Emission of polarized light from liquid crystalline segmented poly(arylenevinylene)s

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SUMMARY: Polyesters with substituted bis(styryl)benzene segments, biphenylene segments, and linear aliphatic spacers in the main chain were obtained by polycondensation. These polyesters show intensive photoluminescence and exhibit thermotropic behavior. UV dichroism, polarized photoluminescene, and polarized electroluminescence were observed when films of the polyesters were cast from solution on rubbed polyimide and subsequently annealed. LC phases get disorders with increasing amount of biphenylene moieties in the main chain. The macroscopic order parameters derived thereof are a nonlinear function of the order of the LC-phase.

Introduction

Solid state photoluminescence and electroluminescence from polymers is, in general, unpolarized. The emission of linearly polarized light, however, is of great interest for instance for background illumination of displays. This requires orientation of the polymer which has been achieved by mechanical orientation[1,2], by rubbing of polymer films[3], by Langmuir-Blodgett films[4], and by conversion of polymer precursors on prealigned substrates[5]. All of these techniques have their own merits and limitations. The orientation of liquid crystalline polymers on rubbed polyimide substrates has received particular attention since this utilizes a well-established technique in display technology[6-8].

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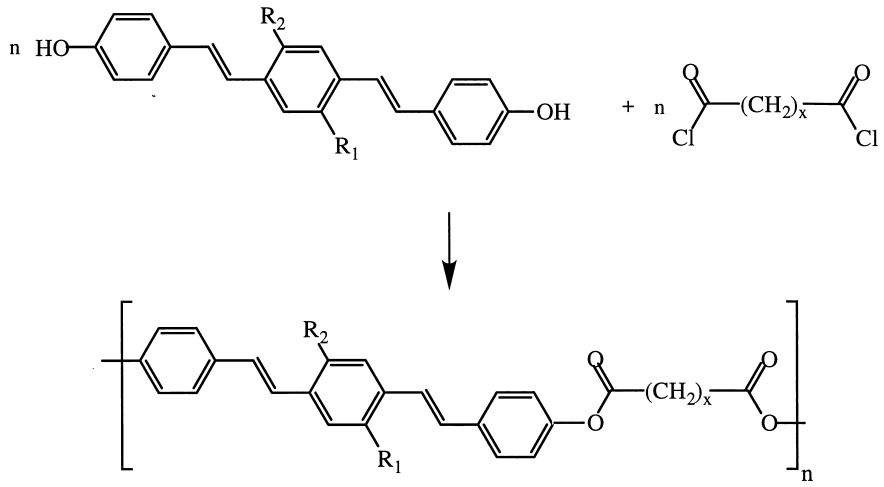
Results and discussion

Light-emitting polyesters were realized by polycondensation of linear aliphatic diacid dichlorides and α,ω-dihydroxy-functionalized bis(styryl)benzenes derivatives (Scheme 1). Details of synthesis and characterization are given in Lit[9]. Particular attention has received the phenyl-substituted polyester **1** with a spacer consisting of 10 methylene units.

Scheme 1



R_1 = phenyl, R_2 = H, x = 10 = polyester **1**

Polyester **1** shows excellent solubility in organic solvents at room temperature, which allows film casting by spin coating. It forms smectic-A phase films as proved by wide angle X-ray scattering[9]. The glass transition temperature is at 77°C. This polyester transforms into the isotropic phase at 179°C without passing through a nematic phase.

The optical properties such as the absorption and emission spectra of this polyester correspond to the optical properties of the bis(styryl)benzene derivative used as monomer. The absorption spectrum is characterized by λ_{max} = 350 nm and the photoluminescence spectrum by λ_{max} = 443 nm. The emission color is blue-green.

Spin coating of polyester **1** on rubbed polyimide (Fig. 1) results in macroscopic orientation as proved by UV-dichroisim (Fig. 2)[6]. In UV-dichroism measurement the absorption was

recorded with a polarizer parallel and perpendicular to the rubbing direction, respectively. The absorption turned out to be large parallel to rubbing direction and small in the perpendicular direction. Consequently, the transition dipole moment of the chromophores is oriented predominantly along the rubbing direction. A macroscopic order parameter S = 0.67 was derived from the dichroitic ratio.

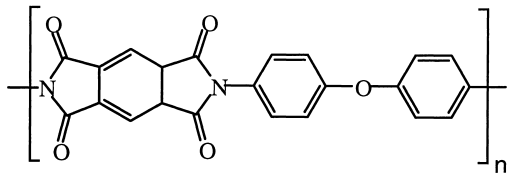


Fig. 1: Chemical Structure of the polyimide used as alignment layer

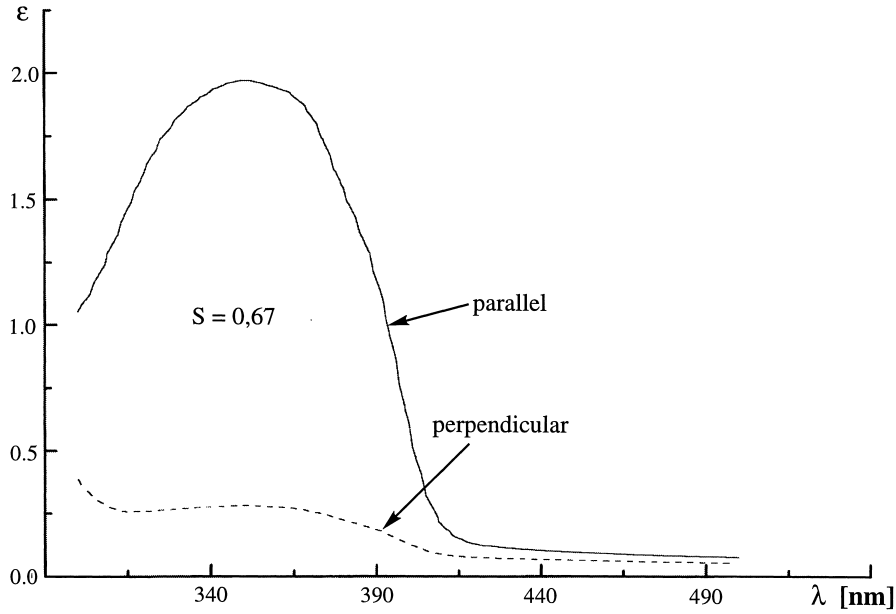


Fig. 2: Absorption spectra of oriented polyester **1** for different angles of the polarizer with respect to the rubbing direction

However, the macroscopic order parameter depends significantly on processing parameters[7]. Key step is annealing of the spin coated polyester film on the rubbed polyimide substrate at about 140°C for at least 30 minutes which can be concluded from measurement of the

macroscopic order parameter obtained from absorption spectra as a function of annealing temperature (Fig. 3) and annealing time (Fig. 4).

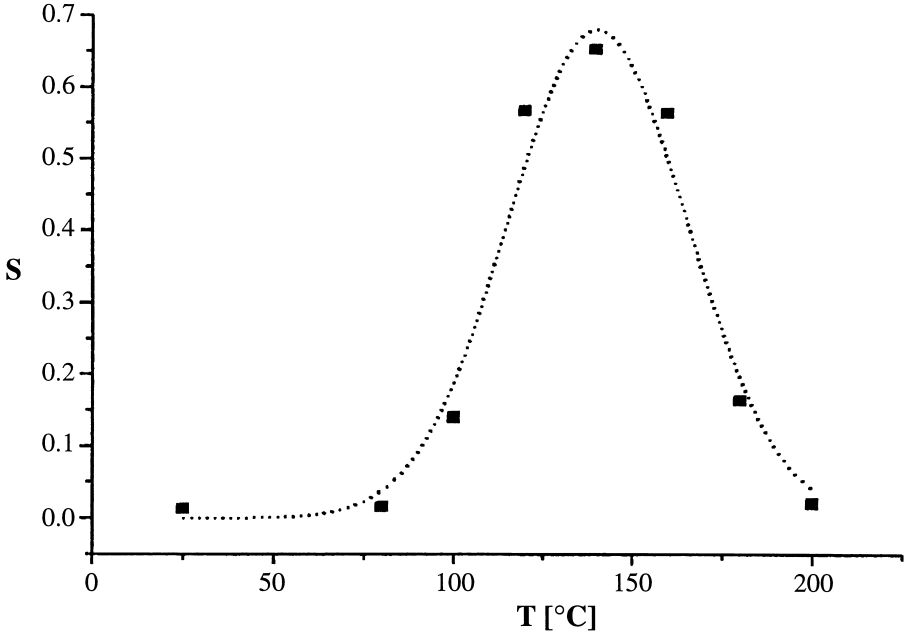


Fig. 3: Macroscopic order parameter as a function of the annealing temperature of polyester **1**

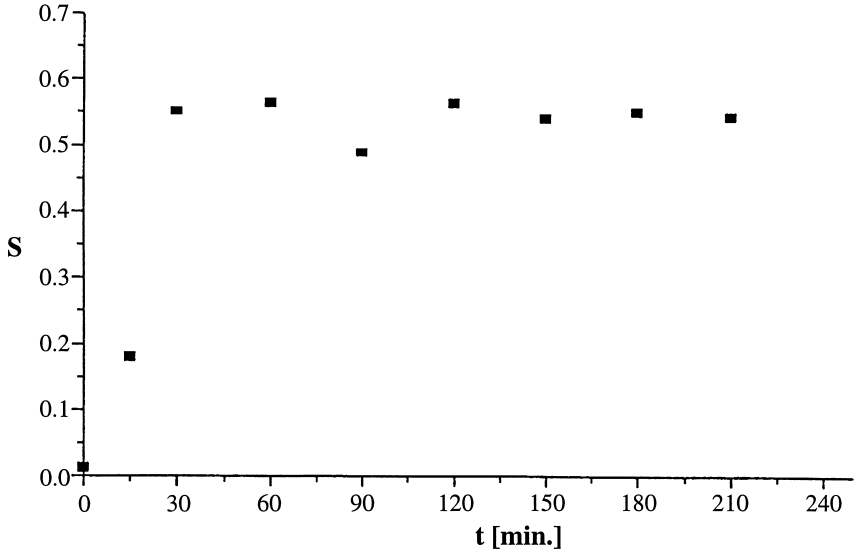


Fig. 4: Macroscopic order parameter as a function of the annealing time of polyester **1**

Macroscopic orientation was confirmed by photoluminescence measurements performed on the samples again using polarizers with different directions relative to the rubbing direction (Fig. 5). The spectra exhibit a substantial difference in the intensity for the polarizer parallel and perpendicular to the rubbing direction.

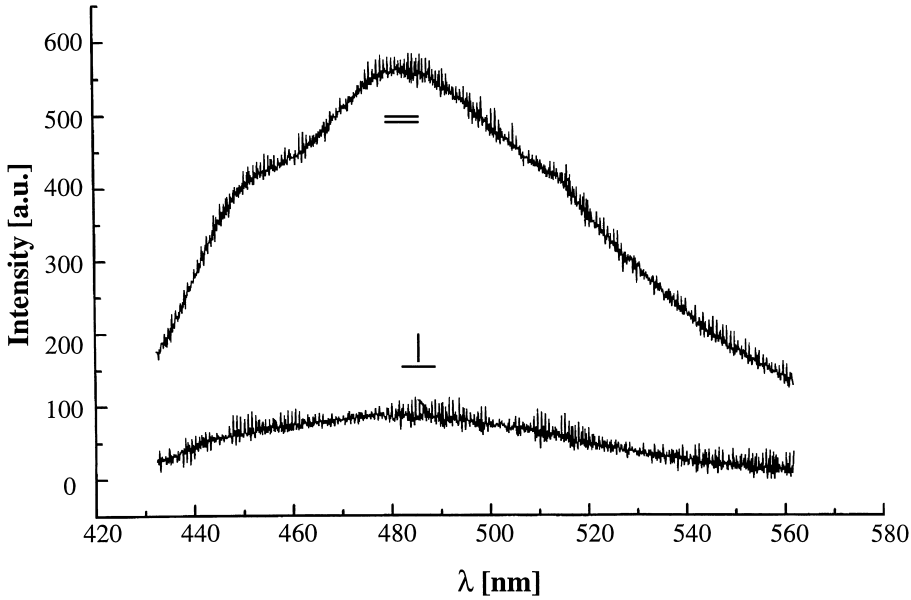


Fig. 5: Photoluminescence spectra of polyester **1** with the polarizer parallel and perpendicular to the rubbing direction

The current-voltage characteristics of a device composed by a polyimide layer sandwiched between an indium-tin oxide (ITO, negative) and an Al (positive) electrode showed the onset of reverse bias injection is 1.8 x 10^6 V/cm and that of forward injection is 1.3 x 10^6 V/cm[7]. (No visible light emission of the polyimide was observed). From this it can be concluded that polyimide is suitable as orientation layer in LED devices allowing charge transport and charge injection.

Multilayer LED devices consisting of glass/ITO/polyimide(rubbed)/polyester **1** (aligned)/Al showed the emission of polarized light[7]. Rubbing of polyimide and alignment of polyester **1** was performed in the same manner as described above. The shape of the electroluminescence spectrum is very similar to the corresponding photoluminescence spectrum. The analysis using the polarizer parallel and perpendicular to the rubbing direction again revealed significant differences of light intensities (Fig. 6). This indicates preferential alignment of the

chromophores along the rubbing direction. The macroscopic order parameter was calculated to be 0.64.

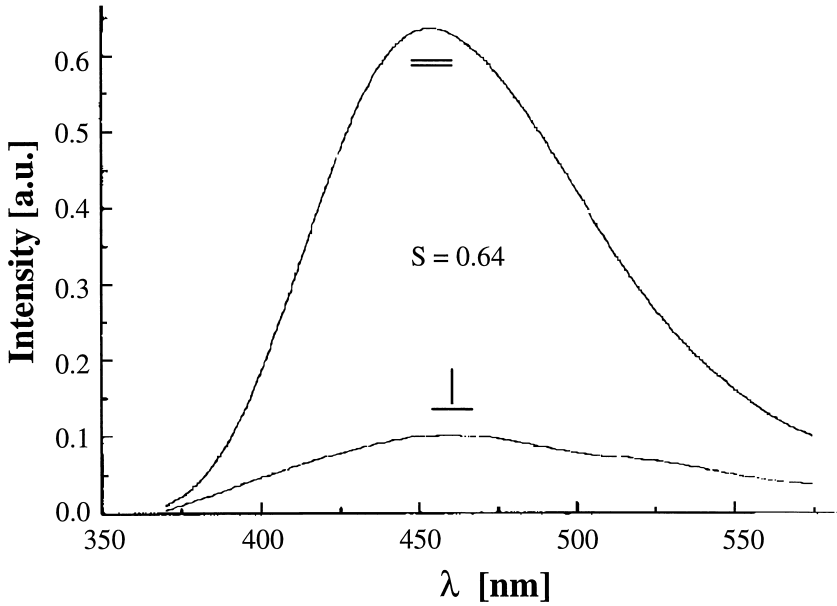
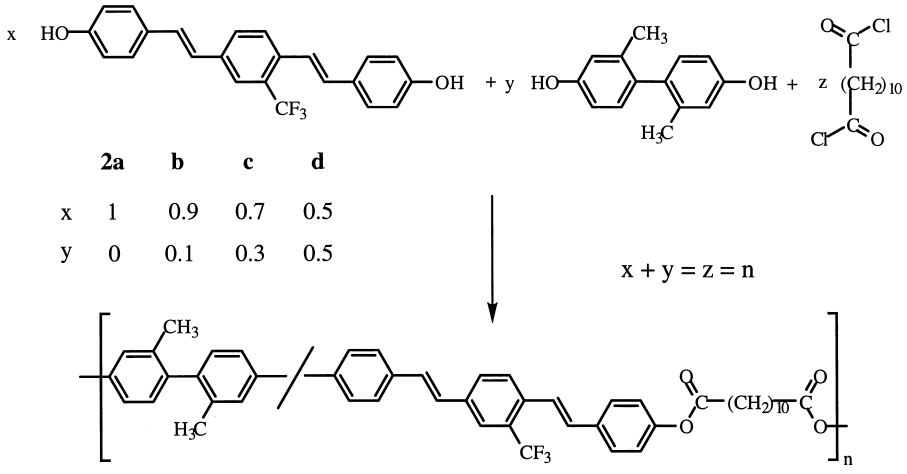


Fig. 6: Electroluminescence spectra of polyester **1** with the polarizer parallel and perpendicular to the rubbing direction

The performance of this device judged with respect to the current voltage-characteristics is satisfactory in spite of the use of segmented conjugated polymer and polyimide layer sandwiched between ITO and the layer of the electroluminescent polymer. The thickness of the polyimide layer amounted to be 30 nm and 130 nm for polyester **1**. The onset field for electroluminescence was 1.3 x 10^6 V/cm. Significant improvement could certainly be achieved by using of modified polyimides as alignment layer with improved hole transport characteristic.

The impact of the state of the mesophase on its ability to achieve a macroscopic orientation by polyimide aligment layers was investigated using the trifluoromethyl-substituted polyester **2a** and its copolyesters **2b-d** (Scheme 2). The synthesis of polyester **2a** was accomplished similar to the synthesis of polyester **1**. For the synthesis of copolyesters **2b-d** varying amounts of 4,4′-dihydroxy-biphenylene as comonomer were used under the conditions of a statistical copolycondensation.

Scheme 2:



	2a	b	c	d
x	1	0.9	0.7	0.5
y	0	0.1	0.3	0.5

2

Polyesters **2** are characterized by excellent thermal stability in the melt-state without solidification (crosslinking), which has been observed with many other poly(arylene vinylene)s in the melt state. The smectic A phase observed for polyester **2a** becomes more and more disordered with increasing content of biphenylene moieties (polyesters **2b-d**) as revealed by the decrease of the heat of transition observed for the endotherm in the DSC heating runs (Fig. 7).

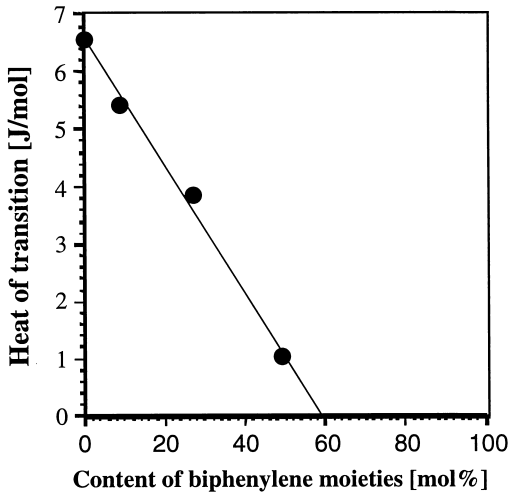


Fig. 7: Heat of transition of DSC endotherm of **2a-d** as a function of biphenylene content

The incorporation of biphenylene moieties in the polyester main chain does not have a dramatic impact on the optical properties, which is shown exemplarily for the photoluminescence spectra (Fig. 8).

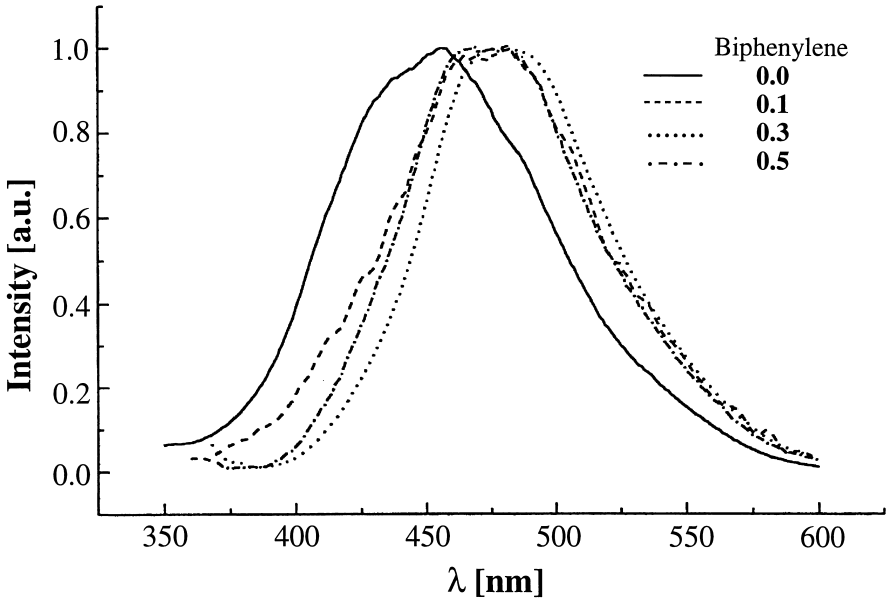


Fig. 8: Photoluminescence spectra of polyesters **2a-d** measured in chloroform solution at 20 °C.

However a dramatic effect is observed according to UV dichroism for the macroscopic order parameter with increasing content of biphenylene moieties (Fig. 9). Polyester **2a** without biphenylene moieties shows near zero macroscopic order. In contrast, polyester **2c** with 30% biphenylene moieties (molar) shows a signficant macroscopic order parameter of S = 0.55. S drops again with further increase of the amount of biphenylene moieties.

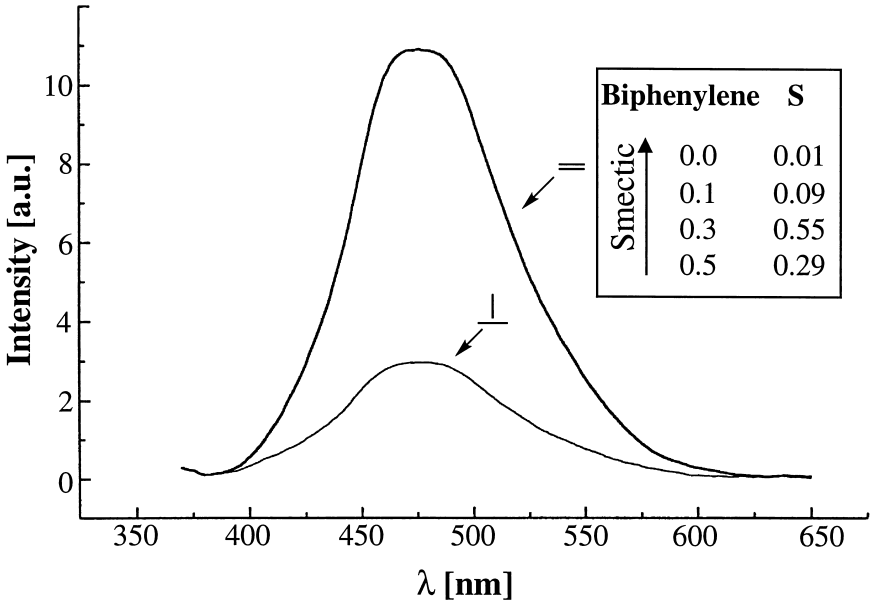


Fig. 9: Absorption spectra of oriented polyester **2c** for different positions of the polarizer with respect to the rubbing direction and macroscopic order parameters as a function of the content of biphenylene moieties

Conclusions

It can be concluded that segmented light-emitting liquid crystalline polymers are well suited for macroscopic orientation on rubbed polyimide substrates. Significant UV-dichroism, polarized photoluminescence, and polarized electroluminescence were observed for these oriented samples. Initial results on the impact of the order within the liquid crystalline phase indicate that a transition state near smectic - nematic transition results in the highest degree of orientation, which in turn results in the highest polarization.

References

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