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Influence of the dopant concentration on the morphology of hole-transporting alignment layers based on a polyimide matrix

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Abstract

Investigations on hole-transporting alignment layers (HTALs) consisting of a polyimide matrix doped with hole-transporting materials (HTMs) at different concentrations by means of low-voltage scanning electron microscopy and atomic force microscopy are reported. These layers were recently used as HTALs for liquid crystalline polyfluorenes in polarized light-emitting diodes. For HTM concentrations below 15 wt%, phase-separation was found to be not significant, and the layer characteristics were dominated by the stiff polyimide matrix. These layers aligned polyfluorene very well, resulting in polarization ratios in electroluminescence of more than 20. On the contrary, the morphology was substantially altered at higher dopant concentrations. Moreover, microgrooves became visible after rubbing, indicating that the degree of imidization of the polyimide matrix was reduced. As a result, increasing the concentration of the HTMs above a certain level resulted in a dramatic decrease of the aligning ability of the HTAL. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Alignment layer; Polarized electroluminescence; Polyimide

1. Introduction

Intense research has been initiated by the discovery of electroluminescence (EL) of conjugated polymers in 1990 [1], and polymer light-emitting diodes (LEDs) are supposed to enter the commercial market in the near future. One interesting aspect of polymer emission layers is that polymers can be aligned by several methods, leading to linearly polarized electroluminescence (LPEL). Polarized LEDs can be used as backlights in conventional liquid crystal displays (LCDs) and replace the light consuming sheet polarizers needed for polarizing the isotropic backlight.

One approach to obtain polarized emission from polymers with good brightness is the direct rubbing of the emissive polymer layer, as shown for the example of precursor poly(*p*-phenylenevinylene) (PPV) by Jandke et al. who achieved a polarization ratio of 12 and a luminance of 200 cd/m^2 [2]. Another promising method is the alignment of liquid crystalline polymers at elevated temperatures on top of a rubbed hole-transporting alignment layer (HTAL). Whitehead et al. used rubbed precursor-route PPV as hole-injecting alignment layer and achieved polarization ratios of 25 at a luminance of up to 250 cd/m^2 when using poly(9,9-dioctylfluorene) as the emitter [3].

We have recently reported polarized emission from a multilayer LED, which was based on the liquid-crystalline polymer poly(9,9-diethylhexylfluorene) (PF26), aligned on rubbed polyimide (PI, Fig. 1) doped with the bulky starburst-type 4,4′,4″-tris(1-naphtyl)-*N*-phenyl-amino-)-triphenylamine (ST638) to provide sufficient transport of holes from indium-tin oxide (ITO) anode to the aligned emission layer [4]. Later, various hole-transporting molecules (HTMs) were tested as dopants in the rubbed PI alignment layer, and the resulting device performance was analyzed with respect to maximum brightness, efficiency and polarization ratio.[3] The comparison revealed that devices with ST 1163 exhibited the largest brightness and the lowest onset voltage [6]. This was attributed to the appropriate HOMO level position close to that of the ITO anode and a high glass transition temperature. LEDs with PF26 end-capped with (4-methylphenyl)phenylamine (PF, Fig. 1) on

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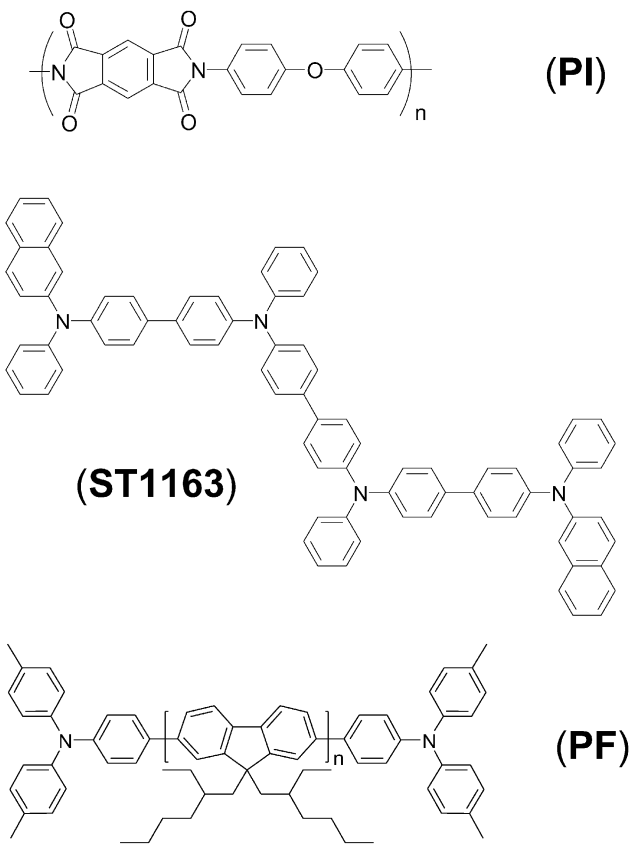

Fig. 1. Chemical structure of poly(phenoxyphenylimide) (PI) and the HTM *N*,*N*′-diphenyl-*N*,*N*′-bis(4′-(*N*,*N*-bis(naphth-1-yl)-amino)-biphenyl-4-yl)-benzidine (ST 1163). Also shown is the structure of poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) endcapped with (4-methylphenyl)phenylamine (PF).

top of polyimide doped with ST 1163 were shown to emit polarized light with a polarization ratio of 22 at a brightness of 200 cd/m^2 and an efficiency of 0.25 cd/A [5]. In the course of this work, a significant dependence of the device performance on the concentration of the HTM in the rubbed polyimide layer was observed. In particular, increasing the concentration from 10 to 15 wt% raised the maximum brightness from 200 to 800 cd/m^2, but at the same time, the polarization ratio decreased from 22 to 15.

In this paper, we present the results of investigations on the morphology of such HTALs, which consist of a polyimide matrix doped with ST 1163 at different concentrations, by means of low-voltage scanning electron microscopy (LV-SEM) and atomic force microscopy (AFM). In particular, we report on the influence of the filler content on the performance of polarized LEDs and on the morphology of the HTALs. To investigate the impact of the rubbing treatment on the film morphology, unrubbed and rubbed layers are compared for different doping concentrations. We show that the influence of the dopant concentration on the achievable polarization ratios can be explained by severe changes in the morphology of the HTALs due to phase-separation, an inherent problem when blending polymers with low-molecular weight compounds [7]. The obtained results manifest an optimum doping concentration balancing between best possible alignment strength and EL performance.

2. Experimental

The fabrication of polarized LEDs is described elsewhere [5]. In short, the emissive layer, poly(9,9-bis(2-ethylhexyl)-fluorene-2,7-diyl) endcapped with (4-methylphenyl)phenylamine (PF), was aligned on top of a rubbed layer of PI, which was doped with ST 1163 (Fig. 1) purchased from SynTec GmbH.[3]

The HTALs were prepared by spincoating a solution of PI precursor and HTM at varying concentrations at 1900 rpm for 50 s. The total solid content of PI and HTMs was 30 g/l in Liquicoat solution (polyimide and Liquicoat solvent were obtained from Merck, ZLI 2650 kit). The solutions were filtered immediately before spincoating ($d = 0.45\ \mu m$) in order to optimize the homogeneity of the films. After a 15 min softbake at 80 °C, the PI precursor was converted to PI at 250 °C for 1 h under rotary pump vacuum. (The film thickness after conversion was between 40 and 50 nm.) Rubbing of the samples was done by means of a rubbing machine from E.H.C. Co., Ltd, Japan. The rotating cylinder (diameter of 70 mm) was covered with a rayon cloth (Yoshikawa Chemical Co., YA-25-N) and rotated at maximum speed of 1400 rpm. The samples were unidirectionally passed twice under the cylinder at a translating speed of 2.2 mm/s. These parameters ensured a relatively high velocity of the rubbing cloth relative to the sample of approximately 510 cm/s. The bending depth of the cloth fibers due to contact pressure was approximately 0.8 mm. For defined surrounding conditions, the rubbing machine was placed in a fume-hood, and rubbing was done under a constant nitrogen flow.

Scanning electron microscopy was carried out with a field-emission gun source, high-resolution low-voltage scanning electron microscope LEO 1530,[4] minimizing the problem of beam-induced radiation damage and charging of the polymers under the electron radiation [8]. All AFM measurements were performed on a Digital Instruments Nanoscope IIIa multimode AFM[5] in tapping mode.

3. Results

3.1. Influence of dopant concentration on the device performance in electroluminescence and on the polarization ratio

Polarized LEDs have been fabricated by the alignment of PF on top of HTALs based on doped PI. Fig. 2 shows

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[4] http://www.leo-em.co.uk.

[5] http://www.di.com.

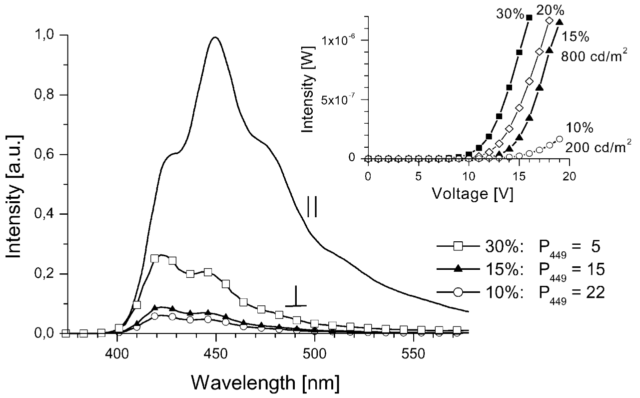

Fig. 2. Polarized electroluminescence for EL devices with an 80 nm thick PF emission layer and different concentrations of ST 1163 in the hole-transporting polyimide alignment layer (thickness 30 nm). (||: emission polarized parallel to the rubbing direction, ⊥ : emission polarized perpendicular to the rubbing direction. Hole-injection layer: 25 nm ST 1163; Ca cathodes). Inset: Intensity–voltage characteristics for the same devices.

polarized EL emission spectra for devices with different ST 1163 concentrations in the alignment layers. The polarization ratio decreased from 22 to 5, when the concentration of the HTMs in PI was increased from 10 to 30 wt%, whereas the intensity increased (at decreasing onset voltage) from 200 to more than 800 cd/m$^{2\cdot}$ These findings demonstrate that the dopant concentration has to be carefully balanced for good EL performance and alignment strength. Devices with 20 wt% doping exhibited the best overall EL performance and showed the highest power efficiency. For higher concentrations, the EL efficiency dropped slightly and the strong decrease in polarization ratio made these devices unsuitable for polarized light-emitting sources.

3.2. Morphology of unrubbed hole-transporting alignment layers

Films with different concentrations of ST 1163 in PI were investigated by means of LV-SEM and AFM. In all cases, blends of the precursor-PI and different concentrations of ST 1163 were spincoated on top of ITO-covered glass substrates to obtain hole-transporting layers of approximately 40 nm thickness after conversion.

Fig. 3 shows scanning electron microscope images of unrubbed layers with different doping concentrations of ST 1163 in PI increasing from 10 to 40 wt%. Looking at the pictures for low filler contents, we find that the appearance of the respective layers is relatively homogeneous. However, at higher filler contents, the surface is covered with increasing density by round spots of growing size. The concentration dependence suggests that these spots are due to HTMs, which phase-separate within the polyimide blends.

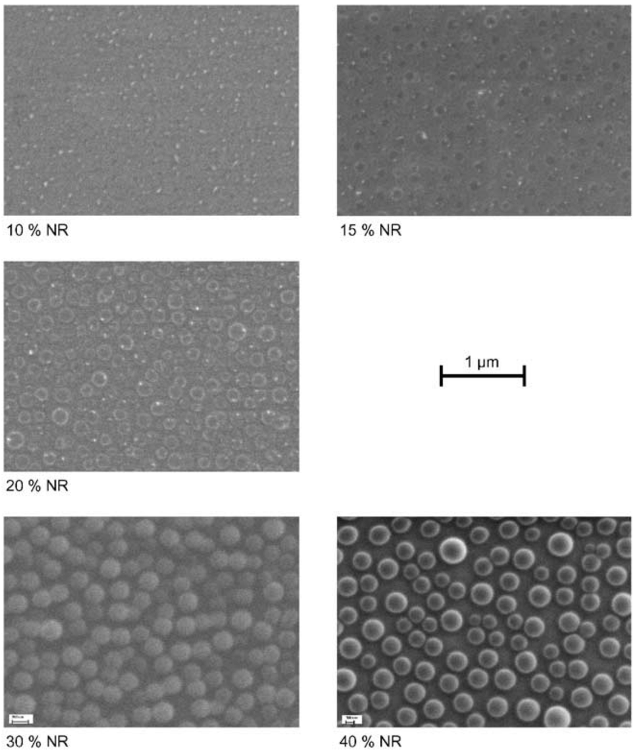

Fig. 3. Low-voltage scanning electron microscope pictures of unrubbed layers (NR) of PI doped with ST 1163 at different concentrations (in wt%).

As shown in the figure, the phase-separated structures are almost not noticeable for dopant concentrations of 10 wt%, and the layer surface is rather flat with a root-mean-square (RMS) roughness of 1.4 nm. At a concentration of 15 wt%, dark spots with a diameter of 60–130 nm can be faintly perceived. When the concentration reaches 20 wt%, the degree of phase-separation starts considerably, and the diameter of these areas varies from 100 to 220 nm. Comparison of the different images reveals that the appearance of the nano-scale features changes with the concentration of the HTMs. While at very low contents, the HTMs are noticed as dark spots, these marks are encircled by bright edges for a content of 20 wt%. The latter indicates that they form crater-like depressions within the PI film, which are surrounded by protruding fringes. According to AFM measurements, the depth of these craters is between 3 and 6 nm (Table 1). When the filler contents further increases to 30 and 40 wt%, the form of the nano-phase-separated structures changes from depressions to globules with heights between 10 and 15 nm and diameters between 180 and 400 nm. The RMS increases to 4 nm (30 wt%) and 6–8 nm (40 wt%), respectively.

In addition to these nano-size features, one observes bright spots of comparatively large size dispersed all over the samples, as clearly visible on images recorded at lower magnification (Fig. 4, left column). The diameters of these spots increase with augmenting filler content from ~700 nm for 10 wt% to ~1650 nm for 40 wt% (Table 1). Due to this concentration dependence, they are interpreted as agglomerates of HTMs. AFM investigations reveal a disk-like shape of these agglomerates with height increasing from 25 nm for 10 wt% to 60 nm for 40 wt% doping.

Table 1
Diameter and depth of phase-separated clusters of HTMs inside of the layer and on top of the layer, respectively, for unrubbed (NR) and rubbed (R) films of PI doped with ST 1163 at different concentrations. The values for the diameter were determined both from LV-SEM and from AFM measurements, and the height (positive val.)/depth (negative val.) was obtained from AFM studies

Dopant concentration in PI (wt%)	HTMs inside of PI film		HTMs on top of PI film	
	Diameter (nm) (LV-SEM/AFM)	Height (nm) (AFM)	Diameter (nm) (LV-SEM/AFM)	Height (nm) (AFM)
10% NR	70–90	−4 to −6	550–850	+25
R	30–70	−4 to −6	Not observed	Not observed
15% NR	60–130	(No data)	800–950	(No data)
R	40–75	(No data)	Not observed	(No data)
20% NR	100–220	−3 to −6	1000–1350	+40 to +45
R	80–160	−4 to −6	1200–1950	+20 to +30
30% NR	180–360	+9 to +11	1200–1500	+50 to +60
R	120–270	−8 to −10	2000–2150	+20 to +25
40% NR	210–400	+8 to +15	1300–2000	+55 to +60
R	170–270	Not measurable	1300–1550	+15 to +20

3.3. Morphology of rubbed hole-transporting alignment layers

Fig. 4 shows LV-SEM images of rubbed layers compared to those of non-rubbed layers of PI doped with ST 1163 at different concentrations. The extent of how strongly the film morphology is altered after rubbing clearly depends on the concentration of the hole-transporting moieties. Figs. 4 and 5 show that for low concentrations of 10 and 15 wt% the matrix of the layers is not noticeably disturbed by the rubbing, and the films are very homogeneous. The layers only show very few single fissures produced by the rubbing procedure. On the contrary, for filler contents of 30 and 40 wt%, the entire film is covered with rubbing grooves (Figs. 4 and 9). For 10 wt% doping, the few microgrooves are approximately 50 nm wide and 5 nm deep, but for a filler content of 40 wt% these values increase to 140 and 15 nm, respectively.

For all concentrations, the average diameters of the nano-size features decreases by rubbing by approximately one third to one fourth (Table 1), suggesting that these features are partially covered during rubbing.

To be more precise, in case of moderate concentrations, at which the features are crater-like depressions within the film, the surroundings are removed by the rubbing, partly covering the depressions and reducing their overall size (as sketched in Fig. 6). However, for high dopant concentrations, where the features appear as blister-like globules, the appearance in the images changes from bright marks to dark spots surrounded by bright fringes. Comparison of surface scans of unrubbed and rubbed samples clarifies this observance. Fig. 7 shows AFM pictures of layers with dopant concentrations of 30 wt%, together with horizontal and vertical scans over the surface along the black lines. In fact, the scans demonstrate that in the case of the unrubbed sample—as mentioned above—the features arch over the surface and form globules of about 10 nm height (for visualization, each area belonging to a single globulus is marked with blue (bold) in the line-scan picture). Contrary, after rubbing, the features remain as crater-like holes with a depth of ~8 nm in the layer, surrounded by fringes, which protrude few nanometers over the surface.

The effect of rubbing and concentration on the above-mentioned large agglomerates, which lie on top of the films, becomes evident from the results both of LV-SEM and of AFM measurements (Figs. 4, 8, and 9). For filler contents of 10 and 15 wt%, these particles—being present before rubbing—are completely removed by the rubbing treatment. In contrary, in the case of dopant concentrations of 20 wt% and more, these agglomerates are smeared to smudgy bands covering the layer surface to a large extent. The increase in diameter and decrease in height, respectively, of the smeared bands relative to the pristine agglomerates is between 40 and 50% (Table 1).

4. Discussion

4.1. Layer morphology

In the following, we like to interpret the cause of the different features observed in images of unrubbed and rubbed layers and to provide explanations for the decrease in alignment strength with increasing filler concentration. Herein, our focus was mainly to describe the impact of the rubbing treatment on the morphology of the alignment layers in a qualitative way, rather than to give a comprehensive clarification of the nature of the process of phase-separation.

One important observation is that rubbing traces appear at high filler contents, which is not the case for low doping concentrations. This outcome suggests that at elevated concentrations, the degree of imidization is too low to yield the stiffness inherent to fully imidized polyimide. A conclusive explanation would require a measurement of the degree of imidization by IR spectroscopy, which has not yet been performed. However, our conclusion is consistent with a report by Han and Im [9] who noticed a lower degree

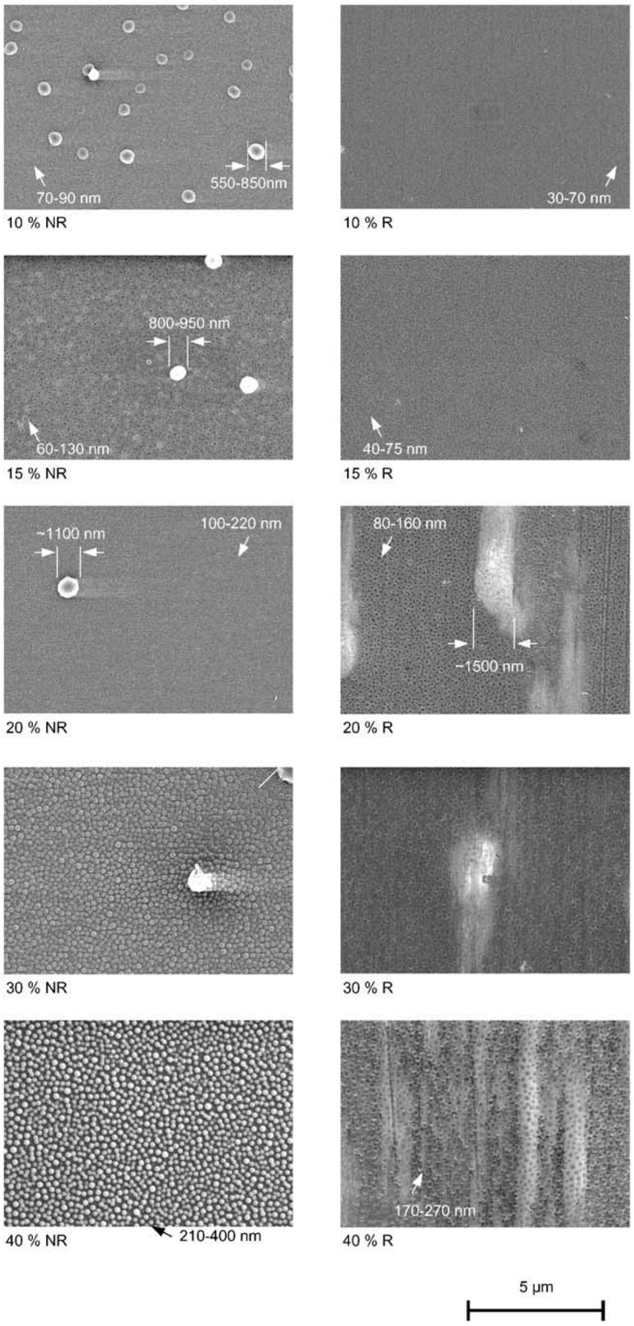

Fig. 4. LV-SEM pictures, showing the comparison of unrubbed (NR) and rubbed (R) layers of PI doped with ST 1163 at different concentrations (in wt%). The size of the nano-structures inside the layers and of the agglomerates on top, respectively, is also shown (as evaluated from LV-SEM and AFM measurements). The direction of rubbing was vertical.

of imidization for higher dopant and lower polyimide contents in comparable conductive polyaniline/polyimide blends. The above-mentioned finding that layers with low doping concentration and insignificant layer irritation yielded the highest polarization ratios (Fig. 2) confirms the well-accepted model [10–15] that LC alignment on rubbed PI is due to molecular alignment rather than to microgrooves, which may be created by the rubbing.

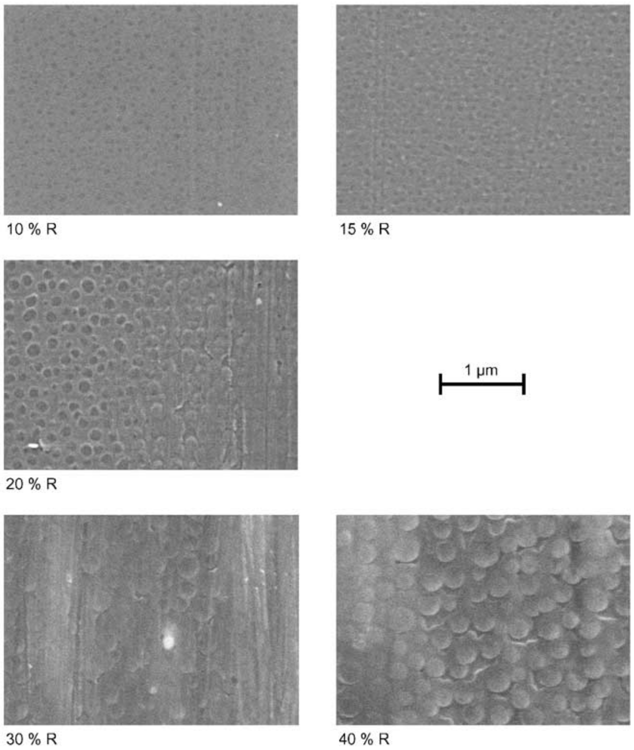

Fig. 5. LV-SEM pictures showing the comparison of rubbed (R) layers of PI doped with ST 1163 at different concentrations (in wt%). The direction of rubbing was vertical.

Second, the images of rubbed and unrubbed layers with different filler concentrations suggest that the *micro-size* features consist of HTMs, which lie ontop of the layer, without being incorporated into the PI matrix. Since those features are absent in images of non-converted layers, we propose that these agglomerates are formed by diffusion of HTM molecules out of the layer during conversion. We could show that these large clusters can be removed by washing the samples in toluene (Fig. 10). As the PI is expected to become stiff and insoluble after conversion, washing with toluene only removes the excess dopants, which are not included in the matrix. The fact that the agglomerates are completely removed after washing supports our interpretation that they consist of HTMs lying loosely ontop of the layer. We had recently confirmed

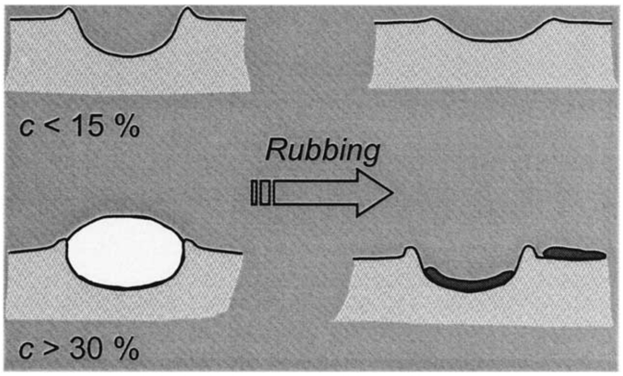

Fig. 6. Cartoon to illustrate the effect of rubbing on HTALs with low and high concentrations of HTMs, respectively.

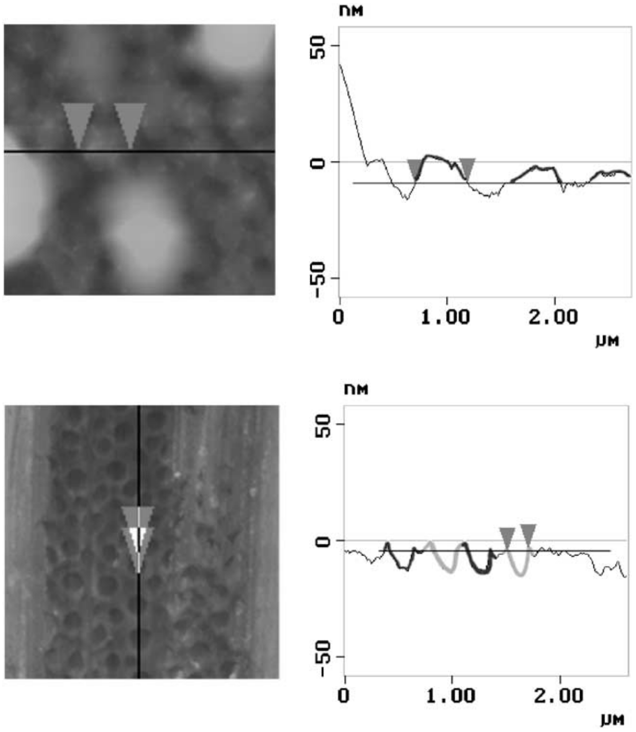

Fig. 7. AFM pictures and line-scans of unrubbed (NR) and rubbed (R) films of PI doped with 30 wt% ST 1163. Line-scans are along the black lines shown in the AFM pictures in horizontal and vertical direction, respectively, and the arrows denote the respective positions in the pictures. For clarity, areas belonging to a single dopant island are marked with bold lines (dark and bright by turns). The black horizontal line in the line-scan pictures indicates the layer surface. The direction of rubbing was vertical.

that spinning off with pure toluene does not affect the electrical properties of such HTALs [4], indicating that the HTMs, which are still dispersed in the PI matrix, are indeed not removed by such a treatment.

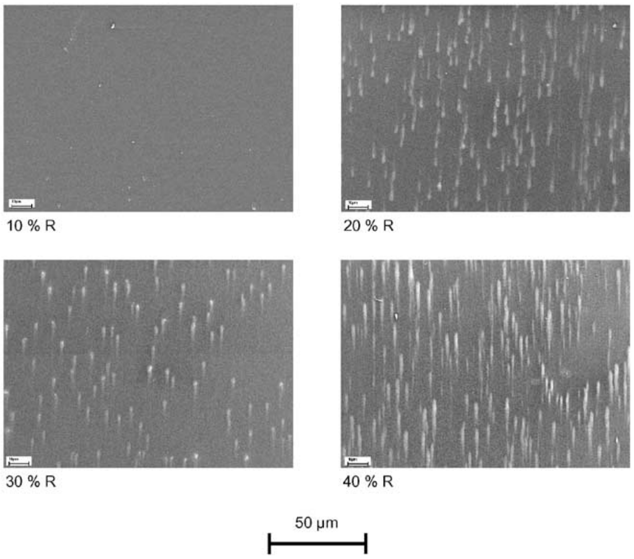

Fig. 8. LV-SEM pictures of rubbed (R) layers of PI doped with ST 1163 at different concentrations (in wt%). The direction of rubbing was vertical.

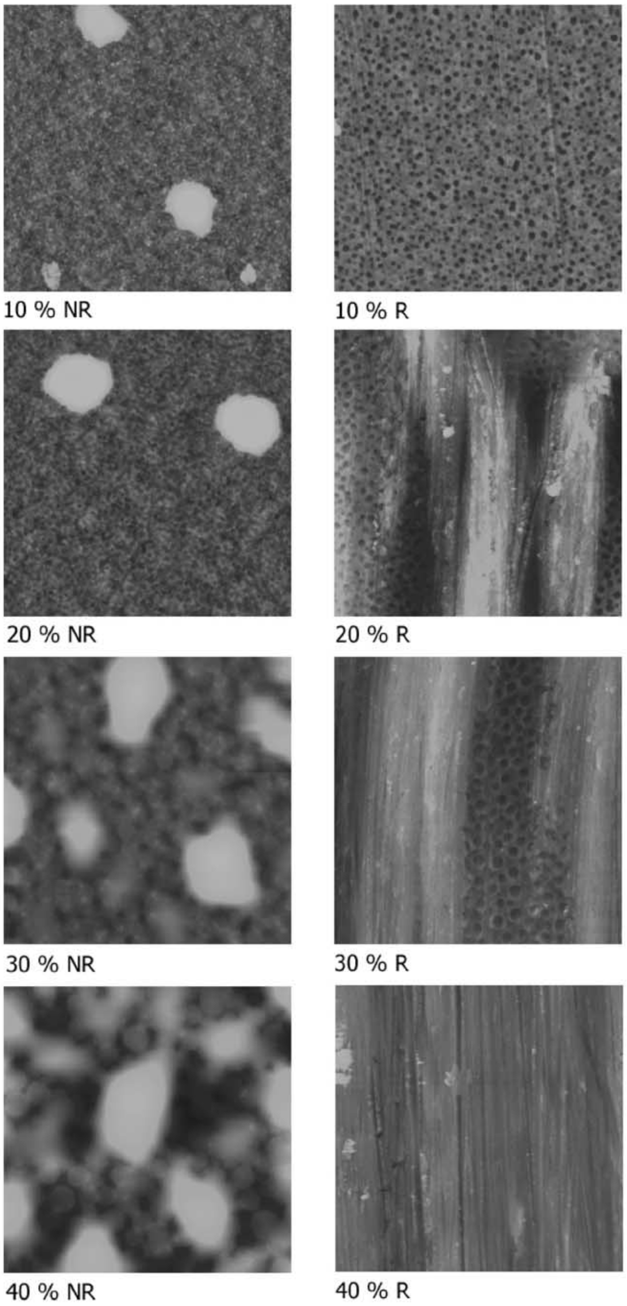

Fig. 9. AFM pictures of unrubbed (NR) and rubbed (R) films of PI doped with HTM ST 1163 at different concentrations. The direction of rubbing was vertical. The length of the square area shown is 5 µm in each case.

The cause and nature of the *nano-size* features is more difficult to understand, and we can only speculate about the driving force for their formation. At low concentrations, those characteristics resemble shallow holes in the PI layer, as shown in Figs. 3 and 4. However, further investigations revealed that in non-converted layers, i.e. before the thermal conversion of the soluble pre-polymer to the insoluble PI, those nano-size features appear as globules rather than as holes. Furthermore, the large micro-size agglomerates described above were only observed in converted layers, but not in the as-prepared layers. Since the total area covered by these nano-size features increases with

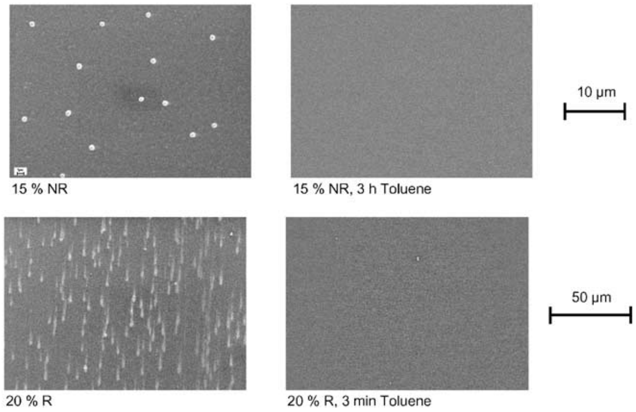

Fig. 10. LV-SEM pictures of unrubbed (NR) and rubbed (R) films of PI doped with ST 1163 at different concentrations without (left) and with (right) additional bathing in toluene. The direction of rubbing was vertical.

augmenting filler concentration, they are most likely caused by phase-separation within the blended layer. However, phase-separation alone cannot explain the formation of the nano-size depressions or even the globules. Their formation might be rather caused by a two-step-process, a combination of phase-separation and diffusion. First, clusters of dopant molecules might be developed directly after spincoating due to microphase-separation. Later, after conversion at higher temperature, a certain fraction of the HTMs in these microphase-separated clusters diffuse out of the layer to form the large agglomerates ontop of the stiff matrix, leaving behind the observed holes in the PI layer. This diffusion might be further driven by the change in surface tension due to the chemical conversion of the polyimide. In case of high filler contents, diffusion might be incomplete, and the converted layers contain nano-size globules rather than holes.

As mentioned in Section 3.3, the investigated layers showed crater-like depressions after the rubbing treatment—even in the case of high concentrations, for which the unrubbed layers had originally been covered with globules. This observation might be understood assuming that rubbing removes the phase-separated clusters from the polyimide layer, and the released HTM molecules are then spread across the layer surface.

One could suppose that the globules at higher filler contents are *completely* filled by hole-transporting material (HTM). This would also imply that rubbing removes the dopants as a whole. The following considerations disprove this hypothesis, however. Estimations of the layers with 30 wt% (Fig. 3) show that under the assumption of massive blobs, at least 15 wt% of the HTM would be incorporated into the microphase-separated features.[6] Thus, less than 15 wt% would be integrated into the bulk of the layer. Current–voltage experiments performed on rubbed PI layers doped with ST 638 at various concentrations, however, have revealed a percolation-type threshold behavior, indicating that a significant fraction of the HTMs is still imbedded into the PI matrix [4]. Also, if the dopants were completely removed during the rubbing procedure, the conductivity of the film would be expected to dramatically decrease after rubbing. However, investigations showed that the electrical performance of such films is not considerably affected by the rubbing treatment, as also evident from the results presented in Fig. 2. Thus, we presume that the nano-size features at high filler concentration are blisters, which are only partially filled with HTMs.

It should be finally noted that the impact both of the dopant concentration and of the rubbing procedure on the morphology are surface effects. Neither the holes induced by microphase-separation and diffusion nor the traces produced by the rubbing penetrate the film deeper than approximately 10 nm (Table 1). These findings are also confirmed by cyclovoltammetric data of the films (not shown here).

4.2. Aligning ability of rubbed layers

One might suggest that the blurred areas of soft HTMs lying on top of the films might explain the pronounced decrease in polarization ratio for polarized LEDs at higher ST1163 concentration in the HTAL. In fact, a large fraction of the surface of the rubbed layer is covered by the smeared areas at high HTM concentration. However, as mentioned above, these clusters are entirely removed by washing the layers with toluene, even if this is done after the rubbing procedure. (This suggests that the agglomerates might also be partly removed by the subsequent spincoating of an emissive layer from toluene solution.) We have investigated the effect of washing the samples with toluene on the aligning ability of the layers (as deduced from polarized absorption and emission experiments on oriented PF layers, which had been aligned ontop of the rubbed HTALs). It was found that even after the concomitant removal of the agglomerates, the alignment ability of films with dopant concentration of 30 wt% and more was still considerably poorer than for layers with moderate filler contents.

Thus, the observed decrease in the degree of PF alignment at higher HTM concentrations cannot be sufficiently explained merely by the HTMs smeared on top of the rubbed layers. We rather believe that it is a consequence of the two morphological changes described above. First, the occurrence of microphase-separation in combination with rubbing leads to a large density of depressions in the layer. As a result, the overall area of contact between the polyimide and the rubbing cloth and, later, between the aligned polyimide and the LC material ontop is reduced. Second, the above-mentioned overall

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[6] In Fig. 3, approximately 120 blisters with an average diameter of ~ 250 nm and an average height of ~ 10 nm are perceived on the area of $\sim 10^{-7}$ cm^2. Assuming massive blisters, they would take up a volume of $\sim 6 \times 10^{-14}$ cm^3 corresponding to a mass of $\sim 6 \times 10^{-14}$ g. The mass of the 40 nm thick polyimide in this area can be estimated to be $\sim 4 \times 10^{-13}$ g. Hence, if the blisters were completely filled with HTMs, this would correspond to a mass ratio ST 1163/PI of 15 wt%.

softening of the PI matrix (as indicated by the appearance of rubbing traces) will reduce the ability of the PI surface to act as aligning material. Recently, a selective reorientation of initially well-ordered polyimide chains upon uniaxial rubbing was proposed from IR spectral analysis [16]. It was also concluded that any chains initially present in a disordered configuration do not respond to the rubbing process. Assuming that doping HTMs at higher concentrations into PI will inhibit the formation of regions with well-ordered polyimide chains, the reduction in the degree of PF chain orientation can therefore be explained by the lack of PI chain alignment in the uppermost PI layer.

5. Conclusion

In conclusion, we have investigated unrubbed and rubbed layers of PI doped with hole-transporting moieties ST 1163 at different concentrations by means of LV-SEM and AFM technique. With such layers incorporated into polarized LEDs, the luminance was enhanced from 200 to more than 800 cd/m^2 by increasing their concentration from 10 to 30 wt%, whereas the polarization ratio decreased from 22 to 5. Investigation of HTALs showed that phase-separation is of minor significance for filler contents of 10 wt% and starts at 15 wt% doping. At these concentrations, the degree of imidization appears to be sufficient and the layer characteristics are dominated by the stiff polyimide, resulting in films with high alignment strength after rubbing and without any remarkable damage by microgrooves.

The morphology is substantially modified by the dopants for concentrations higher than 20 wt%, and phase-separation becomes more and more severe. After rubbing, holes with diameters of more than 100 nm appear, covering a significant part of the layer area. For all concentrations, HTMs agglomerate into large clusters lying on top of the layers. For low concentrations, they are removed during rubbing, whereas at higher filler contents, they appear as blurred stripes covering the whole layer. It was shown that these clusters are entirely removed by a short toluene treatment, and that the resulting alignment power of such layers was still considerably poorer than for lower concentrations. This decrease in aligning ability is most likely caused by the softening of the PI matrix and a reduction of the overall area of aligned PI in direct contact with a liquid crystalline emissive material coated ontop.

Very recently, the formation of blisters and wells in polymer layers have been reported by J.S. Sharp and R.A.L Jones (Adv Mater 2002:14;799–802). However, even though the structures reported by Sharp et al., have a similar appearance as the nano-size features described here, their origin is the partial delamination of the polymer layer from the substrate in a bad solvent rather than phase separation.

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