

3 Abstract

This work focusses on the synthesis, characterization and telomerization of alkylsubstituted oligo-*para*-phenylene-vinylenes (OPVs) (see Fig. 3.1).

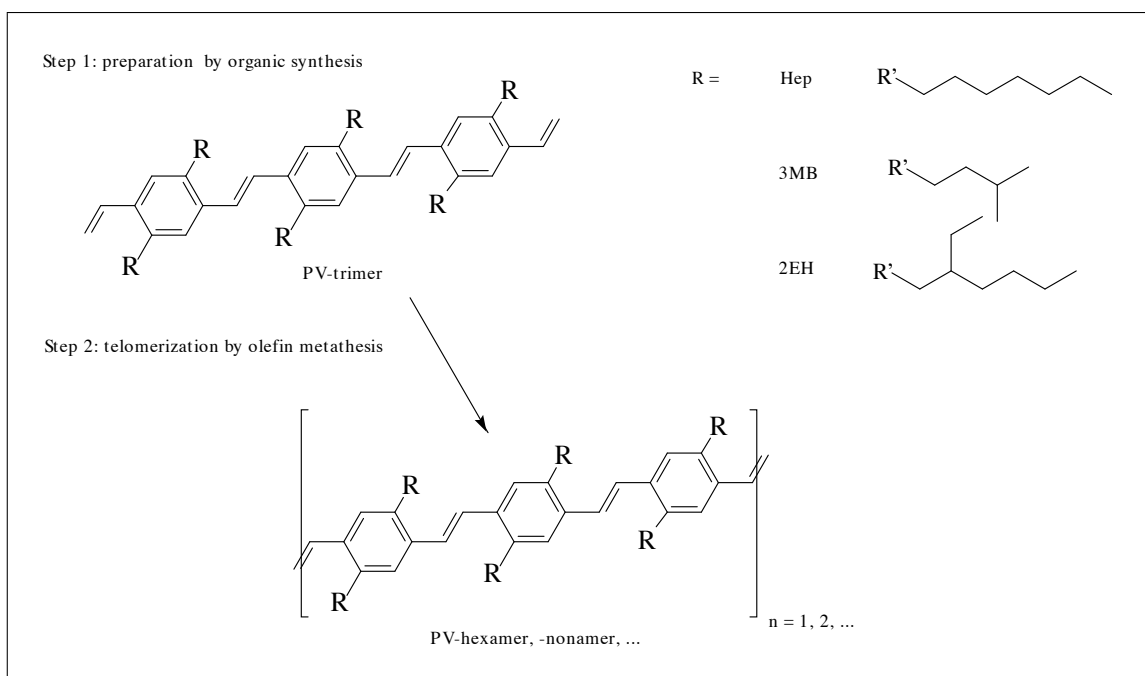


Fig. 3.1: Synthesized alkylsubstituted PV-trimers and their telomerization

Conjugated polymers and the poly-*para*-phenylene-vinylene (PPV) in particular are focussed on by many international scientific groups for the last ten years. For its optoelectronic properties PPV is valuable for several applications.

The oligomeric homologs, the mentioned oligo-*para*-phenylene-vinylene (OPV), show a behavior very much related to the polymeric PPV. Because of their chemical structure

substituted OPVs with integrated side chains (see Fig. 3.1) are known to have a good solubility and to be meltable, in contrast to PPV. Besides they have an interesting morphology like liquid crystallinity or the property of forming sandwiched layered structures. Substituted OPVs also have a well defined and characterizable structure which can be reproduced easily. As a summary, substituted OPVs have remarkable advantages in opposite to the polymer and therefore are valuable substances for fundamental research and technical applications as well.

In the past alkylsubstituted OPVs were synthesized by olefin metathesis of the monomeric alkylsubstituted divinylbenzene. This way of synthesis is not suitable to get higher amounts of OPV, i.e. in the dimension of grams. To achieve this a new synthetic approach was needed and a new synthetic strategy was developed:

- **Step 1:** synthesis of a short alkylsubstituted OPV (dimer or trimer) by **organic synthesis steps**
- **Step 2: telomerization** to higher OPVs by **olefin metathesis**

Multiple grams of different alkylsubstituted OPVs were obtained by organic synthesis. The optimal terms of reaction were determined. Therefore a higher amount of OPVs could be accessed for further investigations i.e. detailed characterization and examinations on the telomerization to OPVs with a higher molecular weight.

The following alkylsubstituted PV-trimers were obtained in a larger scale:

- n-heptyl- (Hep) (linear, unbranched),
- 3-methylbutyl- (3MB) (symmetrical branched)
- 2-ethylhexyl- (2EH) (unsymmetrical branched)

The obtained trimers underwent a detailed characterization. UV/Vis and fluorescence spectrometry were performed on them in different solvents. The absorption behavior of

the trimers showed a bathochromical shift of the absorption maximum in chloroform from unbranched over symmetrical branched to unsymmetrical branched substitution. 3MB-substituted PV-trimer dissolved in cyclohexane showed a hypsochromic shift of the absorption maximum due to the formation of aggregates. 2EH-substituted PV-trimer had a bathochromic shift of the absorption maximum in cyclohexane because of the +I-effect of the 2EH side chains.

No significant influence of the solvent was observed by fluorescence measurements. A bathochromic shift of the emission maxima was observed by changing the substitution from unbranched to branched. Measuring the fluorescence properties revealed the solvation behavior of the excited state. No significant influence of the solvent type was observed.

Alkylsubstituted OPVs have an interesting morphology. X-ray diffraction of powders of a heptylsubstituted homologous series of OPV reveals that the monomer and dimer respectively have a crystalline structure. As found out in this work trimer, tetramer and pentamer have a crystalline and a layered structure as well. From the hexamer on to higher oligomers only a sandwiched layered structure can be observed.

Successful growing of a mono-crystal of DHepPV-trimer and X-ray diffraction of the synthesized monodisperse hexamer strengthened the depicted solid state of the hexamer and higher oligomers. The existence of the layered structure besides the crystalline structure could clearly be assigned to the trimer, tetramer and pentamer (see Fig. 3.2).

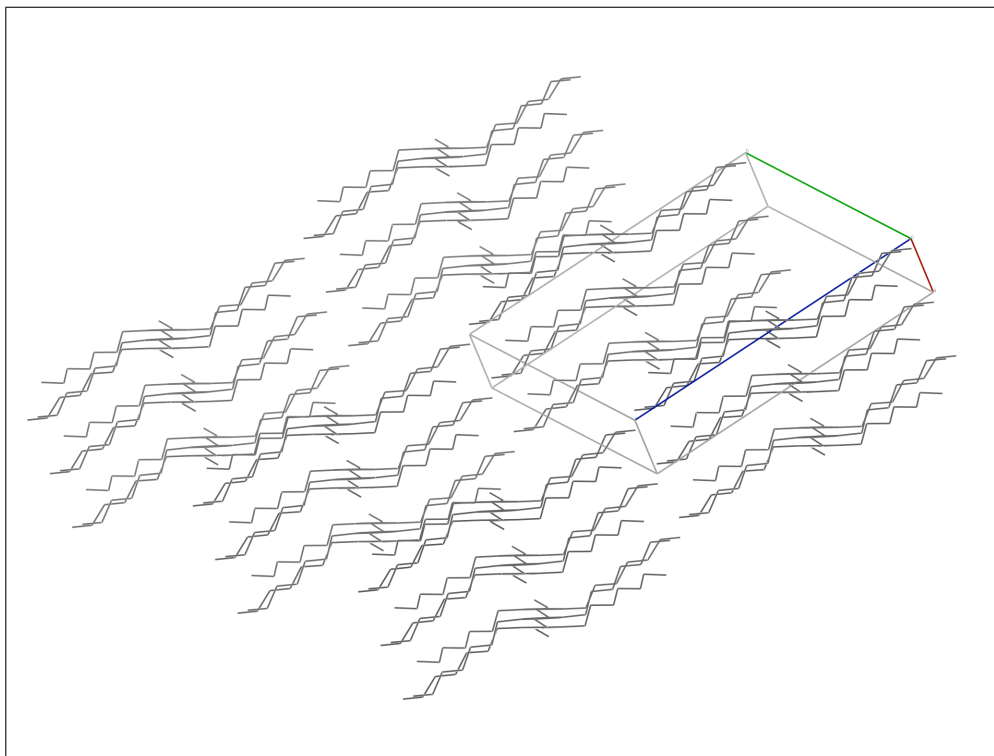


Fig. 3.2: Packing of DHepPV-trimer

As higher amounts of dialkylsubstituted PV-trimer were accessible by organic synthesis investigations of their telomerization of them via olefin metathesis were made. Optimal terms of reaction were worked out. The metathesis was optimized with regard to the selectivity,— attack on the terminal double bonds while sparing the inner double bonds as far as possible—, and with respect to the over all yield. Because of the best balance between activity and selectivity regarding the attack of the different double bonds in the PV-trimer, a metathesis catalyst of the Schrock type was chosen for the telomerization. The best temperature for this reaction was determined to compensate these two effects: high reaction rate at high selectivity. Raising the temperature mostly lead to loss of selectivity because of the activation energy of the splitting reaction at the inner double bonds. This would cause a mixture of oligomers at the end of the metathesis of which the monodisperse oligomers could not be isolated. The advantage of telomerization in comparison to the olefin metathesis of the monomer would be lost.

Best reaction temperatures in methylcyclohexane were found to be:

- DHepPV-trimer **10a**: 0°C, 4 hours reaction period
- DiPPV-trimer **10b**: 25°C, 6 hours reaction period
- DiOPV-trimer **10c**: 25°C, 24 hours reaction period

The depicted OPVs are suitable as discrete materials. Investigations were made in this work whether these OPVs compounded in rubber resist the conditions of a peroxidic curing. DHepPV-oligomer overcomes these peroxidic curing conditions while keeping its fluorescence properties.