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Intermolecular Order of Poly-(2,5-dimethyl-*para*-phenylene vinylene) and Poly-(*para*-phenylene vinylene) – A Comparison

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Summary. Poly-(*para*-phenylene vinylene) (**2b**, *PPV*) and poly-(2,5-dimethyl-*para*-phenylene vinylene) (**1b**) were prepared *via* the formation of a double bond by thermal elimination of an octylsulfinyl side group at 200°C under vacuum. X-Ray diffraction experiments revealed a certain degree of long-range order within both polymers. However, considerable differences in the diffraction pattern were observed, the packing of the polymer chains within the bulk structure being responsible for these differences. Within the crystal structure of **2b**, neighbouring *PPV* chains pack in a zig-zag arrangement (herringbone pattern). Analysis of the diffraction pattern of **1b** on the basis of the crystal structure of a model compound (2,5,2′,5′-tetramethylstilbene) revealed that the molecular planes of neighbouring polymer chains pack parallel to each other. A model for the crystal structure of **1b** is given. The change of packing from a herringbone to a parallel arrangement of the molecular planes is related to the introduction of methyl groups as side chains to *PPV*.

Keywords. Poly-(*para*-phenylene vinylene); *PPV*; X-Ray diffraction; Crystal structure.

Introduction

Poly-(*para*-phenylene vinylene) (*PPV*) and its derivatives are semiconducting, π-conjugated polymers with high potential for future applications [1]. New display technology based on electroluminescence of these materials is an ongoing subject of industrial research. Since pure *PPV* is insoluble in conventional solvents, two methods have been developed to render this material processible for technological use. One way is the coupling of flexible side chains to the *PPV* polymer backbone, poly-(2-methoxy-5-(2′-ethyl-hexyloxy)-*para*-phenylene vinylene), denoted as *MEH-PPV*, being the most prominent among these soluble *PPV* derivatives [2, 3]. The second way is the use of soluble precursor polymers which can be converted by thermal treatment to *PPV* or *PPV* derivative polymers [4].

The amorphous state is preferred for technological use of *PPV* derivative polymers [5]. Depending on the preparation procedure and on the type of side

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chains, the polymer is either amorphous or semicrystalline [6]. Electrical conductivity as well as optical properties depend on the arrangement of neighbouring polymer chains [7, 8]; the orientation of neighbouring *PPV* chains relative to each other and the distance between them are of particular importance [9].

PPV crystallizes in a monoclinic symmetry (space group $P2_1/c$) with lattice constants $a = 8.30, b = 6.05, c(\text{chain axis}) = 6.58\,\text{Å}$, $\beta = 123°$ [10]. The atoms of one polymer chain are arranged approximately in one molecular plane. The molecular planes of neighbouring polymer chains are ordered in a zig-zag arrangement of neighbouring molecules (herringbone pattern), they enclose a tilt angle between 64 and 82° relative to each other [10, 11]. Few experimental data are available for *PPV* derivative polymers; *e.g.*, lattice constants of *MEH-PPV* have been determined [12]. However, the relative arrangement and the distance between the *PPV* backbones are not known. Single crystal investigations on oligomers of *PPV* with attached side chains reveal that the side chains influence the packing of *PPV* backbones considerably [13, 14]. The implementation of side chains promotes the tendency to separate the backbones from each other.

The aim of this study is to characterize two different type of *PPV* polymers which prepared *via* an identical precursor route. The only difference between both *PPV* polymers is the introduction of methyl groups at positions 2 and 5 of the phenyl ring, changing the features of the crystal structure of the polymer drastically.

Results and Discussion

The diffraction pattern of **1b** is given in the upper part of Figure 1. **1b** shows two broad peaks located at $2\Theta = 14.5°(d = 6.1\,\text{Å})$ and at $2\Theta = 25.0°(d = 3.6\,\text{Å})$. The positions of these two diffraction peaks agrees quite well with transmission electron diffraction data on methyl-substituted *PPV* ($d = 6.5$ and $3.6\,\text{Å}$ [20]).

The diffraction pattern of **2b** is given in the lower part of Fig. 1. **2b** shows only one peak at $2\Theta = 20.8°(d = 4.3\,\text{Å})$ and a shoulder at $2\Theta = 27.7°(d = 3.2\,\text{Å})$. Bars on the bottom line in Fig. 1 give the 2Θ-positions and the relative intensities of the main diffraction peaks in crystalline *PPV* ($2\Theta = 20.9°(d = 4.24\,\text{Å})$, $2\Theta = 22.3°(d = 3.97\,\text{Å})$, and $2\Theta = 28.6°(d = 3.12\,\text{Å})$ [11]). A comparison of the diffraction pattern of **1b** with the peak characteristics of crystalline *PPV* leads to the conclusion that **1b** is partly crystalline. The peak intensities of **2b** differ from the expected ratios of *PPV.* Two possible explanations can be given: *i*) within the film, the crystallites of **2b** display a preferred orientation or *ii*) an amorphous part of **2b** exists which would result in a broad peak at about $2\Theta = 20°(d = 4.4\,\text{Å})$ [11].

Although the diffraction patterns of **1b** and **2b** show peaks with a characteristic peak width of several degrees, we conclude that both polymers show a certain degree of long-range order. The experimental diffraction patterns of **1b** and **2b** differ considerably from each other. Obviously, the crystal structure properties of the two polymers are not comparable. Generally, a crystal structure of a molecular material is determined by the conformation of the polymer as well as by the packing of the polymer chains. Therefore, the conformation and packing of **1b** and **2b** have to be analyzed. The results on **2b** are interpreted on basis of crystalline *PPV* [11]. The diffraction pattern of **1b** is analyzed by a comparison with the model substance 2,5,2′,5′,-tetramethylstilbene [21].

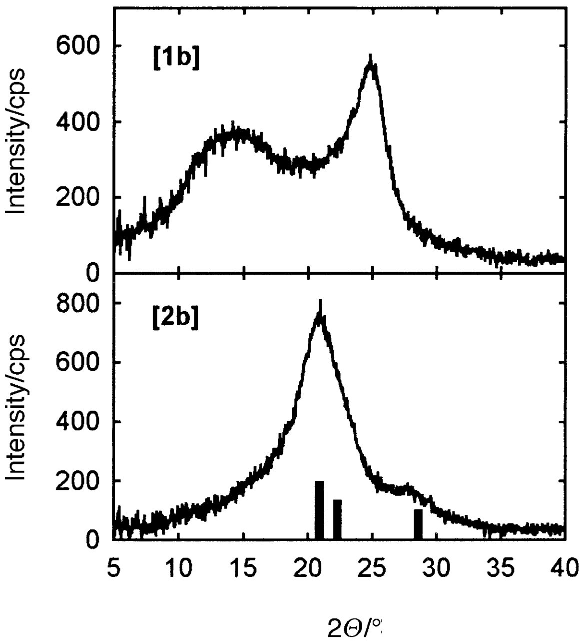

Fig. 1. $\Theta/2\Theta$ – diffraction pattern of **1b** (above) and **2b** (below); the characteristic diffraction peaks of *PPV* with respect to their position and relative intensities are given by bars in the bottom line [11]

Crystal structure studies of *PPV* and of stilbene, a model compound for *PPV*, reveal that the phenyl rings are in *trans*-arrangement to the vinyl unit (*trans*-conformation) [11, 13, 14]. Within a *cis*-arrangement, the adjacent phenyl rings are drastically twisted relative to each other [22]. The *trans*-conformation of the molecules can be characterized on the basis of *PPV*: the neighbouring phenyl rings within one polymer chain are in the same plane, whereas the dihedral angle between the phenyl ring and the vinyl segment is about 10° [11]. It can be concluded that within one polymer chain the atoms are arranged approximately within one molecular plane. The packing of the plain polymer chains to a crystal structure appears in a herringbone pattern. Figure 2 gives the herringbone pattern of *PPV*. The polymer backbones are projected along the polymer chain axes, hydrogen atoms are not depicted. Three different types of net planes which give high intensity reflections in X-ray diffraction experiments are indicated by dotted lines. Since there is a good agreement in the diffraction pattern of our *PPV* and literature data (Fig. 1), the interplanar distances are taken as 4.24, 3.97, and 3.12 Å according to Ref. [11]. Comparison of the crystal structure properties of *PPV* with that of stilbene reveal that the conformation as well as the molecular packing is similar [23]. However, *PPV* and stilbene have different tilt angles of neighbouring molecules: whereas the stilbene molecules are tilted by 60° relative to each other, the tilt angle of adjacent *PPV* molecules is slightly larger.

In contrast to *PPV*, the polymer **1b** has additional methyl groups attached to the *PPV* backbone at positions 2 and 5 of the phenyl ring. The conformation of **1b** within the bulk is deduced from the model substance 2,5,2′,5′-tetramethylstilbene [21]: it is known that the two phenyl rings of the model substance are in one plane;

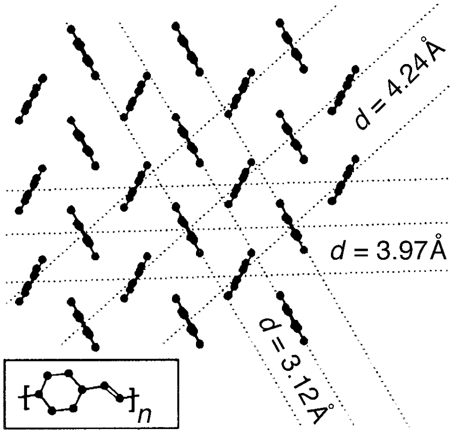

Fig. 2. Herringbone-type packing of *PPV* chains within the crystal structure; the polymer chains are projected in direction of their long axes; the three indicated planes cause the three characteristic high intensity reflections of *PPV*; the inset on the bottom/left side gives the chemical structure of *PPV*

however, the dihedral angle between the phenyl ring and the vinyl segment is 26°. The packing of the model substance within the crystal structure occurs in a parallel arrangement of the molecular planes of neighbouring molecules. The distance between two neighbouring molecular planes is 3.48 Å, the distance between molecular planes of lateral adjacent molecules is 7.7 Å. A similar molecular arrangement is suggested for the crystal structure of **1b** which is depicted in Fig. 3. The molecules are drawn schematically in a projection along the long molecular axes. The net plane between the molecular planes is 3.6 Å, which agrees quite well with the model substance (3.48 Å), a typical distance of two π-stacked aromatic

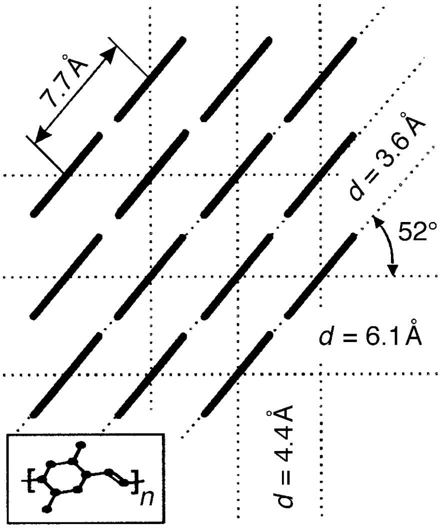

Fig. 3. Model structure of the methyl substituted *PPV* polymer **1b**; the molecules are drawn schematically in direction of their long axes; the distance between two adjacent molecules is 7.7 Å, the distance between two molecular planes 3.6 Å; the three indicated net planes cause high-intensity diffraction peaks; the inset on the bottom/left side gives the chemical structure of **1b**

planes as observed in crystal structures of aromatic molecules [24]. The resulting peak of these net planes show the highest intensity in the diffraction pattern of the model compound as well as of **1b**. One further set of net planes of the model structure which should result in high intensity X-ray diffraction peaks is at 6.1 Å ($2\Theta = 14.5°$). This peak is clearly visible in the diffraction pattern of **1b**. The diffraction peak corresponding to the interplanar distance of 4.4 Å ($2\Theta = 20.2°$) is not clearly visible in the diffraction pattern of **1b**. However, due to the general large peak width, this peak is probably superimposed.

The lateral packing of adjacent molecules is determined by the attached volume of the methyl groups. The lateral distance between adjacent polymer chains is 7.7 Å. This small distance is only possible when the lateral adjacent molecules are shifted along the polymer chain of about a half of the monomer unit length. This shift results in a close packing of adjacent molecules. The lattice constants of the model structure are $a = 6.1, b = 8.8$, and $c = 6.7$ Å. The shift of adjacent molecules along the polymer backbone causes a doubling of the interplanar distance of 4.4 Å to the lattice constant $b = 8.8$. The lattice constant c (along the polymer backbone) is the length of one monomer unit of the polymer **1b**. Within this unit cell, the molecular planes are tiled 50° relative to the *bc*-plane.

The herringbone packing as well as the parallel stacking is generally observed in polynuclear aromatic hydrocarbons of long, thin shape; molecules of larger shape tend to arrange their molecular planes relative to each other [25, 26]. Since it is known that extended molecules tend to adopt a parallel arrangement [24], it can be assumed that in several types of side chain containing *PPV* the π-conjugated molecular planes prefer parallel packing.

Conclusions

Poly-(*para*-phenylene vinylene) **2b** and poly-(2,5-dimethyl-*para*-phenylene vinylene) **1b** were prepared from two slightly different precursor materials and by the same route. The resulting polymers are nearly identical, the difference being only the introduction of two methyl groups at positions 2 and 5 of the phenyl rings. The X-ray diffraction pattern of **1b** and **2b** show different features. The diffraction pattern of **2b** can be explained on the basis of the known crystal structure. A structural model for **1b** is developed on basis of the X-ray diffraction pattern and the crystal structure of the model substance 2,5,2′,5′-tetramethylstilbene. Both polymers show different types of packing of the molecules to a crystal structure. Whereas in **2b** the polymer chains pack in the well known herringbone pattern, in case of **1b** a parallel packing of the polymer chains is observed.

Experimental

The synthesis is based on the precursor method first reported by *Louwet et al.* [15] making use of the formation of a double bond by thermal elimination of a sulfoxy side chain. The main advantages of these precursor polymers are their increased stability as compared to the standard *Wessling* route, solubility in organic solvents, and the elimination of non-corrosive materials under thermal treatment [16]. The modified procedure was used to synthesize the poly-(*n*-octylsulfinyl-2,5-dimethyl-*para*-phenylene ethylene) precursor **1a** and the poly-(*n*-octylsulfinyl-*para*-phenylene ethylene) precursor **2a** [17].

The typical procedure for the synthesis of **1a** is as follows: A solution of 0.178 mol of Na-*tert*-butoxide and 0.181 mol of 1-octanethiol in 300 cm^3 of MeOH is added to a clear solution of 67.1 g *Wessling* salt in 200 cm^3 of MeOH. The mixture is stirred for another 30 min, and solvent is removed *in vacuo*. *n*-Octane is added and removed *in vacuo* (3x). The remaining oil is dissolved in $CHCl_3$ and washed with water and $NaHCO_3$ (1 *M*). The solution is dried over $MgSO_4 \cdot H_2O_2$ and added to a solution of the crude compound together with TeO_2 in 300 cm^3 of MeOH/1,4-dioxane (5:1). After 5 h of stirring the reaction is stopped by addition of 100 cm^3 of a saturated NaCl solution. The mixture is extracted with $CHCl_3$ and dried over $MgSO_4$. Yield: 43.4 g of crude monomer. The monomer α-chloro-α'-octylsulfinyl-*p*-xylene was further purified by crystallization from $CHCl_3$/hexane. 0.106 mol of Na-*tert*-butoxide in 240 cm^3 MeOH are added at once to a mechanically stirred solution of 0.082 mol of α-chloro-α'-octylsulfinyl-*p*-xylene in 570 cm^3 *s*-butanol. After 1 h of stirring the mixture is poured in ice water, neutralized with 1 *M* HCl, and extracted with $CHCl_3$. The solvent is evaporated to remove the *s*-butanol, redissolved in $CHCl_3$, and precipitated in diethylether. The precipitated was collected and dried *in vacuo*. Yield: 14.7 g polymer.

Exactly the same procedure was followed for the synthesis of **2a**. The molecular weight of the precursors were determined by gel permeation chromatography (GPC) in THF against a polystyrene standard. **1a** has a molecular weight (M_W) of 879976 and a polydispersity (*PD*) of 3.26; **2a**: $M_W = 184115$, $PD = 2.48$. The glass transition temperatures (T_g) of the precursor polymers are 44 and 63°C, respectively.

^{1}H NMR (400 MHz, $CDCl_3$ **1a**): $\delta = 0.81, 1.18, 1.63, 1.92, 2.14, 2.25, 2.95, 3.42, 3.65, 3.88$ ppm; ^{13}C NMR (100 MHz, $CDCl_3$ **1a**): $\delta = 14.0, 18.9, 22.5, 22.8, 28.9, 31.6, 34.4, 49.5, 65.5, 129.1, 131.9, 132.4, 133.7, 134.9, 136.2, 136.7$ ppm; ^{1}H NMR (400 MHz, $CDCl_3$ **2a**): $\delta = 0.81, 1.17, 1.59, 1.96, 2.18, 2.26, 3.03, 3.62, 6.94$ ppm; ^{13}C NMR (100 MHz, $CDCl_3$ **2a**): $\delta = 14.0, 22.4, 22.5, 23.0, 28.7, 28.9, 29.0, 31.6, 36.3, 49.7, 65.2, 69.7, 128.4, 128.9, 129.4, 129.9, 131.5, 132.3, 138.2$ ppm.

The conversion to the fully conjugated system was carried out at a temperature of 200°C in vacuum. Figure 1 shows the chemical structures and the thermal conversion of the precursor materials to poly-(2,5-dimethyl-*para*-phenylene vinylene) (**1b**) and to *PPV* (**2b**). Figure 2 displays the absorption and photoluminescence spectra of the conjugated polymer **1b**. The spectra are typical for *PPV* derivative polymers [18, 19].

Films of **1a** and **2a** were prepared from a $CHCl_3$ solution by drop casting onto a silicon single crystal which was cut along a non-reflective direction. This substrate was chosen because of its low background scattering in X-ray diffraction experiments. The precursor films were converted to films of **1b** and **2b** at a temperature of 200°C in a vacuum of 10^{-3} mbar for 3 h. The thickness of the films was approximately 20 µm. After the diffraction experiments the films were lifted off the substrates. Highly flexible, good quality freestanding films were obtained.

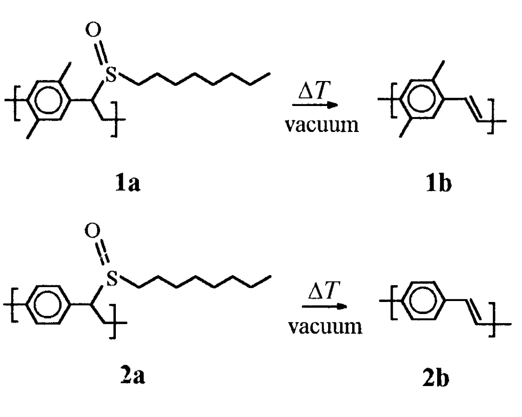

Fig. 4. Chemical structures of **1a,b** and **2a,b**

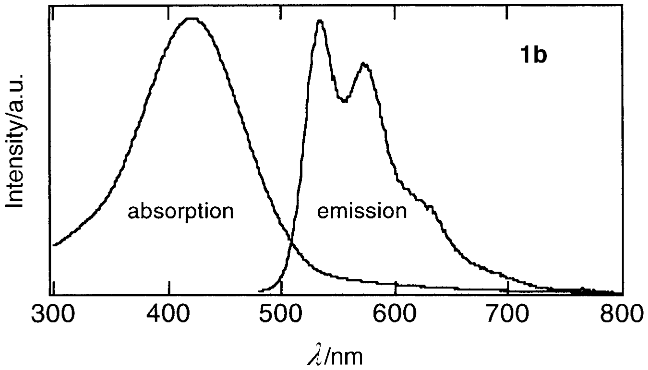

Fig. 5. Photoluminescence and optical absorption spectra of **1b** reveal the typical characteristics of *PPV* derivative polymers

X-Ray diffraction experiments were performed with a Siemens D501 diffractometer in $\Theta/2\Theta$ *Bragg-Brentano* geometry using Ni-filtered CuK_α radiation. The experimental results were corrected for the scattering of the substrate. 2Θ is the scattering angle of the diffracted beam, d gives the interplanar distance corresponding to the diffraction peak calculated on basis of *Bragg*'s equation. The software package POWDER CELL was used to calculate diffraction patterns and to visualize the crystal structures [27].

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