Supramolecular structure and electro-optical properties of functionalized maleic anhydride copolymers

Burkhard Schulz[1]*, Birgit Dietzel[2], Yvette Kaminorz[3]

[1] University of Potsdam, Research Center Thin Organic and Biochemical Films,
Am Neuen Palais 10, 14469 Potsdam, Germany
[2] Institute of Thin Film Technology and Microsensorics, Kantstrasse 55, 14513
Teltow, Germany
[3] University of Potsdam, Institute of Physics, Condensed Matter Physics,
Am Neuen Palais 10, 14469 Potsdam, Germany

SUMMARY: New amphiphilic maleic acid copolymers containing oxadiazole rings as pendent groups were synthesized. Most of them form excellent Langmuir-Blodgett films. The polymers were characterized by UV/Vis- and fluorescence spectroscopy and show electroluminescent behavior in the green-yellow light region.

Introduction

Electron deficient moieties such as oxadiazoles are very often used in organic light emitting devices (OLED) both as emitting layer or as electron transport materials [1-5]. The emission of polarized light is of particular interest because of the possible applications as polarized backlight materials in LC-displays. For the polarized emission of light a high degree of orientation of the electroluminescent active molecules within the layers is necessary. Only few is known about the formation of oriented layers based on oxadiazoles. One possibility is the preparation of Langmuir-Blodgett (LB) films. The application of amphiphilic substituted diphenyloxadiazoles in the Langmuir-Blodgett technique is described in [6]. Because, the stability of the ordered multilayers is limited for some of these compounds which are also active in electroluminescence [7] the synthesis of amphiphilic polymers was investigated. It is well known from [8,9] that maleic acid copolymers containing pendent hydrophobic side-groups form stable LB films. The amphiphilic character of such polymers is caused by hydrophilic groups directly linked to the main chain. Here, we describe the synthesis of amphiphilic polymers containing oxadiazole moieties as pendent groups. These polymers

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form stable monolayers at the air-water interface which can be deposited as LB multilayers on solid substrates. The electroluminescent behavior of the polymers is also described.

Experiments

The synthesis of the oxadiazoles were reported previously [6]. The polymer synthesis were carried out as follows:

A solution of the oxadiazole derivative in N-methylpyrrolidone (NMP) was added slowly under stirring to a solution of maleic anhydride/styrene-copolymer in NMP at room temperature. After the mixture was stirred at room temperature for 2 h, the solution was heated to 120 °C with stirring for 5 h. The reaction mixture was cooled to room temperature and was poured into benzene or water. The resulting precipitate was filtered off, washed with water and dried. The polymers are characterized by elemental analysis and IR-spectroscopy.

The surface-pressure-isotherms (π-A-isotherms) and the deposition of the LB-films were performed in a Nima 611 trough (Nima Technology Ltd. Coventry, UK) with a Wilhelmy plate system. The polymers were dissolved in dimethylacetamide/benzene (2:1) mixture to a concentration of approximately 0,5 mg/ml and were spread onto a subphase of pure Milipore-Q-water. The subphase temperature was held constant at 21°C. The film was compressed with constant barrier speed of 5 cm/min.

The deposition of polymers was carried out at a surface pressure of 30 mN/m onto silicon, gold and quartz. Polymeric films containing several hundred layers were prepared. Using the special trough Nima 622 alternating layers of two distinct polymers were deposited to produce non-centrosymmetric structure.

The photoluminescence (PL) and absorption measurements were carried out in NMP-solution. For preparing an electroluminscent (EL) device a 6 mg/ml solution was spin coated at 1000 rpm for 2 min with additional heating after 1 min on an ITO substrate. On top of the smooth, pin hole free film, an aluminum electrode was evaporated through a shadow mask. The active are was estimated to be 2x2 mm^2.

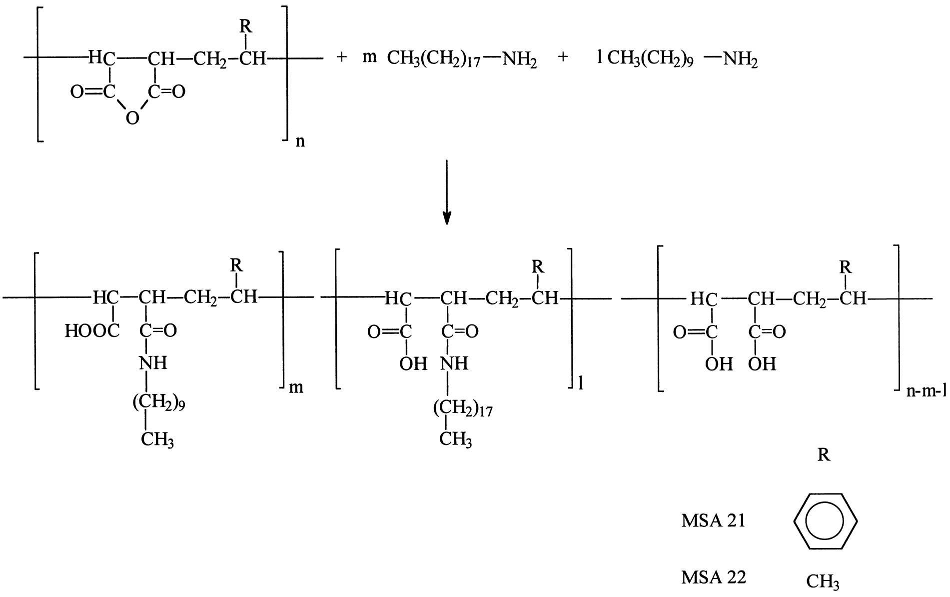
The absorption behavior was investigated with a Lambda 16 UV/ Vis Spectrometer by Perkin Elmer. The polymer solution ($<3\times10^{-5}$ molar) as well as the low molar mass solution of AF148 (5×10^{-5} molar) was measured in a quartz cuvette without reference.

For PL measurements an UV lamp, peaking at 365 nm was used as excitation source. For recording the PL spectra, the emitted light was transferred by an optical fiber (y-shaped) to the solution in a quartz cuvette (MSA39: 4×10^{-3} molar; AF148: 9×10^{-3} molar). From the sample the emitted light was transferred to an InstaSpec CCD detector used with an MS257 monochromator from L.O.T. Oriel Instruments. The same equipment was also used for recording the EL spectrum.

Results and discussion

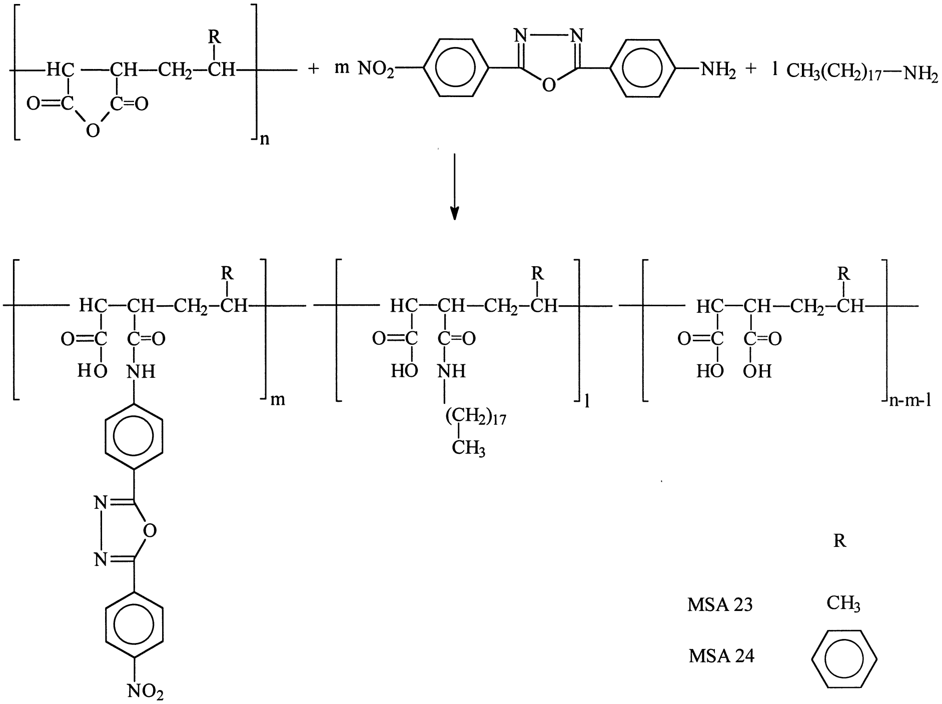
The synthesis of the maleic acid (MA) copolymers was realized via a polymer analogues reactions [13] as shown in the schemes 1-3.

Because of their low amphiphilicity MA-copolymers with styrene or propene cannot be used directly for the LB-technique. Therefore the introduction of additional hydrophobic side chains was realized by reaction of the copolymers with aliphatic amines. But, when only one alkylamine compound is introduced into the polymers the tendency for crystallization at the water surface prevent the formation of stable Langmuir films [8,9]. Therefore, for the synthesis of the copolymers MSA21 and MSA22 alternating copolymers of maleic anhydride with styrene or propene were reacted with a mixture of two alkylamines of different lengths (scheme 1). The polymers are soluble in chloroform and form stable Langmuir films which can be deposited onto solid substrates (see table 1).



Scheme 1

When one of the aliphatic amine in scheme 1 is replaced by an amino substituted oxadiazole derivative the copolymers MSA23 and MSA24 can be prepared (scheme 2). The content of the oxadiazole unit is about 0.5 Mol%. These copolymers form stable Langmuir layers with a high collapse pressure (fig.1). A similar behavior is observed for other amphiphilic MA-copolymers [8,9,10,11].



Scheme 2

The use of the alternating maleic anhydride copolymer with octadecene results in polymers which contain the hydrophobic substituent in each repeating unit (scheme 3). Whereas MSA33 contains 0.9 Mol% oxadiazole containing units, this content is 0.6 Mol% for MSA37and MSA39, respectively. Although the oxadiazole unit is statistically distributed along the main chain of the macromolecules, the copolymers MSA33, MSA37 and MSA 39 form stable LB-films.

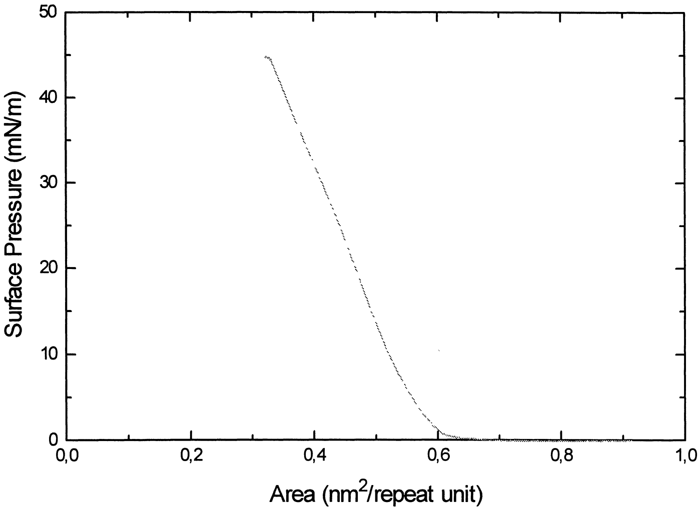
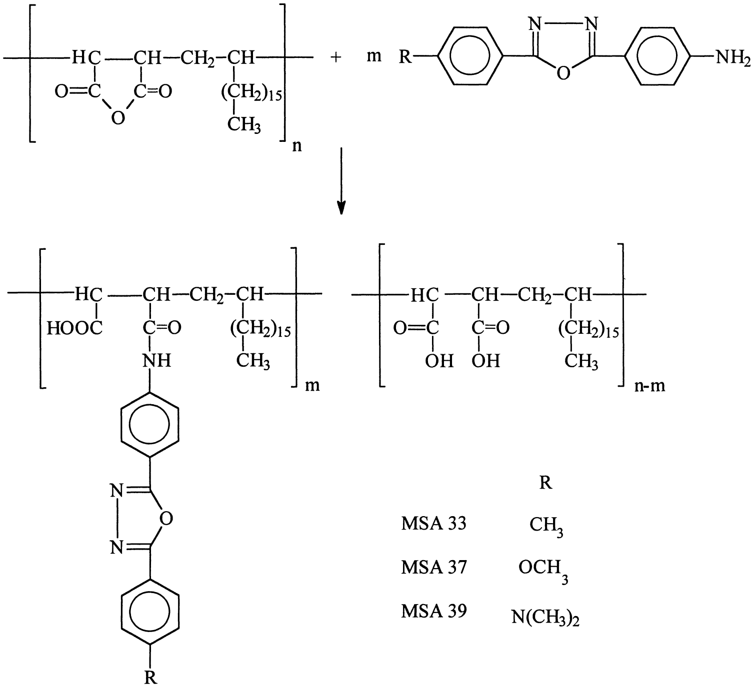


Fig. 1: π-A isotherm of MSA 24



Scheme 3

The investigations of the LB-film structures were performed by a combination of X-ray measurements, AFM (atomic force microscopy) and molecular modeling. The X-ray was recorded for 18 multilayers of polymers. As calculated from the length of the side chains the layer thickness of the MA-copolymers vary between 3 and 4 nm as summarized in table 1.
The Kiessig fringes in the low angle region confirm a smooth surface topography of the film and a successful transfer of the layers [12]. The RMS roughness of 10 layers is between 6 and 70 Å.

Table 1: Layer thickness d of the LB-films measured by WAXS[12].

Substance	m	l	$d_{x\text{-ray}}$ [nm]
MSA 22	0.4	0.4	3,4
MSA 23	0.45	0.45	4,0
MSA 24	0.5	0.4	2,8
MSA 33	0.9	-	3,5

It is well known from our former results that oxadiazole derivatives containing the dimethylamino group as substituent in para position show electroluminescence in single layer devices [7]. Therefore, we have also investigated the absorption, PL and EL of MSA 39. The optical properties of the side chain polymer MSA 39 were compared to that of the corresponding low molar mass amphiphilic compound AF148 (Fig.2). The electroluminescent behavior of AF148 was discussed previously [7].

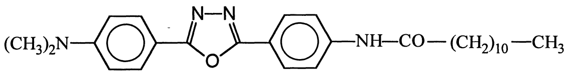


Fig.2: Chemical structure of the MSA39-corresponding low molar mass compound AF148

MSA39 solved in NMP shows the main absorption peak at 341 nm (Fig.3). The absorption of the side chain polymer is comparable in peak wavelength and shape with that of AF148. The PL emission peaks at 485 nm, which is about 30 nm red shifted compared to the PL of AF148. The ITO/ MSA39/ Al single layer device shows also electroluminescence (Fig. 3). Surprisingly, the EL emission of the low molar mass compound AF148 is blue [7] but the EL of the polymer MSA39 is green-yellow to the eye.

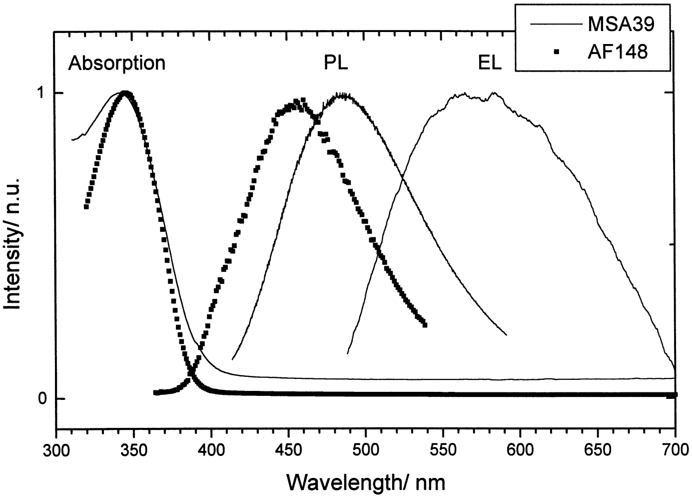


Fig. 3: Absorption and PL spectra of MSA39 compared to that of AF148 (in NMP) and EL spectrum of an ITO/ MSA39/ Al device

Conclusion

New amphiphilic copolymers containing oxadiazole units as pendent groups were synthesized. It has been shown that stable LB-films were formed both by using maleic acid polymers with octadecene as comonomer and by introduction of hydrophobic alkyl chains via amidization reaction on maleic anhydride copolymers.

Polymers containing dimethylamino substituted diphenyl oxadiazole as pendent unit show electroluminescence in the region of green-yellow light which makes them suitable for application in OLED.

References

1. Q. Pei, Y. Yang, *Chem. Mater.* **7**, 1568 (1995)
2. T. Tsutsui, E. Aminaka, H. Tokuhisa, *Synth. Met.* **85**, 1201 (1997)
3. H. Tokuhisa, M. Era, T. Tsutsui, *Synth. Met.* **85**, 1161 (1997)
4. E. Aminaka, T. Tsutsui, S. Saito, *Jpn. J. Appl. Phys. Part 1* **33**, 1061 (1994)
5. S. Yin, Z. Wang, X. Yang, W. Huang, F. Zhang, X. Xu, *J. Appl. Polym. Sci.* **74**, 3535 (1999)
6. A. Freydank, S. Janietz, B. Schulz, *Electroanal. Chem.* **456**, 61 (1998)
7. Y. Kaminorz, B. Schulz, L. Brehmer, *Synth. Met.* **111-112**,75 (2000)

8. R. H. Tredgold, *Thin Solid Films* **152**, 223 (1987)
9. I. P. Aspin, A. M. Barros, P. Hodge, C. R. Towns, Z. Ali-Adib, *Polymer* **36**, 1707 (1995)
10. S. Schrader, V. Zauls, B. Dietzel, C. Flueraru, D. Prescher, J. Reiche, H. Motschmann, L. Brehmer, *Mater. Sci. & Engin.* **C 8-9**, 527 (1999)
11. P. Karageorgiev, B. Stiller, D. Prescher, B. Dietzel, B. Schulz, L. Brehmer, *Langmuir* **16**, 5516 (2000)
12. J. Reiche, in preparation
13. M. Rätzsch, N. Thi Hue, *Acta Polymerica* **30**, 93 (1979)