of a rigid para-linked poly(amic ethyl ester) precursor polymer resulted in a very high DR_{UV} of 15. This value can be compared to values obtained with commercially available flexible polyimide layers, which had a DR_{UV} of only 8. Pretilt angles of selected cells were also measured and were found to be in the range of 0.7 to 5.1°.

Keywords: buffing; dichroic ratio; liquid-crystalline cell; polyimide alignment layers; shear orientation

INTRODUCTION

Full-color liquid-crystalline displays (LCDs) are commonly used in computer monitors, televisions, and mobile phones and are

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commodities for daily life in industrial societies. With the help of LCDs, it is possible to display information in small dimensions based on a relatively simple design [1–3]. LCDs can be realized by using guest–host systems in which a dye, the guest, is mixed with a low-molecular liquid crystal (LC) as host. As a function of the applied voltage on the cell, the molecular orientation of the guest–host mixture and hence the color of the LC cell are changed. These cells show improved color contrast, high brightness, and wide viewing angles [4]. Color contrast and brightness depend mainly on the achieved dichroic ratio (DR) of the used dyes. The DR of a particular dye can be calculated by the ratio of polarized UV-vis absorption parallel and perpendicular to the orientation direction. To improve the DR, research was mainly focused on the modification of dyes, and as a result, often mono-, bis-, and tris-azo dyes were chosen because they are distinct by high order parameters [5–8]. The DR can be correlated to the aspect ratio of the investigated dye molecule, and the DR is higher for dyes with a rigid molecular structure [4].

Polyimide (PI) layers that have been surface oriented by a buffing process are widely used as alignment layers for LCDs [9,10]. In this process, the surface of an alignment layer is buffed unidirectional with a velvet cloth. The DR of guest–host cells is directly governed by the alignment layer used in the LC cell. LC molecules on buffed PI films are, on average, aligned parallel to the buffing direction with a defined tilt angle. This so-called pretilt angle is the angle between LC director and alignment layer surface [10]. The pretilt angle is directly influenced by the inclination angle of the polymer backbone structure, which is oriented along the buffing direction and inclined up from the film surface [10–12]. Thus the pretilt angle is determined by LC anchoring, a complex interplay of steric repulsions and electronic interactions [13,14]. For buffed aromatic PI alignment layers, the pretilt angle is typically below 5° [14].

In this article, we study the influence on the DR of a guest dye in LC cells by varying several parameters forming the PI alignment layer. These parameters are chain stiffness and solution concentration of the PI precursor polymers employed, as well as different layer-aligning methods, such as surface orientation by buffing or bulk shear orientation. To quantify the orientation efficiency of PI alignment layers in LC cells, a nematic dye-containing guest–host mixture was chosen that consists of 0.5 wt% **I** as guest and **II** as host (Fig. 1).

This particular bis-azo dye **II** features a high aspect ratio with an absorption maximum at 390 nm [15]. To quantify the performance of various alignment layers, LC cells were fabricated using these layers, and the degree of orientation is proportional to the DR_{UV} determined at 390 nm using polarized UV-vis spectroscopy.

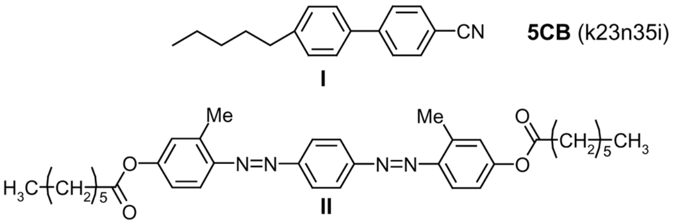


FIGURE 1 LC guest–host mixture consisting of 0.5 wt% of bis-1,4-[4-(4-((4-hexyl-benzoyl)oxy)-2-methyl-phenylazo)]benzene **II** [15] and 4-pentyl-4′-cyano-biphenyl **I** (5CB) was used in this work.

EXPERIMENTAL

Materials

The nematic LC 4-pentyl-4′-cyano-biphenyl **I** (5CB, k23n35i) was supplied by Merck® Darmstadt. Synthesis and properties of bis-l,4-[4-(4-((4-hexyl-benzoyl)oxy)-2-methyl-phenylazo)]benzol **II** are published elsewhere [15]. Poly(amic ethyl ester)s (PAE) **1** and **2** were synthesized according to a previously published procedure [16]. Merck Liquicoat® ZLI-2650 was provided as kit consisting of the precursor Liquicoat® PI-resin (polyamic ester, see Table 1) and Liquicoat® thinner (cyclopentanone) as solvent [17]. All other solvents and starting materials were purchased from Aldrich, Fluka, Lancaster, or Merck and used as received.

Preparation of Alignment Layers by Buffing

Commercial buffing machine LCBM6 (Optron Systems Inc.) with a translating substrate holder, a vacuum chuck, and a rotating roller (d = 70 mm) covered with a velvet cloth was used. The roller-to-stage distance was adjusted by two micrometer set screws. The buffing process was carried out at room temperature (RT), the revolution of the roller was 600 rpm, the pile impression was 0.2 mm, and the substrate was moved in one continuous motion at 1 mm/s. Only two-thirds of each substrate was buffed to create a reference sector (one-third of the substrate) with no buffing treatment.

For preparation of the precursor alignment layers, glass substrates (76 × 26 mm) were coated by a doctor-blading technique. First, substrates were cleaned successively in chloroform and isopropyl alcohol for 10 min in an ultrasonic bath, kept in methyl ethyl ketone steam for about 3 h, and then dried under vacuum at 50°C. A 2 wt% solution of the precursor ZLI 2650 Liquicoat® PI-resin in Liquicoat® thinner and 1.5 wt% solutions of PAE **1** and **2** in NMP were prepared. The solutions were filtered using a 0.45 μm and then a 0.2 μm poly(tetrafluoroethylene) (PTFE) filter. The precleaned glass substrates were heated to 70°C, and the solutions were cast using a 5-μm blade. The layer was soft-baked for 20 min at 70°C, and 1 h at 100°C.

PI alignment layers were obtained from the soft-baked precursor layers by thermal imidization. This curing process was carried out under a N_2 atmosphere using a custom-made hot stage equipped with an Eurotherm 903P controller. A temperature program at 100°C, 200°C, and 300°C with dwell times of 1 h and ramping rates of 10 K/min was used.

Preparation of Alignment Layers by the Shearing Technique

PAE **1** and **2** were dissolved at 10 wt% in NMP at RT and slowly concentrated at 100°C up to 50 wt%. In an analogous manner, 50 wt% solutions of ZLI 2650 in Liquicoat® thinner were prepared. The shearing process was performed with a Tribotrak® machine from DACA Instruments; this technique is described in detail elsewhere [18]. The 50 wt% solutions were sheared with a velocity of 25 mm/s onto a cleaned substrate at 100°C with a sequence of four small 1.5-mm glass rods. Each sample was covered with a glass plate during the shearing process to control the NMP evaporation. The force on the glass rods was applied by a weight of 10 kg. After shearing, the PAE layers were soft-baked at 100°C for 1 h and, if needed, additionally thermally imidized as described previously.

LC Cell Preparation

Each glass substrate covered with alignment layers was cut in half, assembled antiparallel, and fixed with superglue on three edges. The cell gap was adjusted using commercially available thin metal precision wires of 8.3, 12.5, 14, and 19 μm in diameter as spacers. The assembled cells were filled with the isotropic LC mixture at 40°C through the open edge of the cell solely by capillary forces.

Determination of the Dichroic Ratio (DR_{UV})

UV-vis absorption spectra were acquired using a Hitachi U-3000 spectrometer. Polarized absorption spectra were measured on quartz substrates, placing one Glan-Taylor parallel-oriented polarizer in the sample optical path and one in the reference path. To measure parallel and perpendicular absorption spectra, two baselines for each cell containing a particular aligning surface were first recorded by rotating the polarizers 90° but not the samples. Then the sample was replaced by a cell with a 5CB/azo dye mixture, and parallel and perpendicular absorption spectra were recorded. The DRs were calculated at 390 nm by the ratio of the parallel to perpendicular bis-azo dye absorption. To verify the reproducibility of the DR, three identical cells of each alignment layer were built and the DRs averaged; the DR varied at most by ±1. Polarized light optical microscopy was performed on a Leitz Laborlux 12-Pol equipped with a WILD Photoautomat MPS45 and a WILD MPS51 camera setup.

Molecular Modeling

A RMMC (RIS Metropolis Monte Carlo method) module within the Cerius^2 4.6 molecular modeling software was used to calculate the persistence length q of the polymer-chains. The polymer-consistent force field (PCFF) was used for minimizing the monomers and for RMMC calculations. Electrostatic interactions were simulated by a dielectric constant of three. During calculation, 100,000 steps were used in the equilibrium part and 500,000 steps in the production part of the RMMC simulation. A tenfold number of steps did not result in significant changes in persistence length. The *MaxBond* cutoff was set to six. The polymers were built by the random polymer builder with enough repeating units to result in a molecular weight of about 30,000. The reported q values reflect the mean value of the projected end-to-end distance of all backbone bonds by using the RMMC module <a2> output.

Pretilt Angle and Cell-Gap Measurements

The pretilt angle and cell-gap measurements were performed by autronic-MELCHERS GmbH from Karlsruhe (Germany) with the TBA-110^{TM}. In this testing setup, the test cell is rotated in a linearly polarized laser beam, and the intensity of the light transmitted by the analyzer is recorded as a function of the angle of light incidence. The extraordinary and ordinary refractive indices were set to $n_e = 1.7264$ and $n_o = 1.5334$, respectively [19].

RESULTS AND DISCUSSION

Basic Concepts

PI alignment layers are typically prepared from precursor solutions of poly(amic acid)s or PAEs, which are thermally imidized to polyimide layers and finally surface oriented by buffing [13,14,20]. To systematically study the effect of several experimental and structural parameters on the performance of alignment layers, these layers were incorporated in standardized LC guest–host cells, and the DR served as layer performance indicator. In more detail, the alignment layers were prepared starting from research-level polyimide precursor polymers that possess different chain stiffness (rod-like and semiflexible) but that render after imidization the same rigid-rod PI. These materials were compared to a commercially available alignment layer kit consisting of flexible polymers. Furthermore, layers cast from low-concentration solutions (about 2 wt%) were compared to sheared layers obtained from highly concentrated 50 wt% solutions. Additionally, these layers can be oriented by different processes (e.g., conventional buffing for surface orientation or intrinsically bulk oriented by shear forces).

Figure 2 portrays the nature of the final alignment layer on the basis of chain flexibility and sequence of processing steps. In the first pathway, the PI alignment layer is cast from low-concentration precursor solutions (Fig. 2, top). Then a buffing process achieves a surface orientation; this step can be performed before or after imidization. In the second pathway, highly concentrated precursor solutions (Fig. 2, bottom) can be sheared, and a bulk orientation of the layer is achieved, which can be also investigated in LC cells before and after imidization. Additionally, the highly concentrated solutions can be isotropic or lyotropic, depending on the chain stiffness of the precursor polymer, thus introducing another parameter.

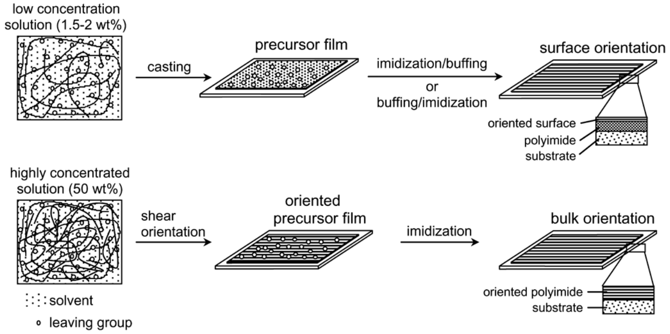
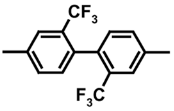
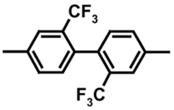
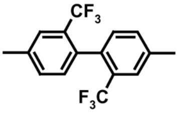
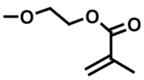
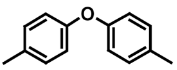
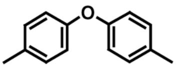


FIGURE 2 Sketch of two different pathways for the preparation of polyimide alignment layers by starting either with a low-concentration precursor solution and subsequently buffing (top) or shearing a highly concentrated solution for bulk orientation (bottom).

To parameterize the chain stiffness of the investigated PAEs and PIs, the persistence length might serve as a key indicator. The persistence length *q* is generally defined [21] as the average projection of the end-to-end distance of an infinite chain in the direction of the first segment along the chain backbone and is experimentally accessible by light-scattering measurements. In this work, *q* was calculated for each polymer structure by molecular modeling [22], and the results are included in Table 1. For the extended, rigid PAE **1** consisting of para-linked aramid and rod-like, noncoplanar diamine units, a *q* of 11.8 nm was computed. This value can be compared to 3.8 nm obtained for the

TABLE 1 Precursor Polymers and Polyimides Investigated in This Work

1,2 3

Polymer	Configuration	−R	−Ar−	η(dL/g)[a]	q[b](nm)
PAE **1**	para	−Et		1.86	11.8
PAE **2**	meta	−Et		0.66	3.8
PI **3**	n/a	n/a		n/a	43.1
ZLI 2650[c] (precursor)	Mixture para/meta			Unknown	0.5
ZLI 2650[d] (polyimide)	n/a	n/a		n/a	2.1

[a] 0.5 g/dL in NMP at 30°C.

[b] Computed persistence length *q* is a parameter proportional to the overall chain stiffness.

[c] Merck Liquicoat® PI-Kit ZLI-2650 is provided as a kit consisting of the precursor Liquicoat® PI-Resin and Liquicoat® thinner (mainly cyclopentanone) as solvent [17].

[d] Structurally identical to Kapton®.

semiflexible PAE **2** with a metalinked aramid unit using the same diamine [16]. For the commercially available Pi-Kit ZLI 2650 from Merck® [17,23] with a much more flexible polymer backbone, a short persistence length of 0.5 nm was calculated. Even though these calculated persistence lengths might not quantitatively match experimental data, they reflect a clear trend in chain flexibility of the investigated polymers.

Dichroic Ratio as a Function of LC Cell Gap

To exclude a cell-gap dependence of DR_{UV} within the investigated range, four LC cells were built with spacer diameters of 8.3, 12.5, 14, and 19 µm each, as described in the Experimental section. The alignment layers were prepared by casting a 2 wt% solution ZLI 2650 in Liquicoat® thinner, imidized, and buffed. Figure 3 shows the polarized UV-vis spectra and lists the calculated DR_{UV} at 390 nm for spacer diameters in the range of 8 to 19 µm.

The averaged DR_{UV} of 8.8 ± 0.3 for all four measurements, irrespective of the spacer diameter, demonstrates that the degree of orientation does not depend on the cell gap in the investigated range. This result is in accordance with published data, where the degree

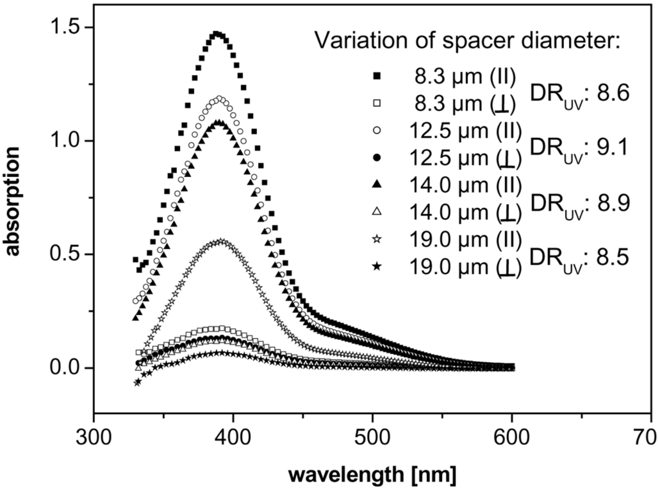


FIGURE 3 Dependence of the dichroic ratio (DR_{UV}) at 390 nm as a function of the spacer diameter in LC cells. Alignment layers were prepared by casting the commercial polymide precursor ZLI 2560 at 2 wt%, imidizing, and buffing. Shown are the polarized UV-vis spectra and the calculated DR_{UV} at four spacer diameters ranging from 8 to 19 µm.

of LC orientation is measured by the variation of birefringence, and a clear increase is observed only for thin cells with a gap of less than 2 μm [24]. All other LC cells in this work were assembled with copper wires of 14 μm in diameter as spacers.

Buffed Polyimide Alignment Layers Prepared from Low-Concentration Solutions

At low concentrations of 1.5–2 wt%, PAEs **1** and **2** form isotropic solutions in NMP; the same holds true for ZLI 2650 in Liquicoat® thinner (cyclopentanone). These dilute solutions were doctor-bladed to precursor films, which then were subjected to different methods of producing alignment layers, indicated in Table 2 by method A, B, C, or D. Precursor polymer (A) and the resulting PI films (B, C) were aligned by buffing, revealing the influence of imidization. Films in method B were oriented as precursor and then imidized, whereas method C uses presursor films without any surface orientation; only the imidized film was buffed. Furthermore, the buffed precursor films were imidized and the DR_{UV} determined without B and with an additional buffing step D. In Table 2, all measured DR_{UV}s are summarized as a function of the orientation method.

For cells with buffed alignment layers of the rigid PAE **1** and semiflexible **2** (method A), a DR_{UV} of 8 was determined, and imidization did

TABLE 2 Dichroic Ratios (DR_{UV}) of Bis-azo-dye **II** in LC Cells (d = 14 μm) at 390 nm

Polymer	Chain stiffness	Conc. wt% in	DR_{UV}			D $PAE_{buff.}$ + $PI_{buff.}$[d]
			A $PAE_{buff.}$[a]	B $PAE_{buff.} \rightarrow PI$[b]	C $PI_{buff.}$[c]	
PAE **1**	Rigid	1.5 NMP	8	—	—	—
PI **3**			—	7	15	12
PAE **2**	Semiflexible	1.5 NMP	8	—	—	—
PI **3**			—	8	9	10
ZLI 2650	Very flexible	2.0 LQT[e]	7	—	—	—
Imidized			—	7	8	8

Note: The investigated alignment layers were obtained with different alignment procedures A–D prepared with low-concentration precursor solutions and surface oriented by buffing.

[a] Precursor film was oriented by buffing.

[b] Precursor film was oriented by buffing and then imidized.

[c] Only the polyimide film was surface oriented by buffing.

[d] Precursor film was oriented by buffing, then imidized, and additionally buffed.

[e] LQT: Liquicoat® thinner (cyclopentanone).

not alter the degree of orientation. After imidization and buffing (C), the rigid-rod PI **3** showed an almost twofold increase in DR_{UV} (15) when starting with **1**, but an almost unchanged value of 9 when starting with the semiflexible PAE **2**. For the very flexible commercial product ZLI 2650, only a small difference in DR_{UV} (7) for the buffed precursor and its imidized polyimide ($DR_{UV} = 7$–8) was found. Evidently, the DR_{UV} values using methods A and B are comparable, indicating that the achieved alignment of the precursors is maintained during thermal imidization and is independent of chain stiffness. However, there is a distinct increase in degree of orientation using PI alignment layers originating from rigid PAE **1** solutions, rendering very efficient alignment layers. Buffing the layer twice (D), meaning first the precursor and then the resulting PI again parallel to the first buffing direction, reveals no change in the measured DR_{UV}s for ZLI 2650 ($DR_{UV} = 8$), a slight increase for the semiflexible PAE **2** (9 to 10), and a lower value for the rigid PAE **1** (12 instead of 15). This suggests that kinks and entanglements of polymers with a flexible backbone impede molecular orientation, which can be compensated by buffing the precursor polymer and additionally the corresponding PI. Consequently, it is of advantage to maximize the chain stiffness of the precursor polymer for PI alignment layers to achieve the highest degree of LC orientation.

To image the quality of the LC alignment layers, the substrates were placed in a polarized light microscope in such a way that the aligned regions could be compared to the unoriented reference polymer layer (Fig. 4). The images parallel to the polarizer are exposed for longer times to visualize possible defects in the layer.

The images in Figure 4 show intense monodomain birefringence at a buffing direction angle of 45° to the polarizer (left image, right upper corner) and no birefringence at an orientation of the LC cell director parallel to the polarizer (right image, right half, black). Buffing the layers twice resulted in some bright spots, indicating defects (not shown); thus the

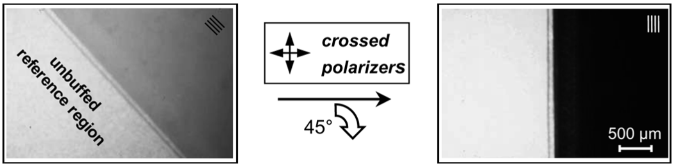


FIGURE 4 Polarized light microscopy of an LC cell. PI **3** obtained from PAE **1** served as alignment layer, which was aligned by buffing after imidization (method C) (d = 14 μm, LC: 5CB **I** with 0.5 wt% bis-azo dye **II**, layer PI **3** from PAE **1**, method C).

polyimide alignment layers were apparently damaged by the additional buffing step. On unoriented PI layers, only multidomains can be observed as bright grainy areas (left image, lower left corner, and right image, left half). Thus the DR listed in Table 2 and the images in Figure 4 demonstrate that buffing the rigid-rod PI **3** prepared from the low-concentration rigid PAE **1** solution results in a very efficient alignment layer for cells with a high degree of LC orientation.

PI Alignment Layers Prepared by Shearing Highly Concentrated Solutions

Bulk-oriented alignment layers were prepared from 50 wt% solutions of rigid PAE **1** and semiflexible PAE **2** in NMP, and ZLI 2650 in Liquicoat® thinner by the shearing technique (see Fig. 2) [18]. Additionally, at such a high concentration, PAE **1** forms a lyotropic solution [16], whereas PAE **2** and ZLI 2650 form highly viscous isotropic solutions. Consequently, bulk-oriented alignment layers prepared by shear were also used to fabricate LC cells before (Table 3, method E) and after imidization (F); the DR_{UV} was determined as described previously.

With shear-oriented alignment layers obtained from lyotropic solutions of PAE **1**, a DR_{UV} of 8 was determined before (E) and after imidization (F). Thus the achieved orientation is comparable to LC cells prepared with commercial PI alignment layers and buffing (Table 2, ZLI 2650, method C). These results indicate that the shearing technique is a suitable alternative method for the preparation of efficient PI alignment layers compared to the established buffing process of

TABLE 3 Dichroic Ratios (DR_{UV}) at 390 nm of Bis-azo-dye **II** in LC Cells ($d = 14\,\mu m$) Obtained with Bulk-Oriented Alignment Layers Prepared by Shearing 50 wt% Precursor Solutions

			DR_{UV}	
Polymer	Chain stiffness	50 wt%	E PAE_{shear}[a]	F $PAE_{shear} \rightarrow PI$[b]
PAE **1**	Rigid	Lyotropic solution in NMP	8	—
PI **3**			—	8
PAE **2**	Semiflexible	Isotropic solution in NMP	6	—
PI **3**			—	7
ZLI 2650	Very flexible	Isotropic solution in LQT[c]	2	—
Imidized			—	2

[a] Precursor alignment layer fabricated by shearing a 50 wt% solution.
[b] Same as (E), then imidized.
[c] LQT: Liquicoat® thinner (cyclopentanone).

cast solutions. However, for layers prepared by shearing a 50 wt% isotropic solution of the semiflexible PAE **2** in NMP, the DR_{UV} is reduced to 6 and 7 for the precursor polymer and the corresponding PI, respectively. Furthermore, alignment layers originated from shearing a 50 wt% isotropic solution of ZLI 2650 in Liquicoat® thinner reveal a very small DR_{UV} of 2 (Table 3, E), which is unchanged by imidization (F). Therefore, lyotropic solutions of the rigid PAE **1** form the most effective sheared bulk-oriented PI alignment layers. For sheared isotropic solutions, the orientation efficiency decreases proportional to the main chain flexibility of PI precursors used (i.e., from the semiflexible PAE **2** to the very flexible ZLI 2650).

In Figure 5, an LC cell with a bulk-oriented PI alignment layer of PI **3**, prepared by shearing a 50 wt% lyotropic solution of PAE **1**, is imaged in polarized light. A monodomain is visible, indicated by a homogeneous dark-grey area without defects (left image, upper right corner, shearing direction positioned 45° to polarizer), which turns black when the polarizer is parallel to the shearing direction (right image, right half). In contrast, the reference regions of native glass surface beside the shear-aligned film show a typical grainy multidomain texture (left image, lower left corner, and right image, left half).

It is known that the shear-oriented alignment layers of PI **3** show striations with a surface relief height of about 30 nm and an average relief spacing of 2 μm [18]. As shown in Figure 5, this surface relief does not visually diminish the quality of the LC cell. The striation might be even beneficial for the viewing angle of such LC cells, because for other systems the resulting director modulations improve the viewing angle [25]. However, for LC cells prepared by shearing the semiflexible PAE **2**, the relief height is almost twice as high [18], and thus the quality of the LC cells is reduced, indicated by slightly brighter lines observed by turning the LC cell director parallel to the polarizer (not shown). For the sheared layers of the very flexible ZLI 2650, polarized light microscopy images revealed only grainy multidomains (also not shown), which is in accordance with a low DR_{UV} of 2.

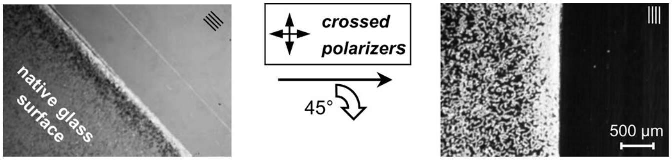


FIGURE 5 Polarized light microscopy of an LC cell with sheared alignment layers of PAE **1** (50 wt% NMP) and imidized to PI **3** (method F) (d = 14 μm, LC; 5CB **I** with 0.5 wt% azo dye **II**, layer; PI **3** from **1**, method F).

In summary, as implied by DR_{UV} measurements listed in Table 3, the efficiency of aligning LCs is very low for layers obtained by shearing flexible precursor polymers but is greatly enhanced for rigid systems.

PI Alignment Layers Prepared by Shearing Highly Concentrated Solutions and Additional Buffing

LC cells were also prepared using sheared alignment layers that had been additionally buffed in different directions after imidization. These experiments were conducted to elucidate the influence of an additional buffing step, inducing surface orientation on top of the bulk-oriented base layer. Bulk shear orientation layers were prepared from 50 wt% solutions of PAE **1**, PAE **2**, and ZLI 2650, imidized and then subsequently buffed either parallel (method G) or perpendicular (H) to the shearing direction. As shown in Table 4, the DR_{UV} measurements of LC cells with these alignment layers demonstrate, in agreement with literature data [26], that the resulting alignment direction is always governed by the direction of the last buffing step.

Comparing the values of Table 4 to buffed alignment layers prepared by film casting (Table 2), we see that now the DR_{UV} values are lower, indicating that the orientation is impaired by the surface profile. However, comparing the DR_{UV} in Table 4 to values obtained with shear-oriented alignment layers (Table 3), we see that the DR_{UV} is increased from 2 to 6 for the very flexible ZLI 2650 by buffing parallel to the shear orientation direction. Conversely, the DR_{UV} for the rigid-rod PI **3** buffed parallel to the shearing direction was found to be at 7 regardless of whether PAE **1** or **2** was used as precursor polymer. This result indicates that the alignment layers prepared by the shearing technique are highly oriented, and that the efficiency in

TABLE 4 Dichroic Ratios (DR_{uv}) at 390 nm of Bis-azo-dye **II** in LC Cells ($d = 14\,\mu m$) Prepared by Shearing a 50 wt% Precursor Solution, Imidizing, and Additionally Buffing Parallel (G) or Perpendicular (H) to the Shearing Direction

	DR_{UV}	
Polymer	G $PAE_{shear} \rightarrow PI_{buff.,\parallel}$	H $PAE_{shear} \rightarrow PI_{buff.,\perp}$
PAE **1** (NMP) → PI **3**	7	12
PAE **2** (NMP) → PI **3**	7	6
ZLI 2650 (LQT)[a]	6	5

[a] Liquicoat thinner (cyclopentanone).

aligning the LC mixture cannot be improved by additional parallel buffing.

Similar results were obtained for the bulk-oriented polyimide layers of the shear-oriented PAE **2** buffed perpendicular to the shearing direction; here the final aligning direction was rotated 90° and now parallel to the buffing direction. The degree of orientation was still in the same range, indicated by a DR_{UV} of 7. A different behavior was found for shear-oriented rigid PAE **1** when the resulting PI **3** was buffed perpendicular to the shearing direction. Here, the determined DR_{UV} (12) was almost doubled compared to DR_{UV}s determined with layers buffed parallel to the shearing direction ($DR_{UV} = 7$). Hence, the different chain flexibility of PAE **1** compared to PAE **2** accounts for the different observed alignment behavior; nevertheless both convert into the structurally identical PI **3** after imidization. This result shows clearly that, for surface and shear orientation, an increase in chain stiffness of the precursor polymer is accompanied by a higher degree of orientation of the resulting LC cell. Additionally, polarized light microscopy was performed on these systems. Figure 6 shows the results using LC cells for which the alignment layer was prepared by method (H). In the left image, a large, almost defect-free LC monodomain is visible as the buffing direction is positioned 45° to the polarizer. In the ellipsoidal insert, the right image is shown overexposed, and now the shearing direction, indicated by slight vertical striations parallel to the polarizer, becomes visible, presumably caused by the surface relief. Here the buffing

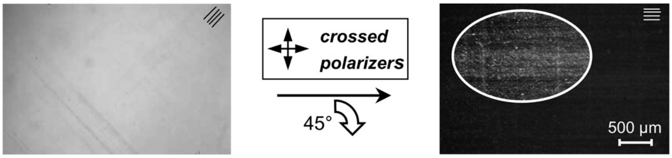


FIGURE 6 Polarized light microscopy of an LC cell with an alignment layer prepared by shearing a lyotropic 50 wt% solution of PAE **1** in NMP. After thermal imidization to PI **3**, an additional buffing step (indicated by four parallel lines) perpendicular to the shearing direction was performed (Table 4, method H). In the left image, the buffing direction is rotated 45° to the polarizer; thus only a bright monodomain on the alignment layer can be seen. In the right image, the buffing direction is parallel to the polarizer: thus the shearing direction is vertical and the final buffing direction horizontal. In the ellipsoidal insert, the same image was overexposed, so that shear-induced (slight vertical striations) and buffing-induced defects (weak horizontal stripe pattern) are visible. (d = 14 µm, LC; 5CB **I** with 0.5 wt% azo dye **II**, layer: PI **3** from **1**, additionally buffed perpendicularly, method H).

direction, schematically indicated in the image by four parallel lines, is slightly visible as a weak perpendicular horizontal stripe pattern produced by the buffing cloth.

Pretilt Angle and Cell-Gap Measurements

Pretilt angle and cell-gap measurements were performed to investigate the tilt bias angle dependency on the different chain stiffness and preparation pathway of used alignment layers. In this measurement setup, the test cell is rotated in a linearly polarized laser beam, and the intensity of the light transmitted by the analyzer is recorded as a function of the angle of light incidence. The pretilt angle values range between 0.7° and 5.1° (Table 5), which are typical for polyimide alignment layers [14].

For LC cells with rigid PAE **1**, the pretilt angle was increased from 2° for the buffed precursor alignment layer (A) to 3° after imidization (B). For the same polymer, imidized and buffed (C), a pretilt angle of 5.1° was measured. For the semiflexible PAE **2**, the pretilt angle of the buffed precursor film (A) at 4.4° is more than doubled and at 4.0° (C) is smaller for the structurally identical buffed alignment layer PI **3**. In contrast, the commercially available buffed PI (C) alignment layer ZLI-2650 exhibits a pretilt angle of only 0.9°, which is very close to that of the shear-oriented PI **3** alignment layer (F) with a pretilt angle of 0.7°. Thus by using PI **3** as alignment material, the pretilt angle can be controlled by different film preparation pathways, meaning a very small angle of 0.7°, obtained by using shear-oriented alignment layers, can be increased to 4.0° by buffing PI films originated

TABLE 5 Pretilt Angle and Cell Gap Measurements of Selected LC Cells ($d = 14\,\mu m$) with Bis-azo-dye **II** (0.5 wt%) in 5CB **I**

Method	Alignment layer	Pretilt angle (°)	Cell-gap (μm)
A	PAE $\mathbf{1}_{\text{buff.}}$	2.0	12.5
B	PAE $\mathbf{1}_{\text{buff.}} \rightarrow$ PI **3**	3.0	15.3
C	PAE **1** $\rightarrow$ PI $\mathbf{3}_{\text{buff.}}$	5.1	11.1
A	PAE $\mathbf{2}_{\text{buff.}}$	4.4	13.8
C	PAE **2** $\rightarrow$ PI $\mathbf{3}_{\text{buff.}}$	4.0	18.8
C	$\text{PI}_{\text{buff.}}$ ZLI-2650	0.9	12.0
F	PAE $\mathbf{1}_{\text{shear}} \rightarrow$ PI **3**	0.7	11.4

Notes: Method A: precursor film was aligned by buffing; Method B: precursor film was aligned by buffing and then imidized; Method C: only the PI film was aligned by buffing; and Method F: shear-aligned polymer precursor layer, imidized.

from semiflexible PAE **2** and might be further increased to 5.1° by starting with the rigid precursor PAE **1**. The cell gap of the selected LC cells was measured between 11.1 and 18.8 µm, which reflects the experimental range in true gap dimensions using spacers of 14 µm. However, as it was shown in Figure 3, the degree of orientation is invariant of the cell-gap dimensions in the range investigated.

CONCLUSIONS

This contribution investigates the influence of chain stiffness of polyimide (PI) precursor polymers, here poly(amic ethyl ester)s (PAEs), on the orientation efficiency of alignment layers in LC cells. Additionally, different alignment layer preparation methods, such as casting from low-concentration solutions and shearing from highly concentrated solutions, were explored. As a result, it was shown that it is beneficial to maximize the chain stiffness of the precursor polymers to obtain highly efficient PI alignment layers. A single-step shearing technique, without buffing, of a highly concentrated lyotropic PAE solution results in alignment layers that are as good as layers fabricated from buffed commercial PIs. Furthermore, cells assembled with buffed rigid-rod PI alignment layers prepared from low-concentration solutions of a rigid PAE result in a very high DR_{UV} of 15. This value is doubled compared to values obtained with alignment layers using a commercial PI alignment-layer kit from Merck. By buffing a PI bulk-oriented alignment layer prepared by the shearing technique parallel to the shearing direction, the efficiency of LC orientation cannot be improved, because obviously the shearing process alone produces highly efficient alignment layers. Conversely, buffing an identically prepared PI layer perpendicular to the shearing direction increases the LC orientation by almost a factor of two. Further, pretilt angles of selected LC cells were measured, and values were found that are typical for PI alignment layers but are clearly a function of the alignment-layer preparation method.

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