Molecular weight dependence of birefringence of thin films of the conjugated polymer poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene]

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We prepared thin films of the conjugated model polymer poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) by the spin coating of polymer samples whose weight-average molecular weight was varied from $10^4 – 10^6$ g/mol. Waveguide prism coupling and polarized optical transmission and reflection spectroscopy were used to determine the refractive index, birefringence, and intrinsic absorption coefficient of each film. We show that these optical constants significantly depend on the molecular weight of the polymers. With decreasing molecular weight, the birefringence is strongly reduced and a nearly isotropic refractive index is approached. We conclude that the molecular weight primarily determines the extent of polymer chain alignment in the film plane. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1739513]

Semiconducting conjugated polymers have outstanding optoelectronic properties which make them attractive materials for applications, such as light-emitting diodes,[1,2] plastic lasers,[3,4] photovoltaic,[5,6] or nonlinear all-optical switching devices.[7–9] These applications require thin films with thicknesses in the range of 50–500 nm, which are often prepared by spin coating. Such films of conjugated polymers frequently exhibit uniaxial anisotropy due to preferred alignment of the polymer chains parallel to the film plane.[10,11] Because the main electric polarizability and transition dipole moment of the conjugated π-electron system are parallel to the chain direction, the anisotropic orientation of chain segments is strongly correlated with significant birefringence of the films, i.e., refractive indices at transverse electric (TE) and transverse magnetic (TM) polarizations differ considerably with $n_{TE} > n_{TM}$. The design of devices clearly needs precise knowledge of the optical constants of thin films, in particular their birefringence which was reported for various conjugated polymers.[10,12–16]

A closer inspection of the frequently investigated model polymer poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene] [(MEH-PPV) see Fig. 1 for its chemical structure], reveals a striking disagreement of the reported refractive indices.[13–17] Our preliminary study[18] indicates that this problematic inconsistency is caused by the large variations of the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the different MEH-PPV samples studied. Most reports of optical properties of MEH-PPV did not pay appropriate attention to the influence of M_n and M_w and frequently, their values are not provided at all.

The main objective of this letter is to reveal the striking influence of the molecular weight of MEH-PPVs on the op-tical constants of thin films, in particular on their refractive index and birefringence. Our results will show that the birefringence is strongly reduced and can be nearly absent at low molecular weight samples. This indicates that the average orientation of polymer chain segments, with respect to the film plane, depends strongly on molecular weight.

A large variation of molecular weight of MEH-PPV can be accomplished by different synthetic routes. The frequently used, so-called Gilch dehydrohalogenation route[19] yields high molecular weight polymers with M_w in the order of $10^5 – 10^6$ g/mol. However, M_w can be reduced by appropriate choice of end-cappers in the synthetic process. Another synthetic approach to MEH-PPV with a very well defined chain structure was realized by using the Horner-type polycondensation route which yields polymers with M_w in the typical order of several 10^4 g/mol.[20] We have investigated the MEH-PPVs (**1**–**8**) listed in Table I. We obtained polymers from different sources and synthetic routes. The MEH-PPVs **2**–**4** and **6** were synthesized as described in Refs. 19
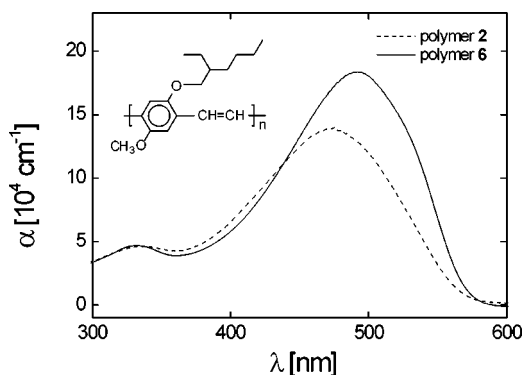

FIG. 1. Spectra of intrinsic absorption coefficient α of thin films of MEH-PPVs (inset shows chemical structure) with different molecular weight. Dashed line—polymer **2**, solid line—polymer **6**.

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TABLE I. Properties of MEH-PPVs from different synthesis pathways and molecular weights. All optical data are from studies of thin films.

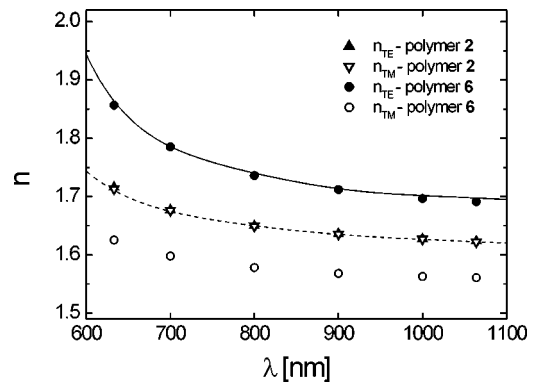| Polymer	Route	M_w (g/mol)	M_n (g/mol)	λ_{max} (nm)	α_{max} (10^4 cm^{-1})
1	Gilch	9.3×10^3	4.8×10^3	472	13.2
2	Horner	1.3×10^4	6.4×10^3	474	13.9
3	Horner	2.5×10^4	9.1×10^3	477	15.0
4	Horner	4.03×10^4	1.41×10^4	489	16.6
5	Gilch	2.65×10^5	8.71×10^4	489	18.2
6	Gilch	2.76×10^5	1.05×10^5	491	18.4
7	Gilch	4.2×10^5	1.08×10^5	495	19.1
8	Gilch	1.6×10^6	1.3×10^5	495	19.4

FIG. 2. Dispersions of refractive indices of MEH-PPVs. Data points are from prism coupling experiments at TE polarization (full symbols) and TM polarization (open symbols). Triangles—polymer **2**, circles—polymer **6**. Lines are from transmission-reflection experiments at TE polarization (dashed line–polymer **2**, solid line–polymer **6**).

and 20. Polymers **1**, **5**, and **7** were obtained from American Dye Source (Quebec, Canada) and **8** was provided by Covion (Frankfurt, Germany). Molecular weights shown in Table I were measured by gel permeation chromatography using polystyrene standards and tetrahydrofuran as eluent.

Thin films on fused silica substrates were deposited by spin coating from freshly prepared and filtered (0.5–1 μm syringe filters) toluene solutions under a laminar flow hood to minimize dust particles. They were subsequently placed in a vacuum oven at elevated temperatures ($T \approx 50\,^\circ$C) for about 6 h to remove residual solvent. The film thickness d was measured with a Tencor Model P10 step profiler. We used films with $d \approx 50$ nm for spectroscopic studies and thicker films (400–800 nm) for optical waveguides. The thickness was controlled by the variation of concentration and spinning speed. However, it was not possible to prepare waveguides from polymer **8** because we were not able to spin coat films thicker than 150 nm due to solubility problems.

Transmission and reflection spectra of thin films ($d \approx 50$ nm) were measured with a spectrophotometer (Perkin–Elmer Model Lambda 900) with the light beam polarized parallel to the film plane. Intrinsic absorption coefficients $\alpha(\lambda)$ and refractive index $n(\lambda)$ were evaluated from the transmission and reflection spectra using the iteration procedure as described previously.[21,22] Typical spectra of the intrinsic absorption coefficient for polymers **2** and **6** are shown in Fig. 1. The values α_{max} and wavelengths λ_{max} of the maximum of the main absorption band are shown in Table I for all investigated polymers. The λ_{max}-data have an estimated uncertainty of ± 2 nm because of broad absorption bands. The experimental error of α_{max} is approximately 5% due to experimental errors in the thickness d. The films of polymers **1**–**8** show a systematic trend to larger values of α_{max} with increasing M_w which is related to changes of the average polymer chain orientation as will be discussed below.

The refractive index of MEH-PPV waveguides with typical thicknesses ranging from 400–800 nm were determined by prism coupling using the *m*-line technique[23] as described earlier.[9] The following lasers were used: HeNe ($\lambda = 633$ nm) and an optical parametric generator which can be tuned in the range of 680 nm–2000 nm (EKSPLA Model PG 501 pumped by the second harmonic of a ps-Nd:YAG laser, EKSPLA Model PL 2143B).

The dispersions of the refractive indices n_{TE} and n_{TM} are shown in Fig. 2 for the MEH-PPVs **2** and **6**. While the high molecular weight polymer **6** shows a typical strong birefrin-

gence, the low molecular weight polymer **2** has a nearly isotropic refractive index. For comparison, spectra of n_{TE} of thin films evaluated from transmission-reflection measurements are also shown. The results of both experiments agree very well. This shows that the refractive index does not significantly depend on the film thickness, at least for 50 nm $< d <$ 800 nm. In Fig. 3, n_{TE} and n_{TM} at $\lambda = 1064$ nm are plotted versus M_w for all polymers **1**–**8**. We emphasize that although MEH-PPVs were synthesized in different laboratories via different routes, the results displayed in Fig. 3 show good reproducibility and a continuous dependence of the refractive index data on the molecular weight. At high molecular weights ($M_w > 5 \times 10^5$ g/mol), the degree of birefringence is very large and seems to approach a saturation limit. The values of n_{TE}, and n_{TM} in this region are in reasonable agreement with those reported recently.[13–15] With the decrease of the molecular weight, the birefringence is significantly reduced and we observe a nearly complete loss of birefringence with a remaining $n_{TE} - n_{TM}$ less than 0.005 at $M_w < 1.5 \times 10^4$ g/mol.

We discuss our results in the context of the average orientation of polymer chain segments with respect to the layer plane. As indicated at the beginning of this letter, there is a strong correlation between average chain orientation and optical constants of thin films of conjugated polymers. The
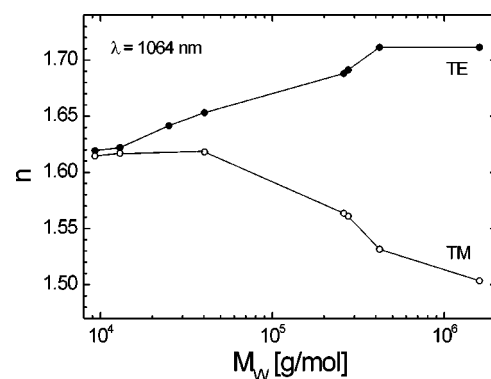

FIG. 3. Molecular weight dependence of refractive index and birefringence of thin films of MEH-PPVs **1**–**7** measured by prism coupling at 1064 nm using TE and TM polarizations, respectively. n(TE) of **8** is measured by transmission-reflection spectroscopy. (n(TM) of **8** is extrapolated from Ref. 15.) The experimental error of n is less than the symbol size.

main electronic $\pi - \pi^*$ transition at $\lambda_{\max}$, and the major electric polarizability which is related to n, are both polarized in the chain direction of PPV. Consequently, $\alpha_{\max}$ and n are largest if the electric-field vector **E** of incident light is parallel to the chain direction. If the PPV chain segments become increasingly aligned parallel to the film plane, it is evident that $\alpha_{\max}$ which is measured at **E** parallel to the film plane and n_{TE} will increase and, correspondingly, n_{TM} will decrease. Our experimental results show this correlated dependence of n_{TE}, n_{TM}, and $\alpha_{\max}$ on M_w quite well. This correlation strongly indicates that spin cast films of MEH-PPVs with a larger M_w have an increasing amount of PPV chain segments aligned parallel to the film plane.

We conclude that the optical properties of thin films of MEH-PPV, in particular their birefringence, are primarily related to the polymer chain orientation which depends significantly on the molecular weight, especially in the range $M_w < 5 \times 10^5$ g/mol. Thin films of *high* molecular weight MEH-PPV have most chain segments oriented parallel to the layer plane (*large* birefringence)—in contrast to *low* molecular weight samples which have nearly random orientation of chain segments (*small* birefringence). We expect that other conjugated polymers with rigid backbones like MEH-PPV exhibit similar effects. This result can have a strong impact on device applications using thin films of conjugated polymers because the polymer chain orientation directly relates to their optoelectronic properties. Therefore, any report of optoelectronic data of conjugated polymers must refer to details of synthesis and molecular weight in order to avoid inconsistencies in scientific literature of these materials.

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