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Polarized electroluminescence of light emitting liquid crystalline polymers

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Smectic liquid crystalline arylenevinylene main chain polymers were used in light emitting diodes (LEDs) to produce linearly polarized electroluminescence. The degree of orientational order induced by a rubbed polyimide layer amounted to $S=0{\cdot}64$, as extracted from the electroluminescence spectra. The great advantages of these LC polymers are their good thermal stability, processability and broad mesophase range, and the possibility of applying established orientation techniques in order to achieve a macroscopic orientation.

1. Introduction

Polymer based light emitting diodes (LEDs) consist, in general, of a substrate, such as glass, coated with Indium–Tin–Oxide (ITO) as the bottom electrode, one or more polymer films and finally a top electrode [1]. The ITO electrode injects holes and the top aluminum electrode electrons into the polymer films. The emitted light is, in general, unpolarized in this case. The emission of linearly polarized light which is of interest, for instance, for applications in the area of background illumination of LC displays, requires orientation of the polymer. Such an orientation may not only affect the state of polarization of the emitted light, but also the charge carrier mobility and diode characteristics such as the onset voltage for emission [2,3].

The orientation has been achieved in the past via mechanical deformation or by making use of the LB technique [4–7]. Our concept is to combine light emitting properties and the self organization of liquid crystalline polymers. We have recently demonstrated that a preferential orientation and consequently polarized photoluminescence can be accomplished by the deposition of smectic light emitting LC polymers (LCPs) onto rubbed polyimide (PI) surfaces [2]. The polymers used were main chain polymers carrying isolated arylenevinylene segments separated by flexible spacers [8]. Lateral substituents were attached to the backbone to enhance their solubility. These systems exhibited a smectic A phase which could be frozen into the glassy state. The macroscopic order parameter $S=<(3/2\cos^2\Theta-1/2)>$, as obtained from UV/VIS and photoluminescence measurements for the compound with the longest spacer ($x=10$, $T_g=77°C$, $T_{cl}=175°C$; see structure **1** in the scheme), was $S=0{\cdot}67$.

The fabrication of a diode requires that the light emitting material is sandwiched between an anode and a cathode. Proper charge carrier injection and transport characteristics of the materials within the sandwich structure of the device are important for a reasonable performance of the LED. A problem might be that the polyimide used for the orientation of the LED polymer diminishes the device performance. This would require the use of hole transporting polyimides as for example suggested by Kakimoto *et al.* [9].

2. Fabrication of LEDs

Based on our previously published work on polarized photoluminescence [2], we report here on the fabrication of LEDs showing polarized electroluminescence. These devices were built of LCPs which were oriented by deposition on a rubbed aromatic polyimide (PI) (see structure **2** in the scheme) that was not specially modified for hole transport. It seems that commercially available polyimide on ITO is suitable for hole injection and hole transport. To produce the LED we deposited a polyimide film by spin coating the precursor solution (PI-kit 'Liquicoat' ZLI 2650, E. Merck) onto a glass substrate sputtered with a conductive ITO layer. The PI film having a thickness in the range 30–40 nm was annealed for one hour at 270°C to achieve imidization. The PI

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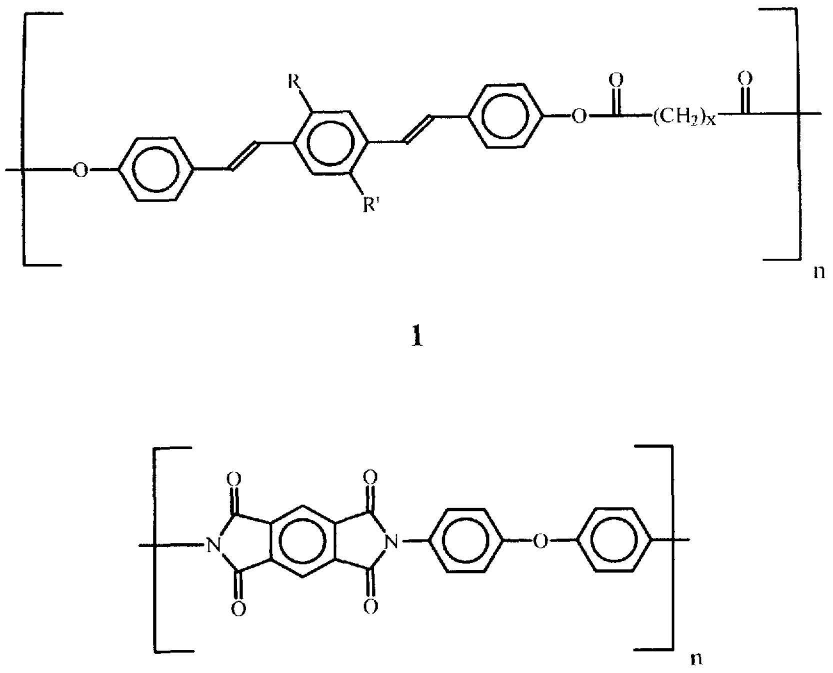

Scheme. Chemical structure of the polymers. **1** LC main chain polymer having R = H, R′ = phenyl, $x = 10$; **2** polyimide.

film was treated for 10 minutes in a rubbing process and subsequently coated with a solution of the LCP (structure **1** in the scheme) in chloroform to produce a second layer. At this stage, the PI film reveals its advantages, namely its good thermal and chemical stability, so that the second layer can easily be coated onto the PI without dissolving the PI film.

To induce the orientational process, we annealed the samples carrying the LC polymer spincoated onto the rubbed PI layer for one hour at different temperatures. The film thickness amounted in all cases to 150 nm. As shown in figure 1 (*a*), a maximum orientation is achieved at 140°C which is 35 K below T_{cl}. No orientation occurred below T_g and above T_{cl}, as expected.

In order to estimate the annealing time necessary to achieve the saturation orientation, we annealed samples with identical film thicknesses at 160°C for different time intervals. Figure 1 (*b*) shows the dependence of the order parameter on annealing time. It is apparent that an annealing time of half an hour is sufficient to obtain the saturation value.

A monodomain resulted in this way, as was apparent from optical investigations. This state of orientation was then frozen in by quenching the sample to temperatures below T_g. To complete the device, a 100 nm thick aluminum electrode was evaporated onto the sample and contacted using a conductive adhesive. The device was then operated at room temperature in air by applying an electric field (i.e. ITO positive, Al negative).

3. Electroluminescence spectra

Figure 2 displays the electroluminescence spectra of a device consisting of a glass/ITO/polyimide(**2**)/LC polymer(**1**) layer configuration. The spectra were recorded using a commercial spectrometer with a polarizer located between sample and detector and with the polarizer aligned parallel and perpendicular to the rubbing direction in the upper and lower curves, respectively, in figure 2.

The shapes of both electroluminescence spectra are very similar to the shapes of the photoluminescence spectra obtained in our earlier work [2]. They exhibit significant differences in the intensities measured in the rubbing direction and perpendicular to it. The transition dipole moments of the chromophores are thus oriented predominantly along the rubbing direction, as expected from our previous results on the UV-dichroism and photoluminescence [2]. The macroscopic order parameter was calculated from the electroluminescence spectrum using the relation $S = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are the values of the intensity of the electroluminescence parallel and perpendicular to the rubbing direction, respectively. It turned out to be $S = 0{\cdot}64$, indicating a rather high degree of orientational order. The maximum of the emission is located at 450 nm, and the sample emits blue–green light.

4. Current–voltage characteristics

To analyse the hole and electron injection characteristics of the PI sub-layer used in the LED device, a

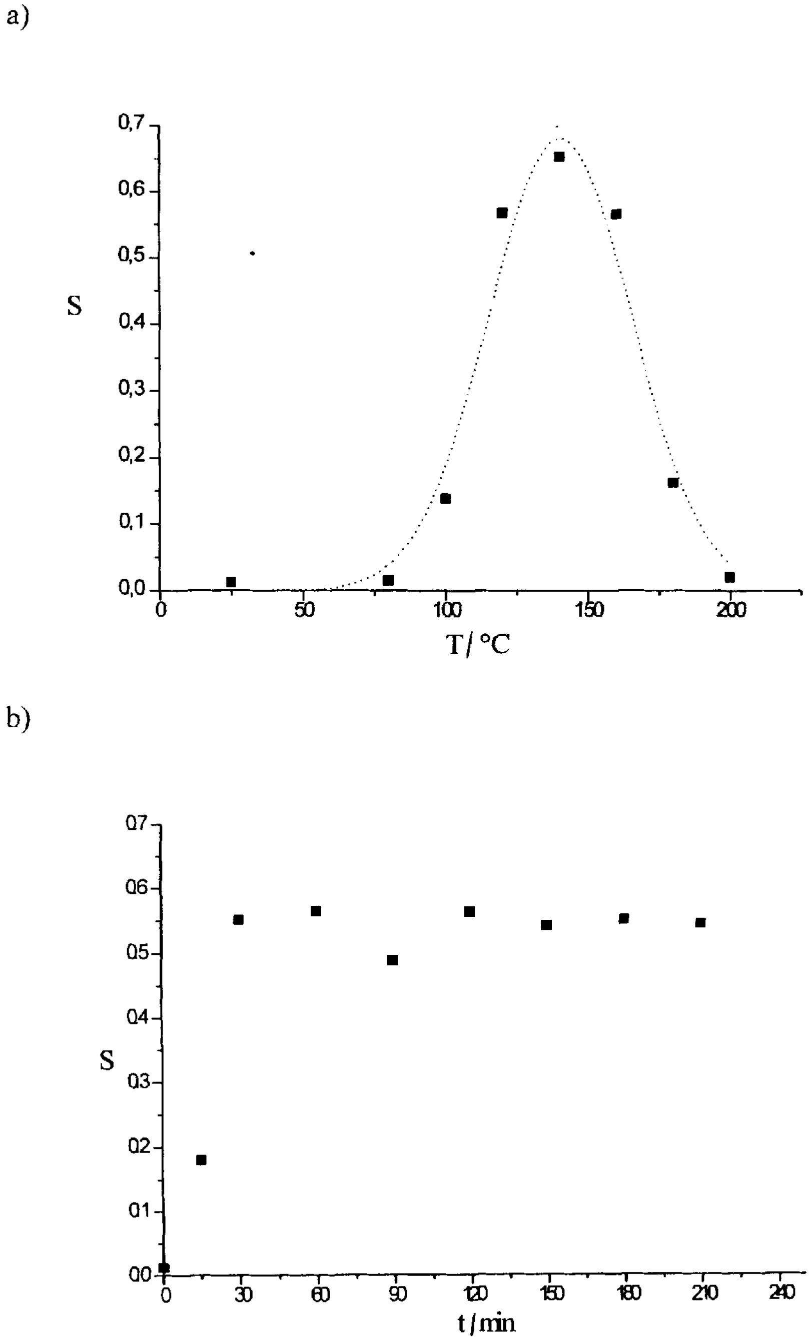

Figure 1. (*a*) Degree of orientational order as a function of the annealing temperature of **1**; samples were annealed for one hour. (*b*) Degree of orientational order as a function of the annealing time of **1**; the annealing temperature was 160°C.

device consisting just of the PI layer sandwiched between ITO anode and Al cathode was prepared. This device was operated with forward (ITO positive, Al negative) and reverse (ITO negative, Al positive) bias. The thickness of the PI film amounted to 165 nm and that of the Al electrode to 100 nm. This device revealed the current–voltage characteristic shown in figure 3. The onset field for reverse bias injection is $1{\cdot}8 \times 10^6\,\mathrm{V\,cm^{-1}}$ and that for forward bias injection is slightly lower amounting to $1{\cdot}3 \times 10^6\,\mathrm{V\,cm^{-1}}$. The PI did not show any emission when operated in these field regions.

We also determined the current–voltage characteristics of the polarized LED device, consisting of the layer sequence glass/ITO/polyimide(**2**)/LC polymer(**1**)/Al. The layer thicknesses were in this case 30 nm for the PI, 130 nm for the LC polymer and 100 nm for the Al

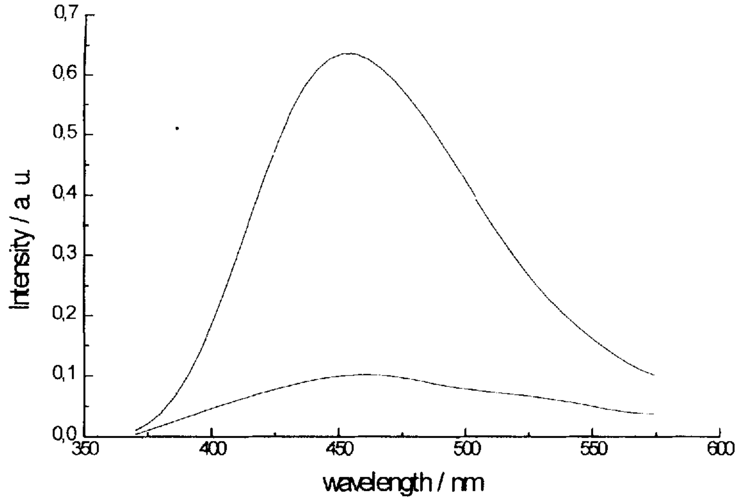

Figure 2. Electroluminescence spectra of **1** with the polarizer parallel (upper curve) and perpendicular (lower curve) to the rubbing direction.

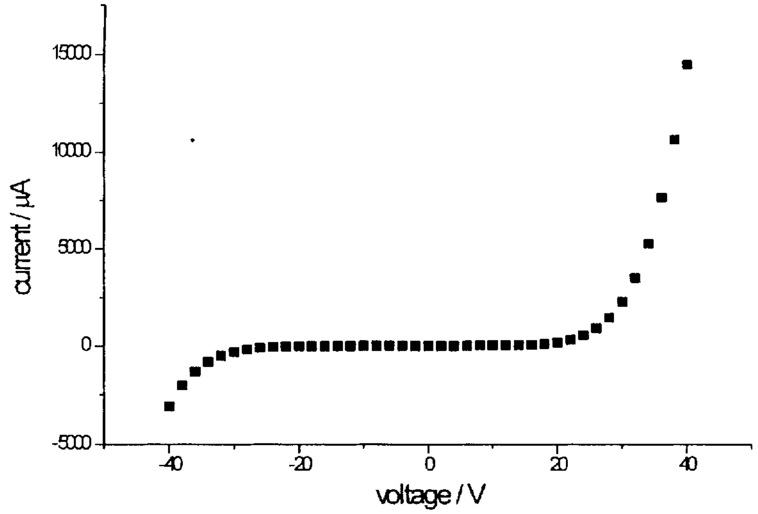

Figure 3. Current–voltage characteristic of a device consisting of ITO/Polyimide(**2**)/Al. The sample thickness was 155 nm (without Al).

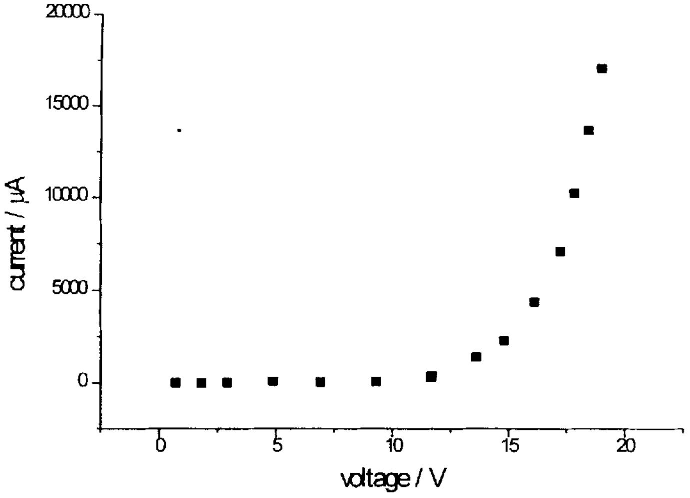

Figure 4. Current–voltage characteristic of the two layer light emitting diode consisting of ITO/Polyimide(**2**)/LCP(**1**)/Al. The sample thickness was 160 nm (without Al).

contact. The onset field for electroluminescence in these devices turned out to be $1{\cdot}3 \times 10^6\,\mathrm{V\,cm^{-1}}$ (figure 4). The expectation that the PI used for the orientation of the LCP may destroy the device performance is thus incorrect.

5. Conclusion

It is apparent that liquid crystalline arylenevinylene main chain polymers can be used in LEDs to produce a linearly polarized emission. The polymer rubbing method applied here is particularly attractive because it can be used in mass production and for manufacturing large area devices. The latter are expected to become an important area of application for polymeric LEDs.

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