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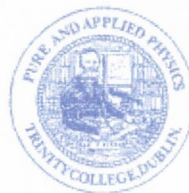
New Conjugated Polymers- Synthesis, Characterisation and Applications

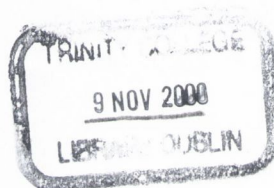
Stefanie Maier

A thesis submitted for the degree of
Doctor of Philosophy
in the University of Dublin



**Department of Physics
Trinity College
University of Dublin
May 2000**





Alsis
5900

Declaration

This thesis has not been submitted as an exercise for a degree to this or any other University.

The work described in this thesis is entirely my own, with the exception of the assistance mentioned in the acknowledgements.

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Stefanie Maier

To my parents and my brother

*It is a much cleverer thing to talk nonsense
than to listen to it.*

*Oscar Wilde
(An ideal husband)*



PPV derivative under UV light

Abstract

A series of conjugated polymers related to poly(phenylenevinylene) have been synthesised and characterised. These polymers contain various substitution patterns. Octyloxy side-chains were attached to the arylene units of the polymer backbone for solubility reasons. Some polymers only contain phenylene units along the polymer chain while in other derivatives naphthalene units were introduced into the backbone. Additionally, some derivatives were prepared by varying *para* and *meta* substitution patterns. For the majority of the materials bulky phenylene moieties were attached to the vinylene unit to obtain very complex systems.

All polymers were chemically characterised by gel permeation chromatography, nuclear magnetic resonance, infrared spectroscopy and Raman spectroscopy to confirm the obtained structures.

The influences of all different structural alterations on the thermal behaviour, the optical properties and electrochemical behaviour are investigated and discussed.

In general, the polymers are temperature stable up to 350°C, emit in the blue to green region of the visible spectrum and contain varying oxidation and reduction potentials depending on the substitution pattern.

With a selection of polymers light emitting diodes and photovoltaic devices have been fabricated and examined.

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Table of Contents

Declaration	
Abstract	
Acknowledgement	3
Abbreviations	9
A short review on the polymer structures	13
1. Introduction	15
1.1. Some historical data	15
1.2. Basic structures of conjugated polymers	16
1.3. Variety of PPV derivatives and related materials	17
1.4. The terminology of conjugated polymers	19
1.5. From non-conjugated to conjugated polymers	21
1.6. Doping	22
1.7. Polarons, bipolarons and excitons	23
1.8. Excitation and de-excitation	24
1.9. Photoluminescence and electroluminescence of conjugated polymers	25
1.10. Light Emitting Diode (LED)	27
Single layer devices	27
Multilayer devices	29
1.11. Photovoltaic devices	31
1.12. Light emitting electrochemical cells (LECs)	33
1.13. Field-effect transistors (FETs)	34
1.14. Lasers	35
1.15. Rechargeable batteries	36
1.16. Other applications	36
2. Research aims	38
3. Results and Discussion	39
3.1. Introduction	39
3.2. Discussion of the employed polymerisation method	40

3.3.	Stereo chemical aspects of the Horner Reaction	41
3.4.	Synthesis of the Ketones	42
3.4.1.	^1H -NMR	43
3.4.2.	^{13}C -NMR	44
3.4.3.	IR spectroscopy	45
3.5.	Synthesis of 2,5-Di-n-octyloxy-1,4-xylene-diethyl-phosphonate-ester	46
3.6.	Horner polycondensation of the PPV derivatives	48
3.6.1.	Gel permeation chromatography	50
3.6.2.	^1H -NMR	50
3.6.3.	^{13}C -NMR	51
3.6.4.	IR spectroscopy	53
3.6.5.	Raman	54
3.7.	Synthesis of 1,5-bis-n-octyloxy-2,6-naphthalene-dialdehyde	56
3.8.	Polymerisation of POPV-ONV	59
3.8.1.	^1H -NMR	59
3.8.2.	^{13}C -NMR	60
3.8.3.	IR spectroscopy	61
3.8.4.	Raman	61
3.9.	Synthesis of the PPV-ONV starting material	63
3.10.	Polymerisation of PPV-ONV derivatives	65
3.10.1.	^1H -NMR	66
3.10.2.	^{13}C -NMR	66
3.10.3.	IR spectroscopy	67
3.10.4.	Raman	68
3.11.	Polymerisation of <i>Pm</i> PV-ONV	69
3.11.1.	Raman	69
3.12.	Synthesis of 2,6-dimethylnaphthalene-bis-(ethyl-phosphonate)ester	71
3.13.	Polymerisation of nonyl- <i>Pp</i> PV-NV	72
3.13.1.	^1H -NMR	72
3.13.2.	^{13}C -NMR	73

3.13.3.	Raman	73
3.14.	Synthesis of halogen containing PPV-NV derivatives	75
3.15.	Thermal Characterisation	76
3.15.1.	Thermo Gravimetric Analysis (TGA)	76
3.15.2.	Differential Scanning Calorimetry (DSC)	76
	Introductory remarks	76
	DSC investigations on the present polymers	78
	Relation between T_g and T_m	81
3.15.3.	Liquid crystalline PPV related material	84
	Introductory remarks	84
	Investigation on liquid crystalline properties using polarising microscopy	85
3.16.	Electrochemical characterisation	88
3.16.1.	Redox behaviour of PPV related material	88
3.16.2.	Cyclic voltammetry measurements of the present polymers	90
3.16.3.	Cyclisation through chemical oxidation	94
3.17.	Optical measurements	96
3.17.1.	Introduction	96
3.17.2.	Absorption measurements in solution	97
3.17.3.	Photoluminescence measurements in solution	101
3.17.4.	Absorption and PL of POPV-ONV	104
3.17.5.	Photoluminescence in films	105
3.18.	Applications	107
3.18.1.	Light emitting diodes (LEDs)	107
	Device preparation	107
	Device characterisation	109
3.18.2.	Photovoltaic devices	112
	Device preparation	112
	Device characterisation	114
4.	Conclusions and Future Work	120
5.	Experimental	125
5.1.	General Remarks	124

5.2.	Synthesis and characterisation	130
5.2.1.	Ketones	130
5.2.2.	Synthesis of the PPV starting material	140
5.2.3.	Synthesis of the <i>para</i> PPV derivatives	143
5.2.4.	Synthesis of the <i>meta</i> PPV derivatives	151
5.2.5.	Synthesis of the POPV-ONV starting material	161
5.2.6.	Synthesis of POPV-ONV	163
5.2.7.	Synthesis of the PPV-ONV starting material	165
5.2.8.	Synthesis of dimethyl-PpPV-ONV	168
5.2.9.	Synthesis of the PmPV-ONV derivatives	170
5.2.10.	Synthesis of PmPV-ONV	176
5.2.11.	Synthesis of the nonyl-PpPV-NV starting material	178
5.2.12.	Synthesis of nonyl-PpPV-NV	180

References

182

Appendix

Abbreviations

λ	wavelength
ϕ	Work function
δ	chemical shift
η	power conversion
ΔE_e	injection barrier of electrons
ΔE_h	injection barrier of holes
Al	aluminium
AM	air mass
b	broad (IR)
Ca	calcium
calc.	calculated
CB	conduction band
CN	cyano
conc.	concentrated
CV	Cyclic voltammetry
d	doublet
D	dye molecule
D^*	excited dye molecule
D^+	oxidised dye molecule
DEPT	distortionless enhancement by polarisation transfer
DMF	dimethylformamid
DSC	differential scanning calorimetry
E	potential energy
e.g.	exempli gratia
$E_{1/2}$	half-wave potential
EA	electron affinity
E-conformation	(german:) entgegen
EL	electroluminescence
E_{pa}	anodic current peak potential

E_{pc}	cathodic current peak potential
Eq.	equation
<i>et al.</i>	et alia
etc.	et cetera
eV	electron volt
FET	Field-effect transistor
FF	fill factor
FT-IR	fourier transform infrared
GPC	gel permeations chromatography
HOMO	highest occupied molecular orbital
Hz	Hertz
I	current
i.e.	id est
I_{opt}	current for maximum power output
IP	ionisation potential
IR	infrared spectroscopy
I_{sc}	Short-circuit current
ITO	indium tin oxide
J	coppling constant
J_{opt}	current density for maximum power output
J_{sc}	Short-circuit current density
K	potassium
L	luminance
LC	liquid crystal, liquid crystalline
LEC	Light emitting electrochemical cell
LED	Light emitting diode
Li	lithium
LUMO	lowest unoccupied molecular orbital
m	medium (IR)
m	multiplet (NMR)
M	molar
MEH-PPV	poly(2-methoxy,5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene

MEK	methyl ethyl ketone, butanone
MISFET	metal-insulator semiconductor field-effect transistor
M_n	number average
M_w	weight average
M_w/M_n	molecular weight distribution
N	electron density
N3	[Ru(4,4'-bis(carboxy)-bpy) ₂ (NCS) ₂], Ruthenium dye
Na	sodium
NBS	N-bromosuccinimide
NC	nanocrystalline
nm	nanometer
NMR	nuclear magnetic resonance
OLED	organic light emitting diode
ox.	oxidised
PA	polyacetylene
Pani	polyaniline
PEO	Poly(ethyleneoxide)
PL	photoluminescence
PNV	Poly(naphthalenevinylene)
PPE	Poly(<i>p</i> -phenyleneethynylene)
ppm	Parts per million
PPP	Poly(<i>p</i> -phenylene)
PPS	Poly(<i>p</i> -phenylenesulfid)
PPV	Poly(<i>p</i> -phenylenevinylene)
Ppy	polypyrrole
PT	polythiophene
red.	reduced
RT	Room temperature
s	singlet
s	strong (IR)
S	singlet state

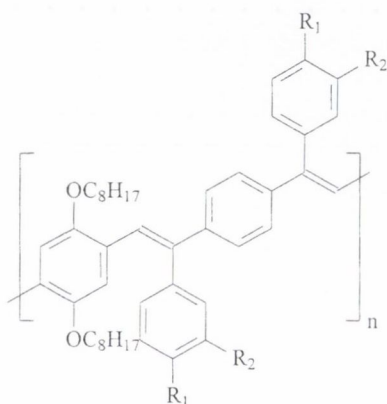
T	triplet state
t	triplet (NMR)
t	Time
T_c	crystallisation temperature
T_{dec}	decomposition temperature
T_g	Glass transition temperature
TGA	thermo gravimetric analysis
theor.	theoretical
THF	tetrahydrofuran
T_m	melting temperature
UV	ultraviolett
V	voltage
VB	valence band
VIS	visible spectrum
V_{oc}	Open-circuit voltage
V_{opt}	voltage for maximum power output
w	Weak (IR)
Z-conformation	(german:) zusammen

A short review on the structures abbreviations of the different derivatives

The figures below contain a review of the structures and the corresponding names of the synthesised polymers.

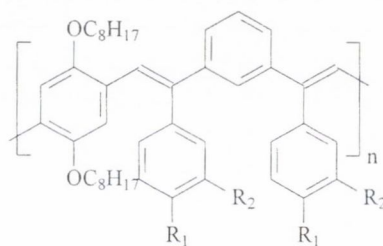
Note that the *PpPV*, *PmPV*, *PpPV-ONV* and *PmPV-ONV* derivatives have an additional prefix to indicate the substitution pattern of the phenylene substitution on the vinylene bond:

e.g.: $R_1 = -CH_3$, $R_2 = -H \rightarrow$ **methyl** or $R_1 = -OCH_3$, $R_2 = -OCH_3 \rightarrow$ **dimethoxy**



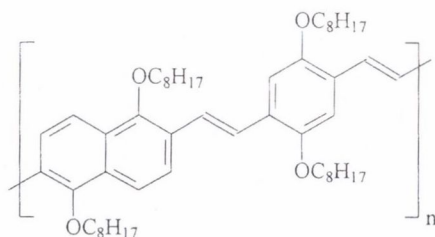
Poly(*p*-PhenyleneVinylene-2,5-di-n-octyloxy-1,4-phenylenevinylene) derivatives

PpPV



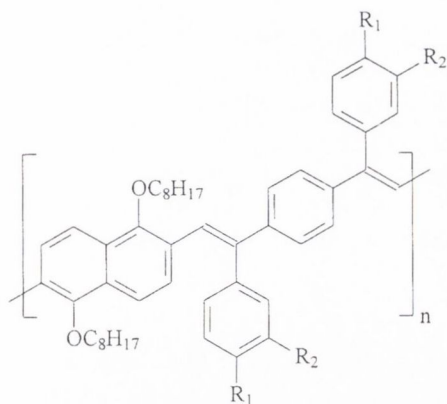
Poly(*m*-PhenyleneVinylene-2,5-di-n-octyloxy-1,4-phenylenevinylene) derivatives

PmPV



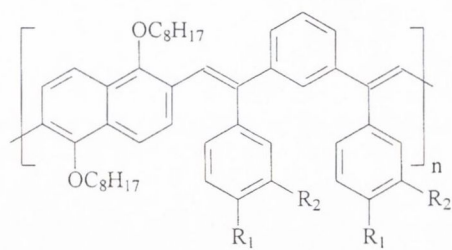
Poly(2,5-bis(*n*-Octyloxy)-1,4-PhenyleneVinylene-1,5-bis(*n*-Octyloxy)-2,6-NaphthyleneVinylene)

POPV-ONV



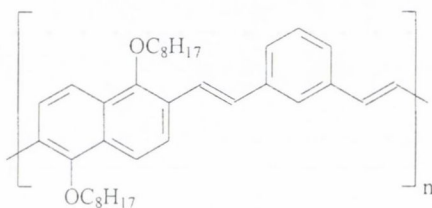
Poly(*p*-PhenyleneVinylene-2,5-di-*n*-Octyloxy-2,6-NaphthaleneVinylene) derivatives

PpPV-ONV



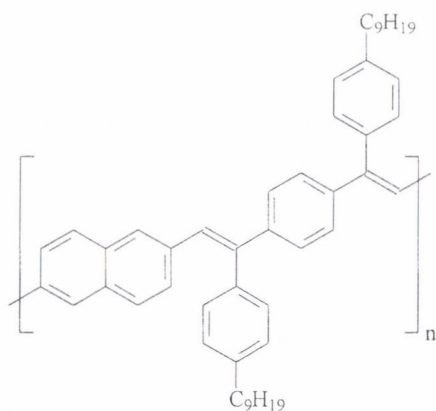
Poly(*m*-PhenyleneVinylene-2,5-di-*n*-Octyloxy-2,6-NaphthaleneVinylene) derivatives

PmPV-ONV



Poly(*m*-PhenyleneVinylene-1,5-bis(*n*-Octyloxy)-2,6-NaphthyleneVinylene)

PmPV-ONV



Poly(*p*-PhenyleneVinylene-2,6-NaphthyleneVinylene) derivative

nonyl PpPV-NV

1. Introduction

1.1. Some historical data

Although inorganic materials have dominated the field of optoelectrical technology in the last twenty years there has long been interest in the possibility of light emission by organic materials. This began with ideas of W.A. Little ^[1] in 1964 proposing theoretically that unsaturated molecules produce a conducting state.

In 1977 a paper describing electronic conductivity of oxidised polyacetylene ^[2] was published and consequently a great effort was made to investigate conjugated polymers for their electrical and optical properties.

Garnier *et al.* ^[3] were able to fabricate the first organic transistor in 1990, and in the same year electroluminescence from conjugated polymers was first reported by Friend *et al.* ^[3a] using poly(*p*-phenylenevinylene) as the single semiconductor layer between metallic electrodes.

Previously, electroluminescence of an organic semiconductor had been first reported by Pope ^[4] in 1963 who observed emission from single anthracene crystals using silver paste electrodes. Then Helfrich and Schneider ^[5] in 1965 used glass tubes filled with liquid electrodes which were cemented to either side of a single crystal. Both devices were rather unattractive due to high drive voltages that had to be applied.

Organic materials are of major interest due to their many advantages. The most evident advantages are the relatively low cost and the ease of fabrication to form integration into devices. The molecular structure can be easily modified which allows property fine-tuning. Also high damage thresholds, low dielectric constant, fast nonlinear optical response and large off-resonance nonlinear optical susceptibilities comparable to inorganic crystals have been reported. ^[6]

Although the device technology is still in its early stages, several organic light emitting diodes have already shown sufficiently high brightness and low driving voltages to be attractive for a number of commercial applications. But still, the question of device lifetime and degradation remains the major issue to be resolved before organic LEDs are ready to enter the commercial marketplace. Although

lifetimes has been reported to be up to several tens of thousands of hours at best in the absence of water and oxygen at RT, these values render them just useful for alphanumeric displays. [7]

1.2. Basic structures of conjugated polymers

Optically conjugated polymer films are often highly coloured with band gaps in the visible region and the colour of the material can be tailored through changes in the molecular structure.

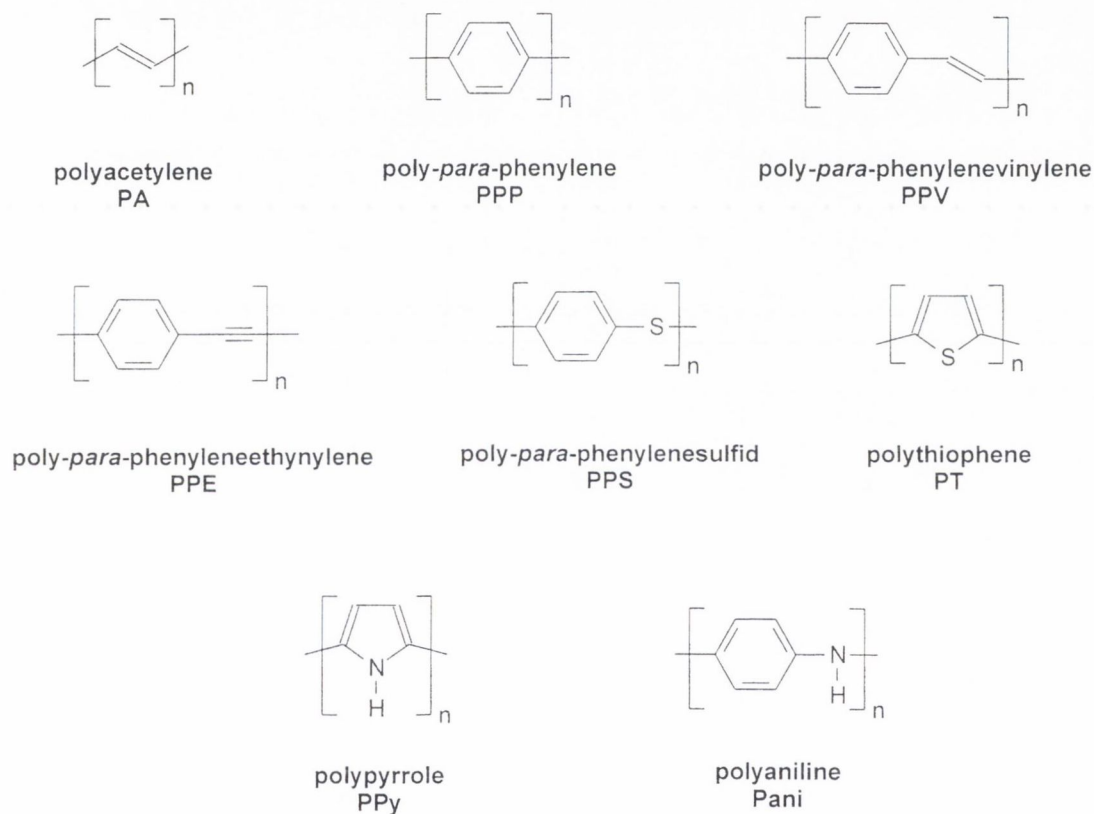


Fig. 1.1: An overview of the molecular structure of some conjugated polymers [8] [9]

Conceptually, the most simple case is that of polyacetylene, comprising an alternating sequence of single and double bonds. Other polymers contain phenyl units as part of the structure, the simplest structure in this case is poly(*p*-phenylene). Then again, these structures can be alternating as is the case for poly(*p*-phenylenevinylene) which can be loosely viewed as a regular copolymer of

polyacetylene and poly(*p*-phenylene) ^[10]. Also, heteroatoms can be introduced into the polymer chain to give, for example, the well investigated polymers polypyrrole, polyaniline, polythiophene and countless others.

Simply on the variety of structure, and also on numerous different synthesis pathways employed for polymer preparation, whole books could be and have been written ^[11-13].

But to understand why these conjugated polymers are subject to enormous efforts in research the present introduction will concentrate on basic phenomena involved in this field and the resulting applications.

The focus will be on PPV related systems since the backbone offers many different substitution locations which are not completely exploited yet.

1.3. Variety of PPV derivatives and related materials

Considerable interest has been devoted to investigating the variety of PPV and related structures.

Starting off from the insoluble poly(*p*-phenylenevinylene) the first step towards easily processible materials was the introduction of long alkoxy chains on the phenylene unit ^[11]. Due to the electron donating character of the alkoxy group the absorption and emission maxima are red shifted compared to the corresponding alkyl-substituted derivative ^[12].

The PPV backbone offers a variety of substitution locations. Not only the character of substitution influences the properties but also where it is attached to the polymer chain. For example, Hanack *et al.* ^[13] report that the location of the cyano group influences the properties of 1,4-bis(α -cyanovinylphenyl)-2,5-di-*n*-hexyloxybenzene and of 1,4-bis(β -cyanovinylphenyl)-2,5-di-*n*-hexyloxybenzene are influenced in such way that moving the α -cyano substitution to the β -cyano substitution causes a significant blue shift of absorption and emission. This is due to steric effects since the β -cyano groups are closer to the hexyloxy unit which causes a deformation of the polymer backbone.

Much effort has been put into the investigation of cyano substituted PPV derivatives ^{[14] [15]}. The strong electron withdrawing CN group is known to reduce the barrier for electron injection to the polymer and therefore improves device

performance. CN-substitution in general induces an overall stabilisation of the electronic levels. This effect has found to be twice as high for CN-substitution on the vinylene bond than on the phenylene unit ^{[14] [16]}. Also, investigation of the strongest known electron withdrawing trifluoromethylsulfonyl (triflyl) units have been carried out. These compounds show a hypsochromic shift, due to sterical influences of the very bulky substituents ^{[20] [21]}.

On the other hand electron-donating groups (e.g. methoxy or amino) produce an asymmetric destabilisation of the top of the valence band and bottom of the conduction band with respect to PPV ^[17]. Therefore the bandgap is narrowed and emission is shifted to higher wavelengths ^[18].

Meta substitution in conjugated polymer systems interrupts the π -conjugation and induces a localisation of the charges on the stilbene building blocks ^{[19] [9]}.

Additionally the incorporation of flexible, non-conjugated segments into a rigid polymer backbone will reduce the stiffness and therefore affect the microscopic molecular order of the polymer ^[20]. In addition to this, the introduction of nonconjugated segments is expected to increase the bandgap, if the length of the conjugated segments becomes smaller than the effective conjugation length. In this case, charges might not be injected into the polymer layer as efficiently. Therefore, the balance of charge injection is altered, too. Another alternative in the design of conjugated polymers involves the variation of the arylene building block itself. Apart from heterocyclic systems which generally have been found to contain a lower bandgap than the corresponding phenylene-substituted compounds ^[21], replacement of the phenylene moiety by the more electron-rich naphthalene unit modifies the band structure. Naphthalene can be linked in different ways ^[22]. The most extensively studied naphthalene system is the one containing a linkage in the 1,4-positions ^[18]. Theoretical calculations have shown that the energy gap of the 2,6-naphthalenevinylene-phenylenevinylene block polymers is very similar to PPV but significantly smaller in 1,4-naphthalenevinylene-phenylenevinylene block polymers ^{[23] [24]}.

Additional phenyl substitution on both the vinylene and the phenylene unit of PPV has been investigated. Alkoxy ^[25] and dialkoxy-phenyl ^[26] substitution on the phenylene moiety has been found to improve the stability to air and light and also the film forming properties.

Phenyl substitution on the vinylene bond has been found to improve the solubility and stabilise PPV related systems against the action of oxygen and light. It is also expected to offer various possibilities for the introduction of electron donating or withdrawing groups via the phenyl rings and it allows manifold structural modifications ^[27].

To date the so called MEH-PPV can be considered as the most exploited PPV derivative since it has been found that it is highly efficient light-emitting material [8] [20] [27-31].

Finally, it should be mentioned that the fundamental properties of these macromolecules are difficult to relate to the microscopic molecular properties due to chemical and structural imperfections as a result of mislinkages (depending on the polymerisation method), saturated sites, molecular weight distributions, the presence of end-groups and conformational defects. Also, it is usually quite difficult to obtain material of high molecular polymer weight due to low solubility of the end-product, recombination and other factors.

Therefore it is common to study well-defined, conjugated oligomers as model compounds for their polymers which in principle can serve as electronic models. It has been found that the oligomer's spectral properties start to converge with that of the polymer at about the five phenyl unit level ^[12].

1.4. The terminology of conjugated polymers

The study of π -conjugated systems is an interdisciplinary exercise involving mainly chemists, physicists and material scientists. Quite often, the different sub-disciplines of the field of conjugated polymers use different terminologies for concepts and phenomena. This is particularly true for the electronic states of neutral and charged polymer chains in the presence of bond relaxation ^[8]. It is appropriate therefore to introduce the nonlinear excitations of conducting polymers, solitons, polarons and bipolarons by drawing parallels between the physics terminology taken from the vocabulary developed in the study of extended systems in solid-state physics, and the chemistry terminology which emphasises the local molecular geometry in the vicinity of spins and charges on the polymer chain.

Although the energy band theory explains how conjugation can lead to semiconducting properties, it has its limits. For example, problems occur in describing electron-electron interaction in the solid state causing localisation of electronic states ^[8].

Baessler *et al.* ^[32] clarified the nature of the lowest optically allowed transition in PPV. Their results support the exciton concept and indicate the failure of one-electron theories for treating the lowest excitation states of conjugated polymers.

Table 1.1 shows a selection of frequently used physics terms and their corresponding chemical terms.

Physics terms	Chemistry terms
Undoped state	Neutral state
Work function	Ionisation potential
Electronegativity	Electron affinity
Valence band	π -band, HOMO, bonding level
Conduction band	π^* -band, LUMO, anti-bonding level
Doping	Redox chemistry
p-type	Oxidation
n-type	Reduction
p-type dopant	Oxidising agent
n-type dopant	Reducing agent
Polarons	Radical ions
Positive polaron	Radical cation
Negative polaron	Radical anion
Bipolarons	Dications
Positive bipolaron	Spinless dication
Negative bipolaron	Spinless dianion

Table 1.1: Conventional names for observed phenomena in conjugated polymer systems ^[8]

1.5. From non-conjugated to conjugated polymers

In the case of non-conjugated polymers, the carbon atoms along the chain are sp^3 -hybridised and therefore the electrons highly localised. Due to the absence of π -orbital overlap they are excellent insulators.

In conjugated polymers the carbon atoms along the chain are sp^2 -hybridised and the orbitals overlap to form an extended π -electron system.

A complete delocalisation of the electrons in conjugated polymers would make them one dimensional metals with a half filled energy band. According to Peierls^[33] such one dimensional metals are unstable and a conjugated system is arranged by alternating double and single bonds since this conformation is of lower energy than the completely delocalised electron system. Therefore the electrons in conjugated polymers are partially localised which makes them semiconductors with the fully occupied valence band (π -band) and the empty conduction band (π^* -band) separated.

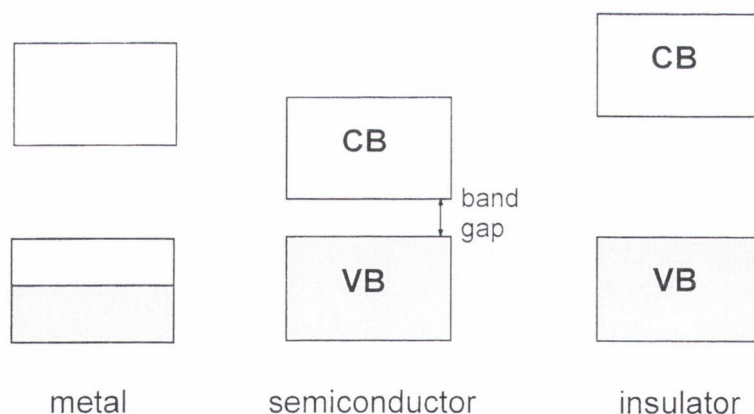


Fig. 1.2: Schematic band structure: when a large number of atomic orbitals are brought together, they overlap to form allowed energy bands; depending on the nature of the bonding this can result in a half filled band (metal), a filled band with a small gap (semiconductor) or a filled band with a large gap (insulator)

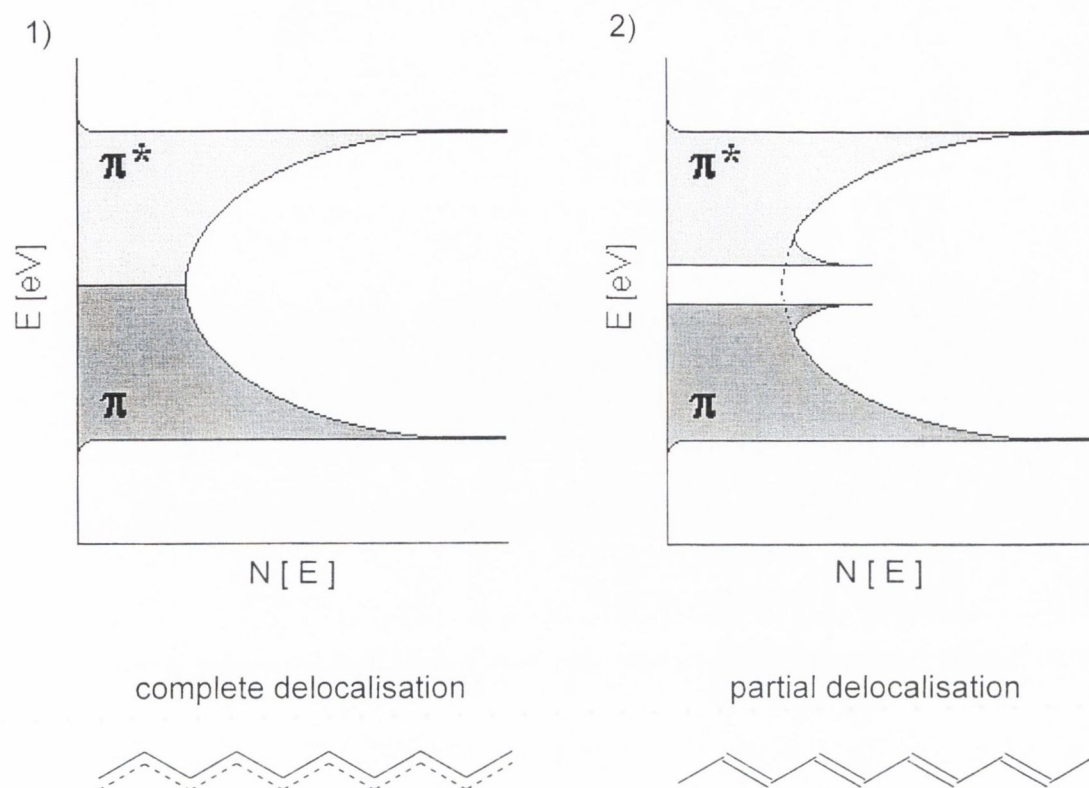


Fig. 1.3: Depiction of Peierls distortion in polyacetylene (E: potential energy and N: electron density)

The energy of the bandgap between the occupied π -band and the unoccupied π^* -band of conjugated polymers lies in the visible (1-4 eV, 1240-310 nm) ^[34] and varies with the alternations.

1.6. Doping

The easiest way to increase the charge density of an organic material is charge injection i.e. doping. A variety of doping methods are available, e.g. via charge transfer redox chemistry, electrochemically, acid-base chemistry doping, photo doping and the most common method employed for device preparation, the charge injection at a metal-semiconducting polymer interface.

Suitable dopants find it energetically favourable to transfer charge to the organic material through oxidation or reduction. Oxidising agents such as I_2 , PF_6 and BF_4 accept electrons from the polymer chain and act as p-type dopants. Alternatively,

reducing agents such as Na, Al, K, Li or Ca donate electrons to the chain and act as n-type dopants.

1.7. Polarons, bipolarons and excitons

The vast majority of conjugated polymers have a non-degenerate ground state. An example of a degenerate ground state polymer is polyacetylene since the order of the alternating double and single bonds does not change the total energy of the polymer chain.

In non-degenerate polymers, such as PPV and PPP, the lowest total energy is reached by the aromatic configuration, which for PPP are single bonds between neighbouring phenyl rings. The system of higher energy in these systems is called quinoidal configuration. The PPV configuration is shown in figure 1.4.

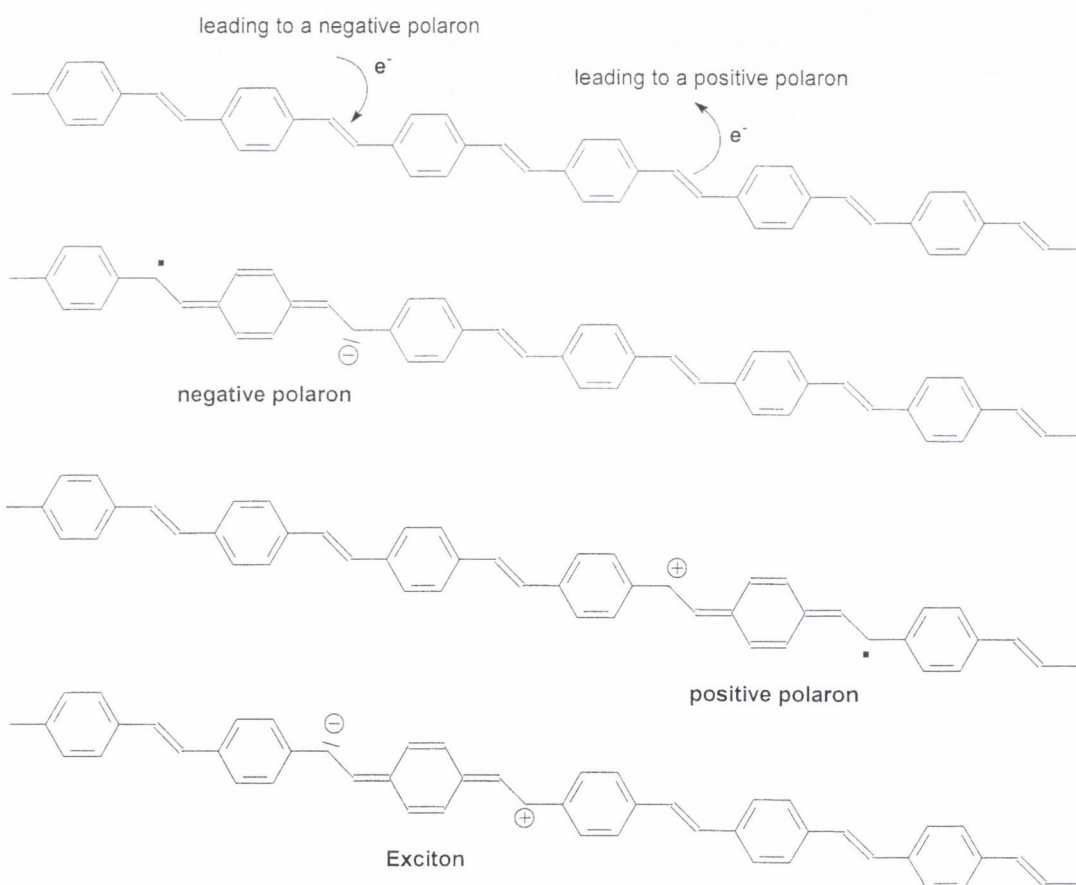


Fig. 1.4: Polarons and excitons shown at the PPV backbone

Injection of an electron into the PPV backbone leads to a negative charge, called negative polaron whereas removing an electron leads to a positive charge, called positive polaron. In both cases a local rearrangement of bond alternation introducing a the quinoid section, is obtained ^{[35] [36]}.

A bipolaron is the coupling of two charges to the chain. It costs less energy to form one bipolaron than two polarons so bipolarons dominate at high local polaron density.

Excitons can be formed by absorption of light and also in a light emitting diode by the recombination of an oppositely charged polaron pair with the opposite charges approaching each other ^[37].

1.8. Excitation and de-excitation

Excitation of an electron from a lower to a higher molecular quantum state leads either to chemical re-arrangement, chemical fragmentation or to physical de-excitation since the excited state is not indefinitely stable.

De-excitation will occur through radiative, non-radiative or quenching processes.

Of major interest for the present work is de-excitation through radiative processes involving the emission of electromagnetic radiation when the excited molecule returns to lower energy states. De-excitation from the singlet state is called fluorescence. Phosphorescence transition from a triplet state is generally less intense than fluorescence transition, less rapid, because the triplet state is more stable and at longer wavelength. Since for fluorescence there is no change of spin multiplicity, the transition is spin allowed and occurs on relatively fast timescales. Typical timescales are in the sub nanosecond to microsecond range. Typical timescales for phosphorescence lie in the microsecond to second range.

The scheme below provides an overview about the absorption and emission process.

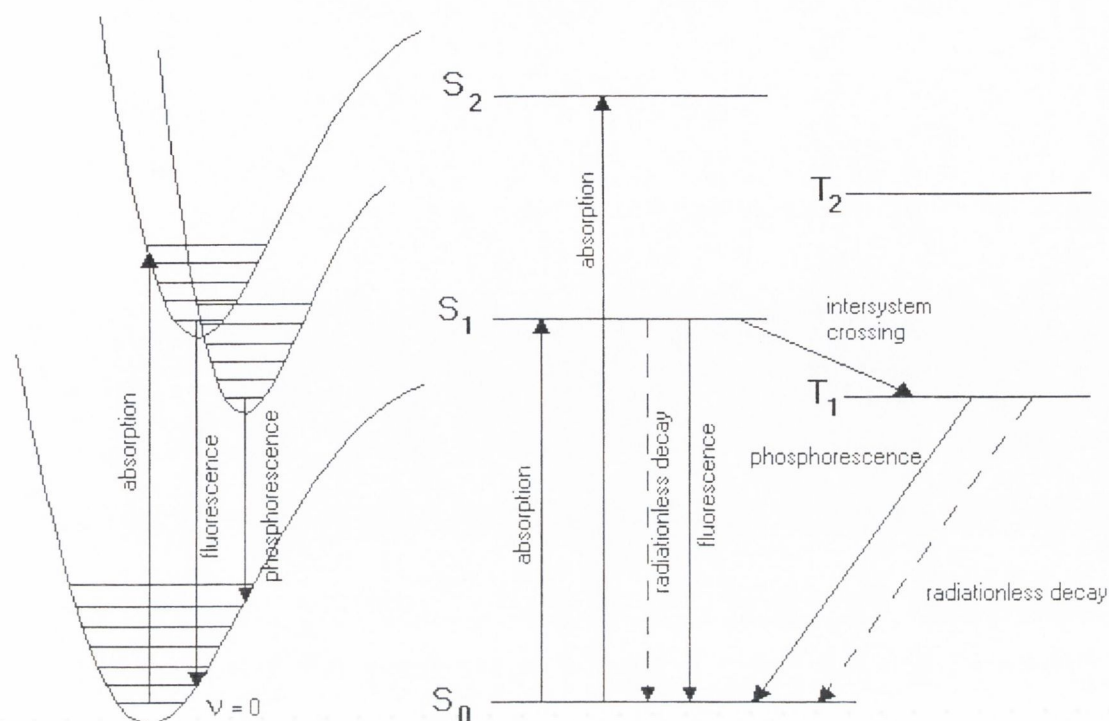


Fig. 1.5: schematic illustration showing the absorption and emission of a molecule with the singlet ground state S_0 , the first and the second excited singlet state S_1 and S_2 , the lowest triplet state T_1 and the excited triplet state T_2 ^[38]

The absorption and emission also will always occur from the lowest vibrational states ($v = 0$).

Due to nuclear vibrational relaxations in the excited state the emitted radiation is usually at longer wavelengths than that used to create the excited state. The difference between the absorption and emission wavelength is called Stokes shift.

1.9. Photoluminescence and electroluminescence of conjugated polymers

Photoluminescence:

When a photon of the appropriate energy interacts with an electron in the ground state, the electron is promoted from highest occupied molecular level (HOMO) to

the lowest unoccupied molecular level (LUMO). This process creates a singlet exciton which can decay radiatively.

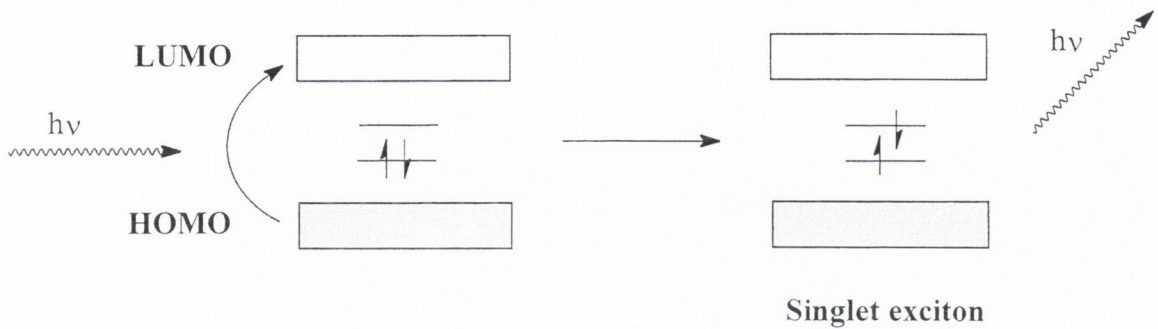


Fig. 1.6: Photoluminescence

Electroluminescence:

The injection of an electron into the LUMO on one end of a polymer chain and the injection of holes into the HOMO at the other end can lead to recombination of the hole and the electron to form a singlet exciton if they interact with each other in an electric field. Again, any singlet exciton formed can de-excite by giving rise to radiation.

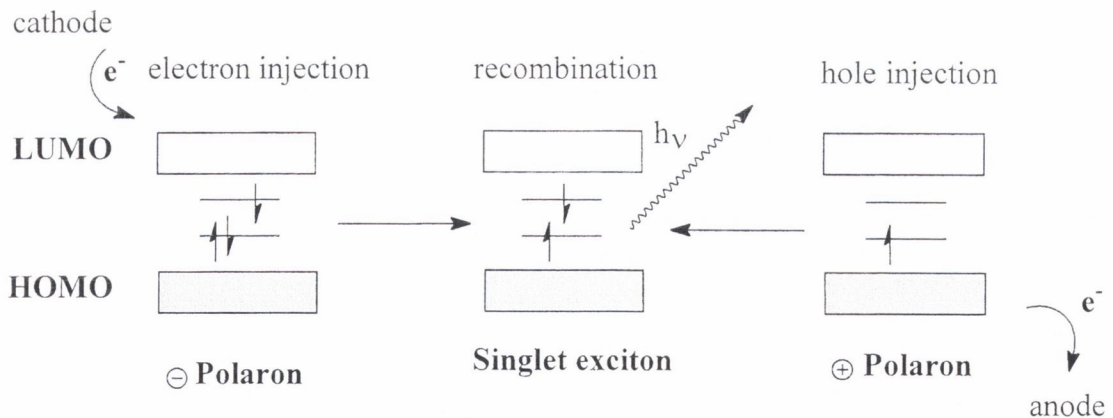


Fig. 1.7: Electroluminescence

1.10. Light Emitting Diode (LED)

Single layer devices

The simplest organic LED's employ one active layer such as PPV or a derivative of PPV and two injecting contacts, one of which is substantially transparent.

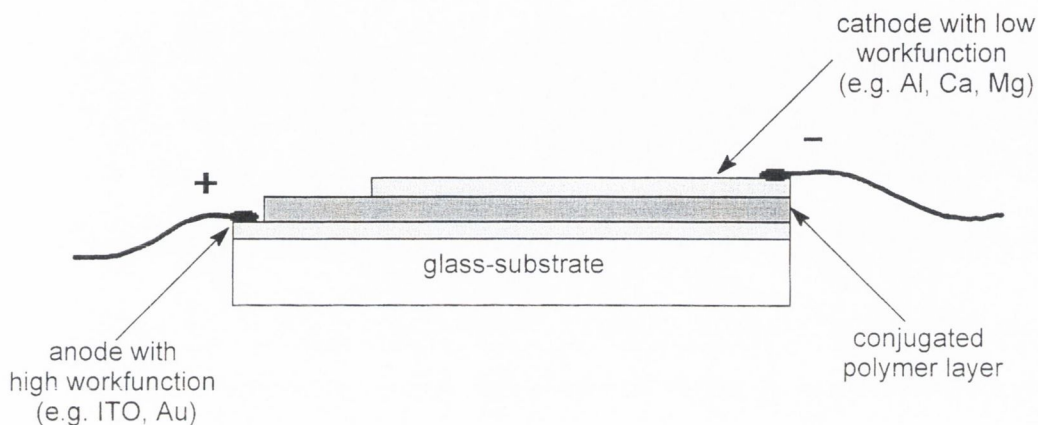


Fig. 1.8: Schematic structure of a single-layer organic LED

For efficient charge injection certain energy barriers have to be overcome. These energy barriers are dependent on relative positions of the energy levels of the polymer and the work function of the electrodes.

The workfunction of the cathode material is usually low (equivalent to electron affinity of the polymer) to facilitate efficient electron injection, whereas the workfunction of the hole-injecting semitransparent anode is preferably high (equivalent to the ionisation potential of the polymer).

For low work function cathode material Ca, Al or Mg are usually employed; whereas ITO is used as high workfunction anode material.

The operation of the device requires that electrons and holes are injected from opposite electrodes. Electrons are injected into the conduction band states of the polymer and holes into the valence band states. Note that there are potential barriers at the electrodes for injection of both electrons and holes from the aluminium and ITO electrodes, respectively. It is difficult to make accurate predictions about the barriers to electron and hole injection. Making reasonable assumptions about the polymer ionisation potential and electrode work functions, it

is clear that the barrier to injection of electrons from aluminium must be significantly larger than the barrier to injection of holes from ITO ^[39]. The majority of the current is therefore expected to be due to holes. Electroluminescence, however, requires the simultaneous injection of electrons, and the quantum efficiency will therefore depend strongly on the barrier to electron injection.

Also, most organic materials used in thin-film LED's do not transport both carrier types with comparable mobilities (generally there is a large disparity between electron and hole mobilities and hole mobility is usually larger) it is inevitable that the recombination must occur close to one of the electrodes ^[40]. This is critical since in this region (which can extend over a distance as large as several hundred angstroms) the nonradiative quenching by the metal has found to be significant ^[8] ^[41]. Electrons and holes capture in the simple case one another within the polymer film and form either singlet or triplet excitons, but only the singlet excitons decay radiatively ^[42].

The schematic diagram of the energy levels of an ITO/PPV/Al LED is shown in the figure below.

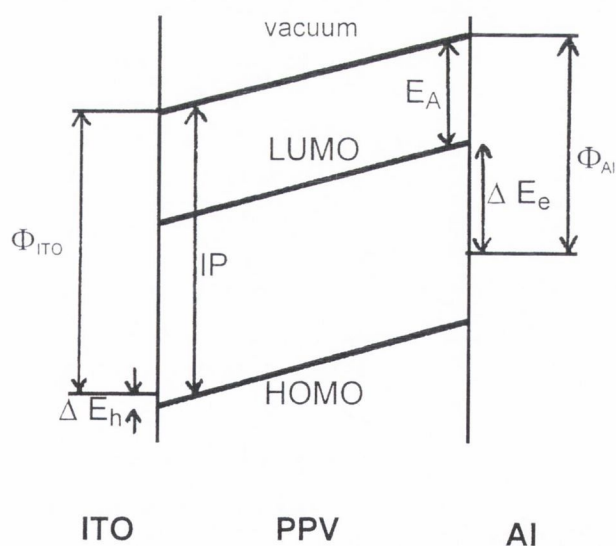


Fig. 1.9: Schematic energy level diagram for an ITO/PPV/Al LED, showing the ionisation potential (IP) and electron affinity (EA) of PPV, the work functions of ITO and Al (Φ_{ITO} and Φ_{Al}) and the barriers to injection of electrons and holes (ΔE_e and ΔE_h)

The operating characteristics of the single layer LEDs can be improved upon by separating the emission and transport functions, facilitating carrier confinement and carefully designing the emissive layer to have a very high quantum yield. This is achieved using multilayer devices.

Multilayer devices

The use of two-layer structures to control injection rates of electrons and holes by introducing barriers for charge transport at the heterojunction between the two semiconductor layer is now well established and a variety of different multilayer devices has been published [39] [43-46].

In multilayer organic LEDs it is advantageous to confine at least one of the injected carriers at an interface to enhance the probability of radiative recombination with the other carrier species.

With a combination of PPV and a cyano derivative of PPV, Greenham *et al.* have obtained internal efficiencies of ca. 4% whereas the single layer PPV device has been found to be much less efficient [47].

The structure of this two layer device is shown in figure 1.10.

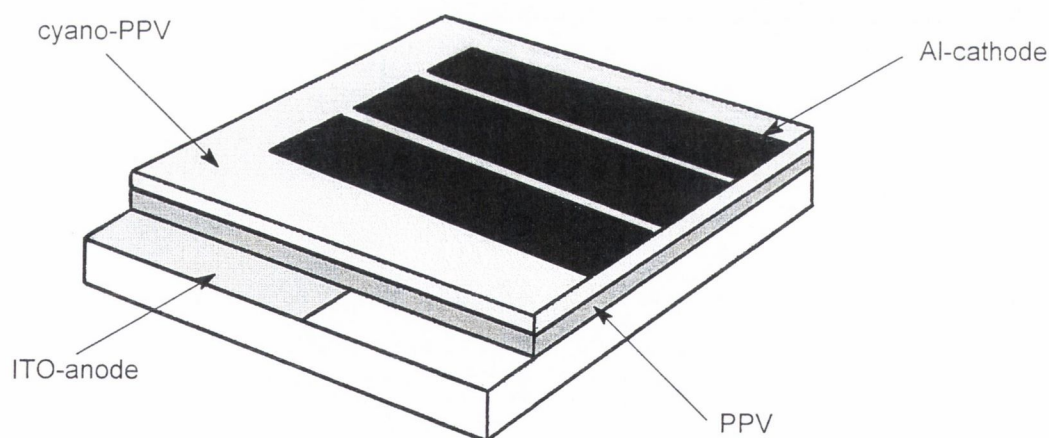


Fig. 1.10: Two layer ITO/ PPV/ CN-PPV/Al LED

At the interface between the two polymers there are offsets in the energies of the HOMO and the LUMO for the PPV and CN-PPV layers. Under forward bias, as illustrated in figure 1.11, injection of holes from the ITO into the HOMO of the

PPV layer results in transport of holes to the heterojunction, at which they are confined by the potential barrier, which must be surmounted if they are to progress into the CN-PPV layer. Similarly, electrons injected from the cathode are confined at the heterojunction by the potential step formed at the interface. This results in the build up of space charge on either side of the heterojunction. Tunnelling across one or the other barrier will allow electron/hole capture and the resulting electroluminescence.

One of the advantages of this device is that higher work function metals like Al instead of Ca can be employed.

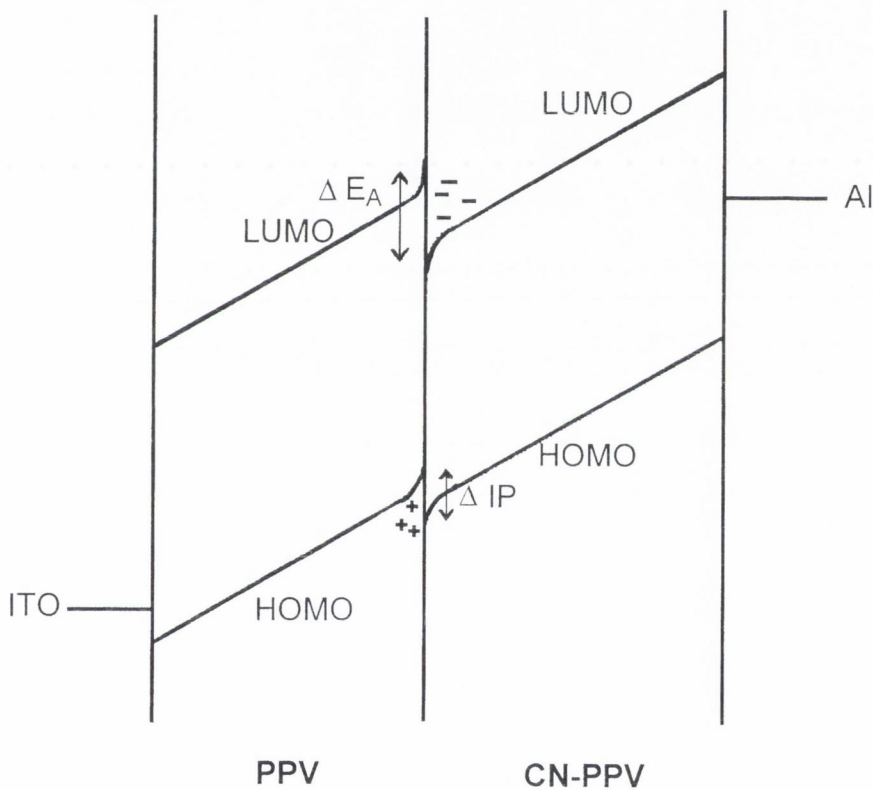


Fig. 1.11: Band scheme for the two layer ITO/ PPV/ CN-PPV/Al LED under forward bias

1.11. Photovoltaic devices

Polymer based photodiodes use the photovoltaic effect, by which electrons and holes are produced, separated by a built in voltage and subsequently collected at electrodes when a semiconductor device is illuminated.

The first problem that has to be considered with the use of organic molecular semiconductors is that the excited states produced by photon absorption are usually excitons that have relatively high binding energies and so do not easily dissociate to give electrons and holes. Exciton ionisation in the bulk is therefore not a promising method to follow. However, interfaces between molecular semiconductors or with electrodes, similar to the ones that have been shown in the previous section, can provide the correct energy differences to allow charge separation.

Two difficulties are commonly encountered. Firstly, carrier mobilities in these conjugated polymers are low, so that power loss is likely to be problematic at high levels of illumination. Secondly, the absorption depth is usually greater than the diffusion range of the excitons created by the absorption process. Thus, only a fraction of the excitons generated find the interface between the two semiconductors at which ionisation can occur.

Feldrapp *et al.* ^[48] and Yu *et al.* ^[48a] have shown that the photovoltaic effect in poly(*p*-phenylenevinylene) can be increased by an effective charge separation in PPV and C₆₀ blends.

Friend *et al.* ^[49] state that the 'active' region in PPV/C₆₀ blends is about 8 nm long and equals the diffusion length of the excitons which are photogenerated in the PPV. The active region is the area at the heterojunction between PPV and C₆₀ in which photogenerated excitons are most likely to result in charge generation through exciton dissociation. Efficiency of these devices is limited by low exciton diffusion range in relation to the optical absorption depth.

Sariciftci *et al.* ^[50] report that the transfer from PPV to C₆₀ is about 1000 times faster than the competing radiative and non-radiative processes and therefore the photoluminescence of PPV is expected to be quenched.

Combination of polymer, e.g. polythiophenes and poly(*p*-phenylenevinylenes) with colloidal nanocrystals of TiO₂ or CdS have been investigated ^[51]. Following the

example of the Graetzel cell, a ruthenium dye-sensitised nanocrystalline TiO_2 solar cell ^[52] ^[52a], the dye-electrolyte combination has been replaced by a single conjugated polymer layer bringing together the functions of light-absorption and hole transport.

Recently it was shown that thin layer $\text{SnO}_2/\text{flat-TiO}_2/\text{MEH-PPV/Hg}$ cells show a photovoltaic effect. To suppress recombination of injected electrons and holes the presence of an internal electric field at the interface of $\text{TiO}_2/\text{polymer}$ is necessary. This internal electrical field ensures fast transport of electrons through the TiO_2 and holes through the conjugated polymer layer, thus preventing recombination. An internal field is created by contacting a p-type material with a high workfunction with an n-type semiconductor yielding a region depleted of mobile charge carriers which has been demonstrated for the $\text{TiO}_2/\text{polymer}$ cells ^[31]. $\text{TiO}_2/\text{MEH-PPV}$ cells have been found to exhibit a photovoltaic effect with $V_{oc}=0.92\text{ V}$, $I_{sc}=0.32\text{ mA/cm}^2$ and a fill-factor of 0.52 under AM 1.5 illumination ^[53]. The theory behind these values will be explained in section 3.18.2.

Figure 1.12 below shows a schematic diagram of the operation mechanism in the solar cell device that was built for the present work.

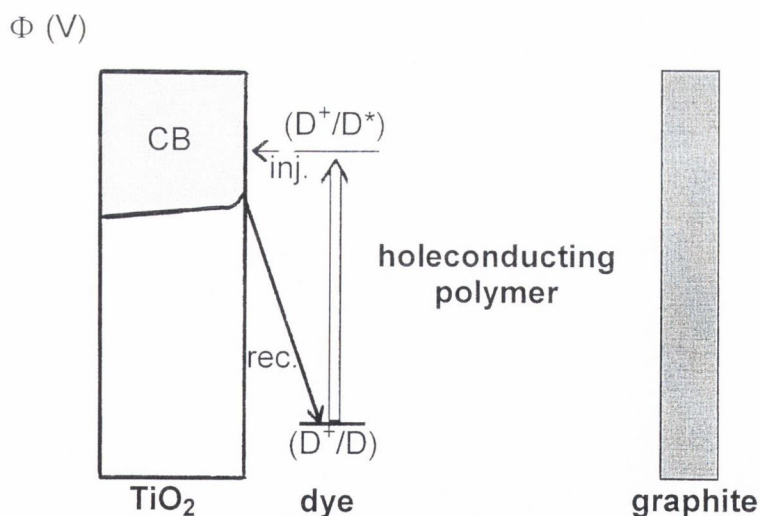


Fig. 1.12: Scheme for the electron-transfer processes (inj.= injection, rec.= recapture, also regeneration of the dye through the hole conducting polymer) occurring in the dye sensitised heterojunction

Visible light absorption by the ruthenium dye (which is shown in fig. 1.14) is followed by electron transfer to the conduction band of TiO_2 . The dye is regenerated by hole injection into the polymer layer:

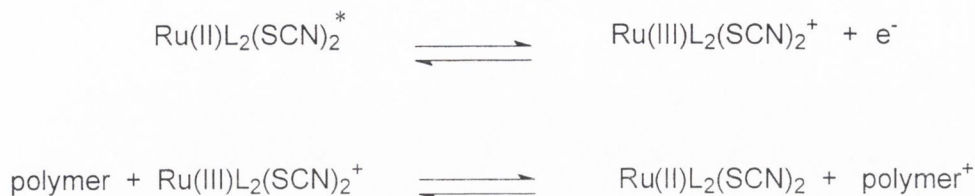


Fig. 1.13: Scheme of dye oxidation and regeneration

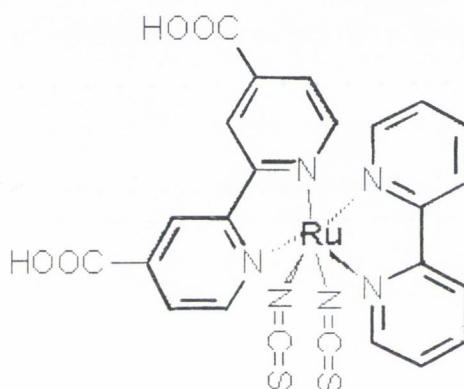


Fig. 1.14: $[\text{Ru}(4,4\text{-bis(carboxy)-bpy})_2(\text{NCS})_2]$, so called N3 ^[54]

1.12. Light emitting electrochemical cells (LECs)

Polymer light emitting electrochemical cells provide an alternative approach to obtaining light emission from semiconducting polymers. Between the two contact electrodes is a layer of a polymer blend of a luminescent conjugated polymer and a solid electrolyte, usually an ion transport polymer plus salt. When a voltage exceeding the potential difference between the HOMO and the LUMO is applied, the conjugated polymer is electrochemically doped n-type near the cathode and p-type near the anode. The counter ions from the electrolyte redistribute to compensate the charges on the oxidised and reduced polymer. Since the p- and n-

doped regions of the luminescent polymer are good conductors, the polymer/electrode interfaces become ohmic contacts and electrons and holes can be injected and transported to the insulating region near the centre of the film where radiative recombination occurs.

This is a very rough explanation of an LEC, more detailed explanations have been published by Heeger *et al.* who invented this type of light emitting device ^[55] ^[56].

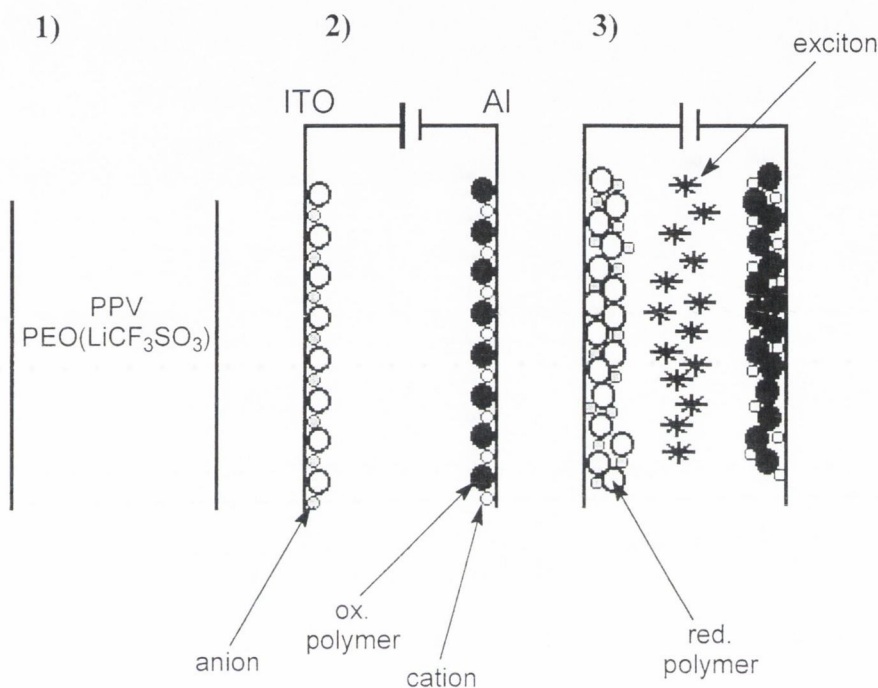


Fig. 1.15: Schematic diagram showing the operating mechanism of polymer LECs, 1) the cell before applying a voltage, 2) doping opposite sides as n-type and p-type and 3) charge migration and radiative decay

1.13. Field-effect transistors (FETs)

Conjugated polymers can be used in the construction of field effect transistors although charge carrier mobilities tend to be too low for most serious applications ^[8]. In a field-effect transistor, the voltage applied to the gate electrode determines the conductivity of a semiconducting channel which connects two other electrodes, the source and the drain. In a metal-insulator semiconductor (MIS) FET (shown in fig. 1.16) the gate electrode is separated from the semiconducting channel by a thin insulating layer ^[57]; the three layers form a MIS capacitor. Applying a voltage to

the gate modulates the conductivity in the semiconducting channel by altering the charge density in the semiconductor.

Although semiconducting polymers are not suitable for replacing silicon as the semiconductor for high-speed microelectronics, they are very promising for cheap high-volume microelectronics such as electronic identification tags, credit card encoding etc. For these applications, simple processing and mechanical flexibility are more important than high carrier mobility.

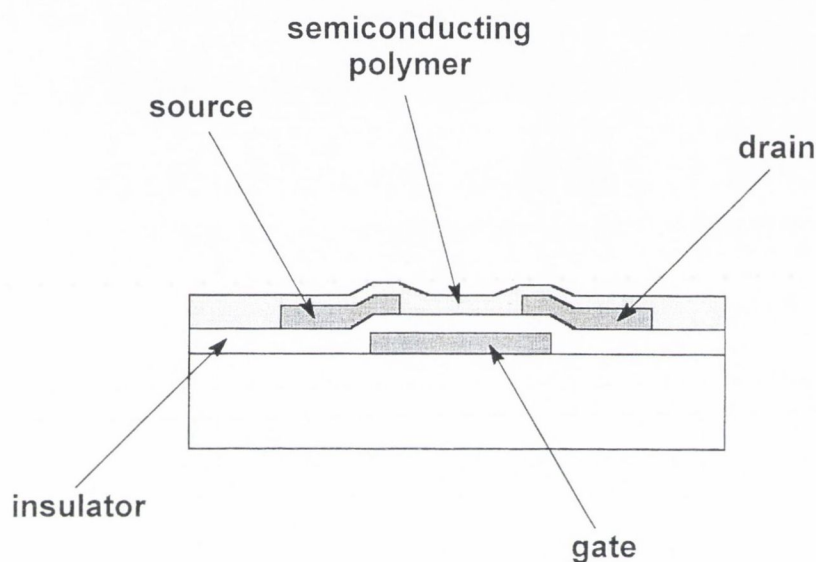


Fig. 1.16: Schematic structure of a polymer MISFET

1.14. Lasers

The nonlinear properties of PPV derivatives may prove useful in such applications as optical switches and electromodulators^[58].

As PPV is highly crystalline^[59], films tend to scatter light, which is a major problem for optical devices.

One solution has been found to use PPV/sol gel composites, where the optical quality was found to be much improved^[60]. PPV derivatives have also been investigated for use in waveguides^[61] and third-order nonlinear susceptibility in conjugated polymer solutions^{[28] [62] [63]}.

Laser action has also been reported in microcavities of MEH-PPV dispersions with TiO₂ nanoparticles that act as strong scatterers and provide a feedback mechanism

to achieve lasing ^[30]. Also Friend *et al.* ^[64] reported stimulated emission of PPV films incorporated into a microcavity structure.

1.15. Rechargeable batteries

The attraction of employing conducting polymers in rechargeable batteries lies in the specific weight of polymers, which is considerably lower than that of ordinary inorganic materials, as well as potential environmental benefits ^[65].

In principle there are three different types of batteries. The active polymer electrode can be used either as cathode, as anode, or as both cathode and anode.

The polyacetylene cell has been intensively researched and first published by MacDiarmid *et al.* ^[66]. Initially, p-doped PA was used as active electrode and Li as anode.

Although in principle, the properties of PA are promising, its commercial prospects are less. This is chiefly due to the chemical instability of PA. Other conducting polymers, like e.g. Ppy and Pani have been investigated and found quite promising.

A battery with a thin film of PPV derivative on Pt as cathode material and Li as anode in LiClO₄/CH₃CN electrolyte has been published by Hoerhold *et al.* ^[67].

1.16. Other applications

Some rather exotic applications, mainly based on employing Pani as the conducting polymer can also be found in literature ^[68].

Due to the fact that conjugated polymers can be easily modified after synthesis through doping to enhance their separating abilities they were investigated for their gas liquid separation abilities in membranes ^[69]. Pani has also been studied for the use of anti-corrosion coatings ^[70] and gas ion sensors ^[71].

Another possible application has been found to be employing conducting polymers as chemical sensors to convert the chemical potential energy of a targeted analyte into a proportionate measurable signal using the ability of these polymers to undergo a wide range of molecular interactions ^[72].

The need for electrically conducting textiles for electromagnetic interference shielding, static dissipation, resistive heating and even radar shielding for military

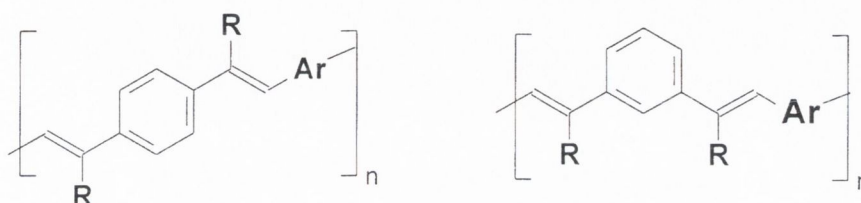
applications has initially employed metals such as brass and aluminium which were woven into the garment. Conducting polymers offer an interesting alternative to coated or filled plastics and textiles ^[73].

And finally, the use of conducting polymers in artificial muscles has been investigated. Redox properties and changes in potential of these polymers promote fast reversible changes in volume and length and therefore could be employed for micro robotics and micro machinery ^[74].

2. Research aims

The focus of this thesis was to synthesise and characterise very complex PPV related polymers and to investigate their application in optical devices.

Therefore, a variety of materials of the following structure was synthesised:



R = differently substituted phenyl moieties

Ar = substituted naphthalene and phenylene units

To make these complex structures it was necessary to introduce bulky phenylene side-groups (R) into the polymer structure to investigate the resulting very complex PPV systems. As already mentioned, these phenyl substitutions have been found to improve the stability to air and light and also the film forming properties. Additionally, the structural modifications on the polymer backbone were studied by altering *para* and *meta* substitution of the centre phenylene unit and also by varying arylene units.

Some polymers without bulky side-groups were synthesised to compare these complex materials with rather plain structures.

The influences of all the different structural alterations on the optical properties, also electrochemical and thermal behaviour had to be investigated, not only for characterisation purposes but to see if this would lead to any applications for optical devices which had to be fabricated.

3. Results and Discussion

3.1. Introduction

This chapter presents the syntheses of both the starting material and the obtained polymers. Also the characterisation (to some extent) and also device preparation will be presented.

First of all, the polymerisation route and the reaction conditions of the chosen method will be discussed. Then, the preparation of the ketone starting material will be presented, followed by the synthesis pathways chosen for the different phosphonate ester starting materials of each polymer group. The final polymerisation will be presented separately for each polymer group or each single polymer with the basic characterisation (GPC, ^1H -NMR, ^{13}C -NMR, FTIR and Raman) results attached to the syntheses.

The results of the thermal, optical and electrochemical characterisation will be presented in subchapters for all polymers together in order to discuss the investigation by comparing the different polymer groups. Finally, the preparation and characterisation of LEDs and solar cells will be shown.

3.2. Discussion of the employed polymerisation method

A number of synthetic approaches for PPV materials have been reported in the literature: Wessling-Zimmermann route ^[75], Wittig reaction ^[76], aryl/ethylene coupling via Heck ^[77] or Suzuki-reactions ^[78], McMurry ^[79], the Gilch route ^[80] and numerous others.

Polymers synthesized by these methods contain small amounts of structural defects as a result of incomplete elimination, cross-linking or other side reactions during polymerisation. These reactions also have the disadvantage that alternating copolymers with different arylene vinylene units cannot be prepared.

Hanack and co-workers employ the Knoevenagel condensation polymerisation ^[22] ^[81]. This method is not suitable for the required polymers since only polymers with electron-withdrawing groups on the vinylene bond are accessible via this route.

Both Wittig and Horner are heterocoupling-processes and therefore these polycondensation routes are suitable for the synthesis of well-defined strictly alternating copolymers.

Horner-ylides are more reactive than the corresponding Wittig-ylides which frequently do not react with ketones ^[82].

Furthermore the Horner reaction resulted in better yields in previous investigations ^[83] ^[84] and the phosphorous product is soluble in water which makes it easier to separate from the alkene product.

Hence this route was finally chosen for the synthesis of the polymer for this work.

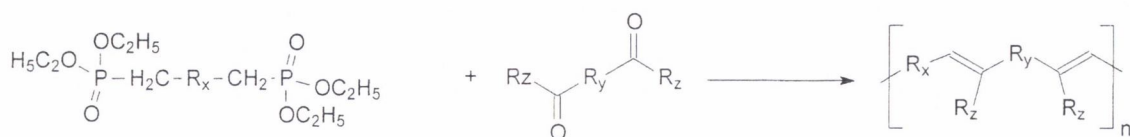


Fig. 3.1: Schematic Horner synthesis

The phenyl substitution R_z on the vinylene bond make the polymers soluble and protect them against degradation due to the action of oxygen and light. Additionally phenyl substitution is expected to offer various possibilities for the

introduction of electron donating or withdrawing groups via the phenyl rings and allow diverse structural modifications. [27].

3.3. Stereo chemical aspects of the Horner Reaction

Another issue that has to be taken into consideration for the characterisation of the polymers is the formation of the *E/Z*- or *cis/trans*-configuration.

The following figure 3.2 shows the two intermediates on the example of methyl-*PpPV*.

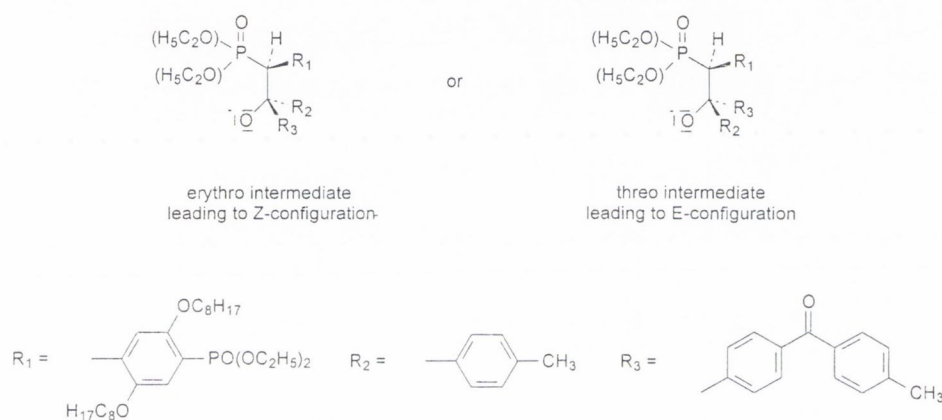


Fig. 3.2: Erythro and threo intermediates of methyl-*PpPV*

In the Horner reaction the major product is usually the *E*-alkene. Increasing amounts of *Z*-alkene are obtained as the steric bulk of the substituents on the carbonyl compound and the phosphonate ester increases [87].

This is in agreement with the observations made by Hoerhold *et al.* who found that the Horner reaction result in unsubstituted vinylene double bonds in an all-trans configuration whereas phenyl-substituted double bonds were found to possess increased *E/Z*-configuration [88] [89].

The stereochemical outcome of the olefination-reaction has been extensively studied. In general, factors leading to the predominance of the *E*-isomer are elevated temperatures, apolar solvents, stabilising salts (lithium or sodium halides), electron-rich phosphorus atom [-PO(OR)₂] and excess base. Formation of the *Z*-

isomer is promoted by lower temperatures, polar (aprotic) solvents, salt-free solutions and an electrophilic phosphorus atom [PPh₃] ^[90].

For PPV it has been found that *cis* configuration influences the solid state emission efficiency; a higher proportion of *cis* bonds gives a higher emission efficiency, presumably as a consequence of reduced interchain interactions ^[63].

Observations in our research group were made that for the purification of carbon nanotubes poly(*m*-phenylenvinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene) batches with high ratio of *trans*-configuration are required since they tend to wrap around the carbon nanotube. Modelling studies indicate that the all-*trans* polymer chain coils in a regular manner with a coil diameter of 20 Å and a pitch of 6 Å (in vacuum). The introduction of *cis* linkages into the polymer chain results in a more random coiling ^{[91] [92]}.

Attempts were made to employ the present polymers for purification of nanotubes but as expected, they do not interact in the manner poly(*m*-phenylenvinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene) does.

The *E/Z*-ratio have been estimated from relevant ¹H-NMR, IR and Raman peaks in various publications ^{[19] [27] [93]}.

For the present work the *cis-trans* ratios for the polymers were not estimated from either method due to the very complex polymer systems causing overlapping peaks.

3.4. Synthesis of the Ketones

All ketones were prepared by orthodox Friedel-Crafts reactions. The reaction of either terephthaloyl-chloride or isophthaloyl dichloride with two equivalents of an aromatic hydrocarbon in the presence of anhydrous aluminium chloride gave the required aromatic ketones. The synthesis is shown in figure 3.3.

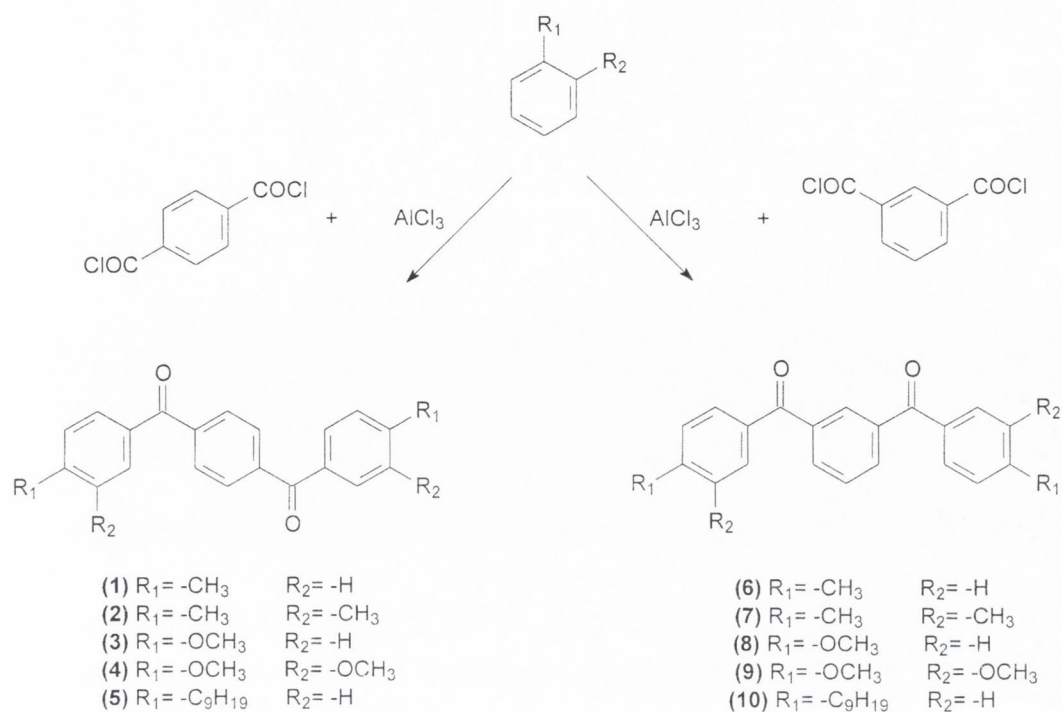


Fig. 3.3: Friedel- Crafts Acylation of either terephthaloyl-chloride or isophthaloyl dichloride with different alkyl- and alkoxy-benzenes

Generally an excess of the aromatic hydrocarbon was used as a solvent for the reaction.

However, syntheses using isophthaloyl dichloride tended to dry out and therefore dichloromethane was added. Additionally, isophthaloyl dichloride was found to be more reactive and had to be handled more carefully than terephthaloyl-chloride.

3.4.1. 1H -NMR spectroscopy

The ketones can be divided into two groups: the 1,4-substituted diketones and the 1,3- substituted diketones. For the 1,4-substituted diketones the characteristic singlet peak for four protons of the centre phenylene unit appears at 7.83-7.89 ppm. 1,3-substituted diketones show one singlet at 8.09-8.16 ppm, one doublet at 7.95-7.99 ppm and one triplet at 7.60 ppm.

The peaks of the aromatic protons of the outer phenylene unit vary with the substitution pattern. For the mono-substituted phenylene groups two doublets (integrating for four protons each) occur, whereas for the di-substituted adducts the

aromatic region shows two doublets and one singlet (integrating for two protons each). The aliphatic region of the spectrum shows either one singlet peak around 2.4 ppm for methyl groups and around 3.9 ppm for methoxy groups or a number of peaks for long-chain alkyl or alkoxy side groups.

3.4.2. ^{13}C -NMR

The peaks of ^{13}C -NMR-spectra were interpreted with the help of increment calculations.

All spectra show peaks of the keto-groups at 194.7-196.0 ppm. The two characteristic peaks of the centre phenyl ring of 1,4-substituted ketones appear at 140.7-140.9 ppm (arom.C-C=O) and at 129.9-130.8 ppm (arom. =CH-).

Spectra of 1,3-substituted ketone show four different peaks:

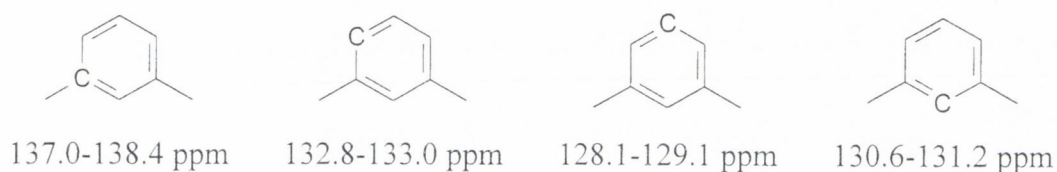


Fig. 3.4: ^{13}C -NMR data of the centre phenylring of the 1,3-substituted ketones

potassium bromide. The reaction is very sensitive to any kind of impurity and produces a greenish-brown sludge if not handled properly. The flasks were soaked in dilute HCl for 24 h before and dried. All NMR spectra of this product show that the reaction did not produce mono-substituted derivatives. In the final step, the Arbuzov reaction of 1,4-bis(bromomethyl)-2,5-di-n-octyloxybenzene (**12**) with triethylphosphite gave 2,5-di-n-octyloxy-1,4-xylene-diethylphosphonate-ester. This reaction is carried out without solvent.

Since this reaction route is very well known ^{[19] [83] [85] [86]} it is not necessary to go into the characterisation in great detail. All steps gave good yields, were easily purified and characterised by common methods.

3.6. Horner polycondensation of the PPV derivatives

Both toluene and DMF are frequently employed in this reaction. The product and starting material are soluble in both solvents. Previous investigations have shown that the crude product obtained from the DMF reaction was easier to purify and therefore resulted in higher yields.

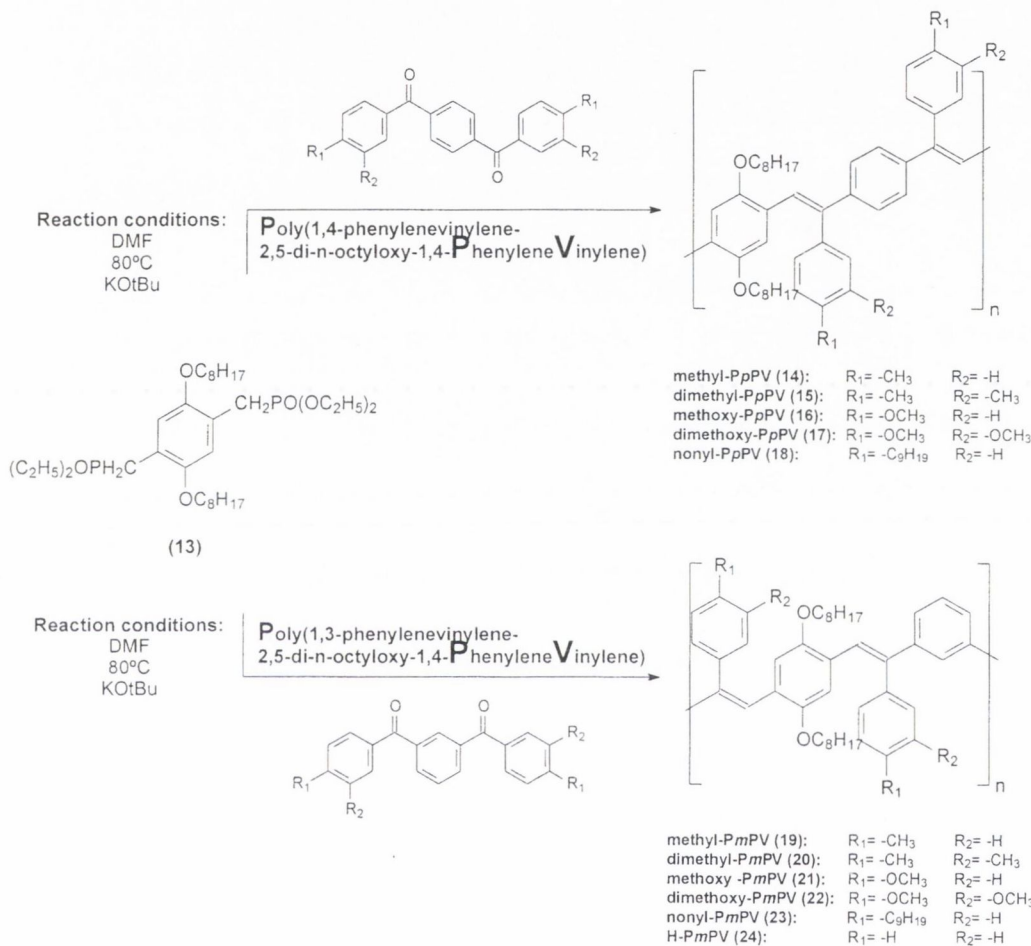


Fig. 3.6: Horner polycondensation of 2,5-di-n-octyloxy-1,4-xylylene-diethyl-phosphonate-ester with different diketones

Also the influence of temperature on this reaction was investigated ^[84]. It was found that for a range of reaction temperature from 50-110°C the best yields and largest M_n with lowest M_w/M_n were obtained at 80°C. It was also found that between 50-75°C and 90-110°C 10-40% of starting material remained unreacted. Therefore the reaction was carried out at 80°C.

Ten different PPV derivatives were successfully synthesised by the Horner reaction route. All ten are soluble in common solvents e.g. chloroform, toluene, dichloromethane, trichlorobenzene, THF and DMF.

Additionally, the synthesis of the following polymer was unsuccessfully attempted:

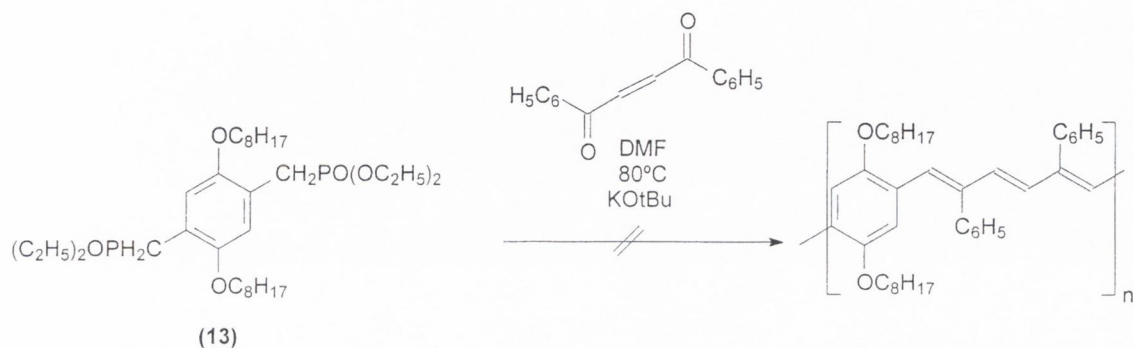


Fig. 3.7: Unsuccessful Horner polycondensation

Although the polymerisation was carried out several times, only brownish slime was obtained.

3.6.1. Gel permeation chromatography

	M_n	M_w	M_w/M_n
methyl-PpPV	5436	46730	8.60
dimethyl-PpPV	5025	31025	6.14
methoxy-PpPV	4532	8259	1.82
dimethoxy-PpPV	5499	9217	1.68
nonyl-PpPV	2099	5355	2.55
methyl-PmPV	2980	5042	1.69
dimethyl-PmPV	4293	10225	2.38
methoxy-PmPV	3864	9980	2.58
dimethoxy-PmPV	3220	6516	2.02
nonyl-PmPV	4557	8653	1.90
H-PmPV	1870	2402	1.28

Table 3.2: Molecular weight details of the PPV derivatives (polystyrene was used as the calibration standard)

On average the molecular weight is more in the range of oligomer molecular weight. The poly-dispersivity of the material is low except for methyl- and dimethyl-PpPV although they were prepared, purified and soxhleted under the same conditions.

Even with optimised reaction conditions diarylketones are not very reactive. Also sterical effects have to be taken into consideration because of the bulky side groups which complicate formation of the intermediate.

3.6.2. $^1\text{H-NMR}$

In general the polymer spectra show very broad peaks in the aromatic region (low-field), whereas the aliphatic (high-field) signals exhibit sharp peaks. Due to overlapping it was difficult to distinguish specific aromatic peaks.

According to $^1\text{H-NMR}$ -calculations the proton of the vinylene unit appears between 6.92-7.19 ppm depending on the substitution pattern. The aromatic proton in ortho

position to the octyloxy side-chains appears at 6.25-6.27 ppm for the alkyl-PPVs and at 6.31-6.33 ppm for the alkoxy-PPVs.

The methylene groups adjacent the oxygen of the octyloxy group show a signal at 3.98-4.01 ppm and the signals of the remaining protons of the alkyl chain appear between 1.84-0.87 ppm. Depending on the substitution pattern additional peaks appeared in this area.

3.6.3. ^{13}C -NMR

Although even in ^{13}C -NMR the peaks are broad, more information could be obtained than from ^1H -NMR. For the present polymer systems peaks are shifted and broadened due to the different positions of the respective carbons in the chain and different chain lengths.

The spectra of all PPV derivatives show that all starting material was removed by purification. The characteristic peaks of the starting materials were not found: (i) carbon peaks of the keto group at 195 ppm, (ii) methylene carbon adjacent to the phosphorous at 34.1 ppm and (iii) the methylene peaks adjacent to the oxygen in the alkoxy groups at 61.6 ppm.

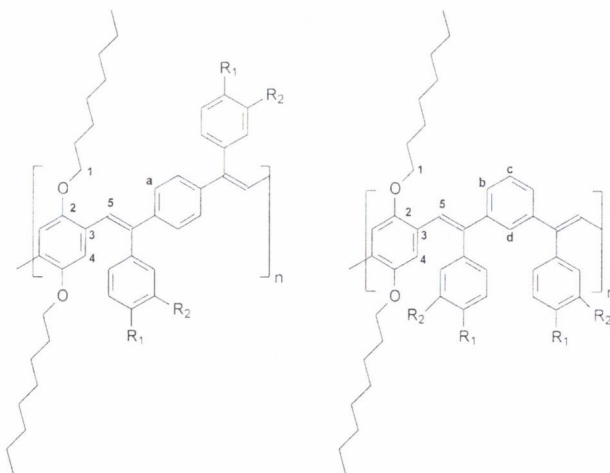


Fig. 3.8: Structure of *para* and *meta* PPV derivatives

Also, seven signals of the alkyl chains of all PPV derivatives dominate between 14-32 ppm, the methylene carbon adjacent the oxygen (1) appears at 68 ppm.

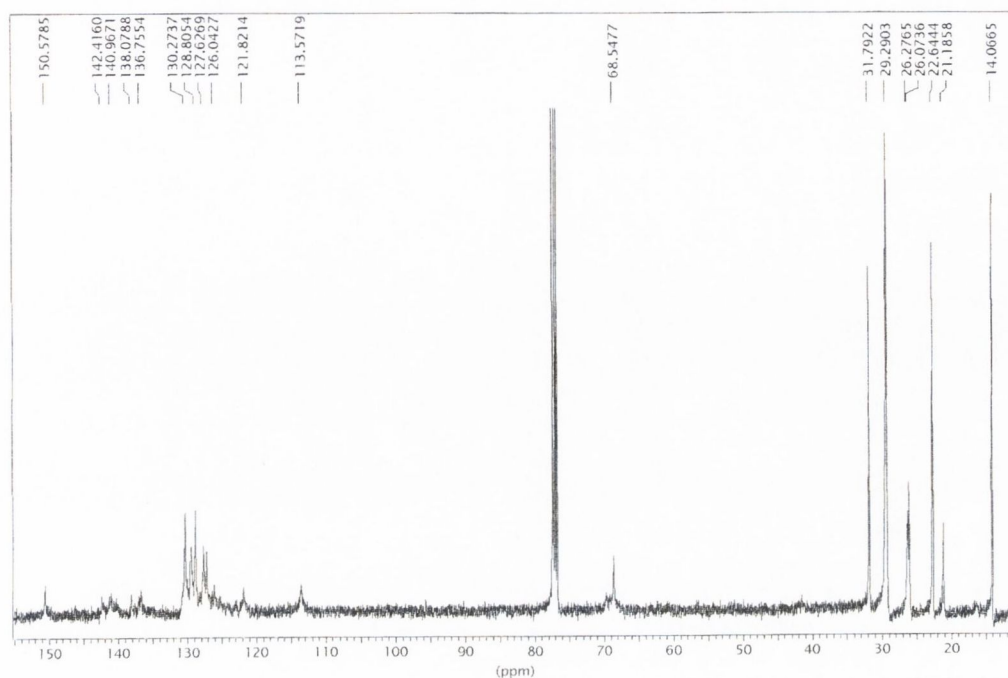


Fig. 3.9: ^{13}C -NMR of methyl-PpPV (100MHz / CDCl_3)

The characteristic aromatic modes derive from the protonated carbon at the vinyne unit (5) at 122 ppm, the protonated carbon (4) adjacent to the octyloxy substituted carbon at 113.6 ppm, the unprotonated carbon atom (3) linked with the vinyne unit typically shifted upfield at 126 ppm and the unprotonated carbon substituted with the octyloxy group at 150 ppm.

The unprotonated carbons obviously do not appear in the distortionless enhancement by polarisation transfer (DEPT) spectrum.

The DEPT of methyl-PpPV is shown in figure 3.10.

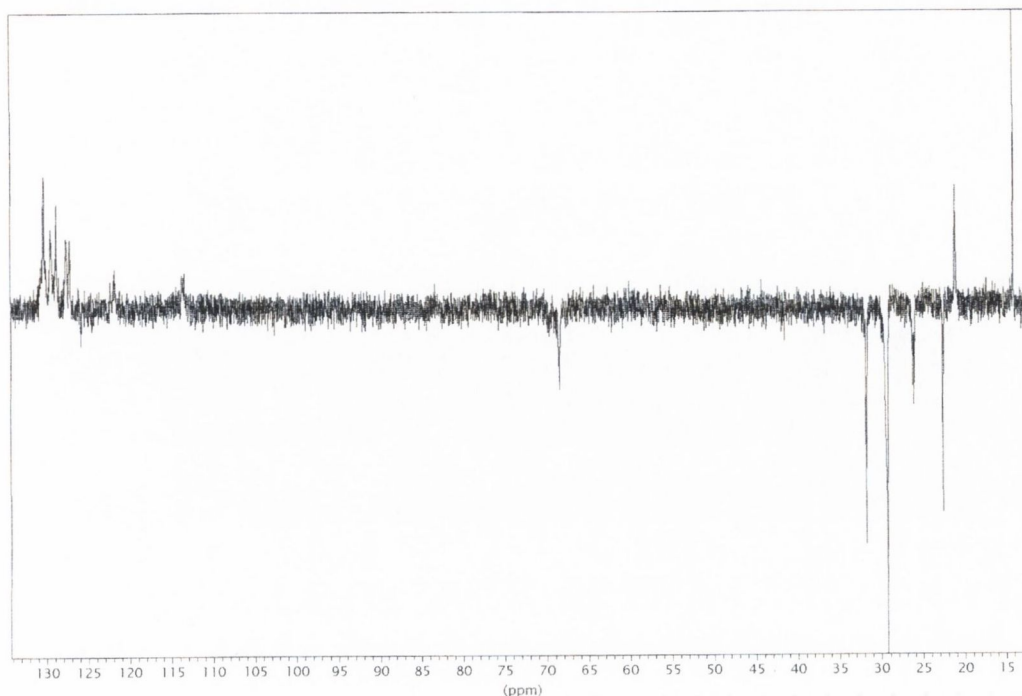


Fig. 3.10: DEPT 135 of methyl-PpPV (100MHz / CDCl_3)

The *p*-substituted phenyl ring only shows one strong mode for the aromatic carbon (a) at 127 ppm whereas three non-equivalent aromatic carbons (b, c, d) appear for the *m*-substituted phenyl ring at approximately 128, 127 and 126 ppm.

3.6.4. IR-spectroscopy

On the one hand, IR is a more sensitive method to investigate if the purification was successful and all starting material was removed^[94]. On the other hand, due to the quite complex system of the present polymers many overlapping modes are expected. Therefore IR-characterisation was mainly employed to search for remaining starting material.

Very strong alkane C-H stretching vibrations were found in the region of 2925-2850 cm^{-1} . The spectra also show the characteristic C-H stretching vibration of aryl compounds at 3020 cm^{-1} .

The modes of the fingerprint region are broader due to overlapping especially around 1600-1450 cm^{-1} (in plane skeletal vibrations of the aromatic rings). The C=O modes at 1669, 1654, 1644 cm^{-1} that were found in the ketone IR-spectra

either disappeared or only very weak peaks were found. This could be due to the end-groups. The C=C stretching vibration is expected around the same region but is less intense than the C=O stretching vibration; it appears at $1598\text{--}1608\text{ cm}^{-1}$.

Another characteristic mode was identified to be the alkyl-aryl ether C-O stretching vibration at 1040 cm^{-1} .

The phosphonate ester starting material shows a strong characteristic mode at 1280 cm^{-1} (P=O) which was not found in any of the polymer graphs.

3.6.5. Raman

In addition, Raman spectra were recorded. The most intense infrared bands are usually those arising from polar bonds such as O-H, N-H, and C=O, while the most intense Raman bands are usually those arising from bonds having nearly symmetrical charge distribution, such as C-C, C=C or S-S. Thus, infrared spectroscopy is usually preferred for studying the substituents in a polymer while Raman spectroscopy is preferred for studying the backbone conformation of a polymer.

The Raman lines that appear in the region of $1070\text{ to }1300\text{ cm}^{-1}$ arise from vibrations of the -C-C- backbone and are absent in the IR. These Raman active skeletal modes are quite useful in characterising polymers since they are likely to be sensitive to micro-structural changes^[95].

Despite large numbers of degrees of freedom, the Raman spectra of even these complex PPV derivatives are extremely simple. The spectra show a few characteristic lines with distinct positions depending on the substitution pattern.

The spectra of all PPV derivatives show broad but weak peaks for the C-H stretching vibrations modes of the alkyl chains around 2880 cm^{-1} .

Raman measurements of the starting materials show two weak peaks (doublet) between $1570\text{ and }1590\text{ cm}^{-1}$ for 1,4-di-n-octyloxybenzene (11), whereas 2,5-di-n-octyloxy-1,4-bis(bromomethyl)-benzene (12) and 2,5-di-n-octyloxy-1,4-xylylene-diethyl-phosphonate-ester (13) exhibit strong peaks in the same region.

For the polymers the aromatic C=C stretching vibrations exhibit a very strong peak, which is probably the overlaying peak of the doublet, in the centre of the spectrum at approximately 1580 cm^{-1} .

The *E*-vinylene C-H deformation vibration appears at 1290 cm^{-1} and the *Z*-vinylene vibration at 1230 cm^{-1} .

The pattern of the peaks between 1180 cm^{-1} and 1090 cm^{-1} appears to be very characteristic for the PPV-derivatives and their substitution pattern. Aromatic in plane and out of plane ring or C-H deformation vibrations occur in this region and also aliphatic C-C skeletal and C-H vibrations.

For the *para* substituted polymers two peaks at 1180 and 1130 cm^{-1} were found, whereas *meta* substituted polymers either give rise to one signal at 1160 cm^{-1} (methoxy-PmPV, methyl-PmPV) or no mode (dimethoxy-PmPV, dimethyl-PmPV). Also characteristic for the *m*-substitution are also two peaks at 885 cm^{-1} and 985 cm^{-1} , whereas *p*-substituted derivatives show only one peak at 885 cm^{-1} .

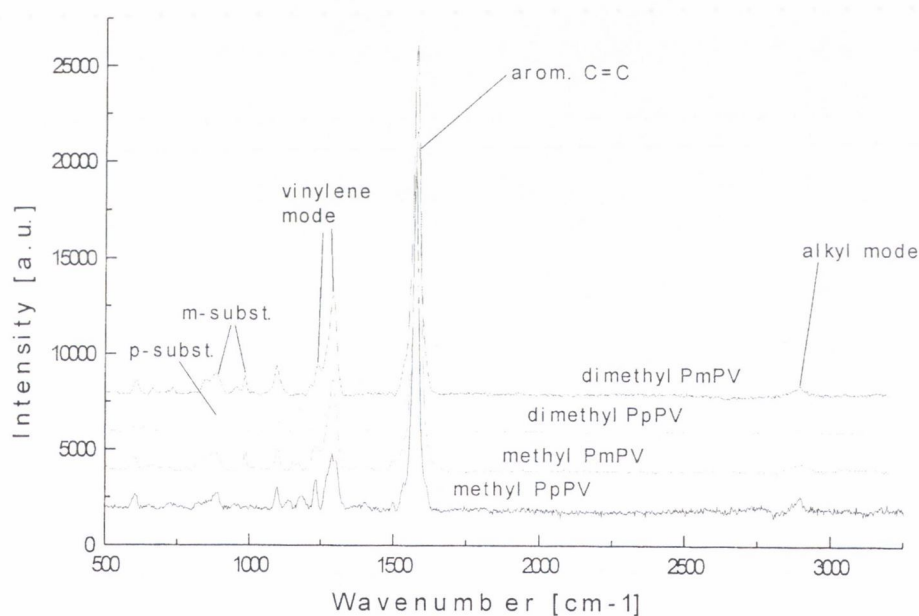


Fig. 3.11: Raman spectra of *p*-/*m*-substituted methyl and dimethyl PPV (in CHCl_3 solution)

3.7. Synthesis of 1,5-bis-n-octyloxy-2,6-naphthalenedialdehyde (25)

Although dioctyloxy-benzene was easily methyl brominated to obtain 1,4-bis(bromomethyl)-2,5-di-n-octyloxybenzene, the same reaction was not successful for the synthesis of the corresponding naphthalene derivative:

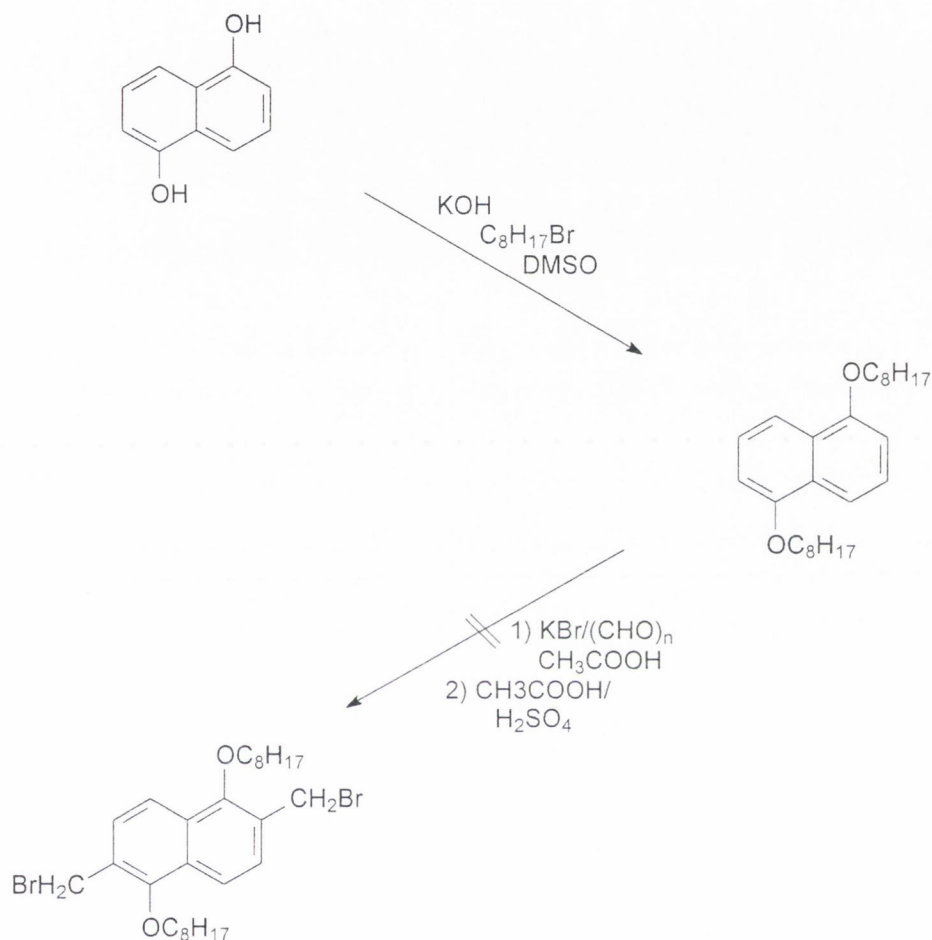


Fig. 3.12: Alkylation and unsuccessful methyl-bromination of di-hydroxy-naphthalene

Hanack *et al.* report ^[22] the synthesis of 1,5-bis(n-hexyloxy)-2,6-naphthalenedialdehyde: In a four step synthesis 1,5-dihydroxy-naphthalene was brominated, the resulting 1,5-dihydroxy-2,6-dibromo-naphthalene was hexylated to yield 1,5-dihexyloxy-2,6-dibromonaphthalene. Treatment with copper cyanide leads to the dicyano-derivative that upon reduction with DIBAL-H yielded the required dialdehyde. This four-step reaction was improved by the same group ^[96].

Fig. 3.13 shows the complete reaction route for 1,5-bis-n-octyloxy-2,6-naphthalenedialdehyde.

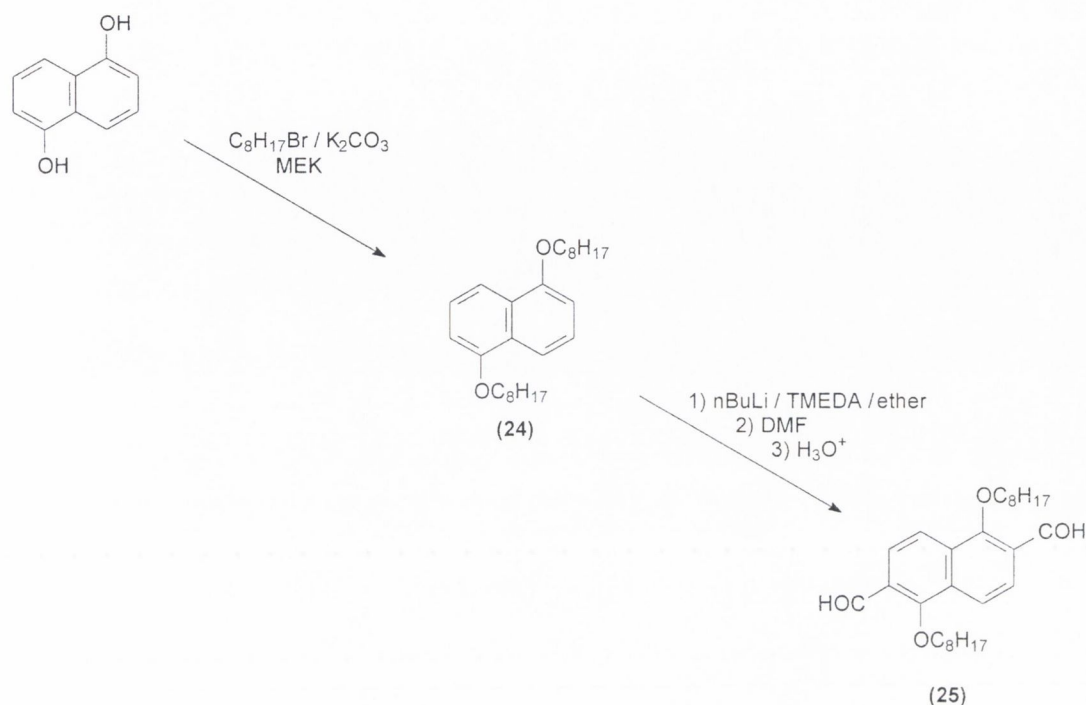


Fig. 3.13: Synthesis route of 1,5-bis-n-octyloxy-2,6-naphthalenedialdehyde

The first two steps of this synthesis were carried out during a short time scientific mission to the 'Arbeitskreis Prof. Dr. Dr. h.c. M. Hanack, organisches Institut II, Eberhard-Karls-Universitaet, Tuebingen/Germany'.

It was found that alkylation of 1,5-dihydroxynaphthalene employing K_2CO_3 in methyl ethyl ketone (MEK) ^[97] is more suitable for the naphthalene compound than the method that was used for 1,4-hydroquinone (KOH in DMSO). Alkylation with KOH in DMSO resulted in not only in a high amount of mono substituted product but also remaining starting material product whereas reaction with K_2CO_3 yielded only traces of mono substituted product. It was also found that the choice of solvent has a great impact on the purity of the product. Initially the reaction was carried out in ethanol to give a brownish-black solid in a brown oily solution that has to be purified by re-crystallisation and column chromatography. The same reaction in MEK resulted in a greenish-yellow suspension. The product was re-crystallised

once to give bright yellow crystals. The second step, ortho-lithiation followed by formylation is more demanding. It requires very careful heating and cooling procedures and still failed several times. NMR spectra of the crude product showed impurities of starting material and monosubstituted product. The impurities were easily separated over a short column (silica gel/ether). The collected fractions were left standing until the characteristic white balls crystallised from the solution. The ^1H -NMR shows that these fractions contain no mono-substituted by-product since only the expected two doublets for **2** and **3** appear due to the integration:

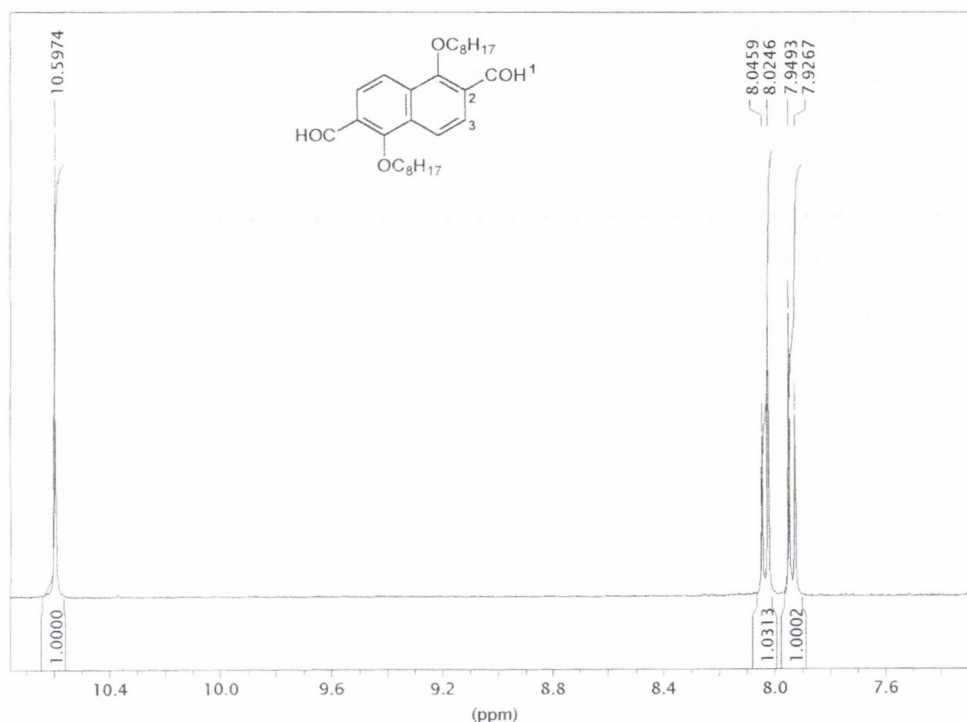


Fig 3.14: Section of the aromatic peaks in the ^1H -NMR of 1,5-bis(n-octyloxy)-2,6-naphthalenedialdehyde

3.8. Polymerisation of Poly(2,5-bis(n-Octyloxy)-1,4-PhenyleneVinylene-1,5-bis(n-Octyloxy)-2,6-NaphthyleneVinylene (36) (POPV-ONV)

POPV-ONV was synthesised under the same reaction conditions as the PPV derivatives.

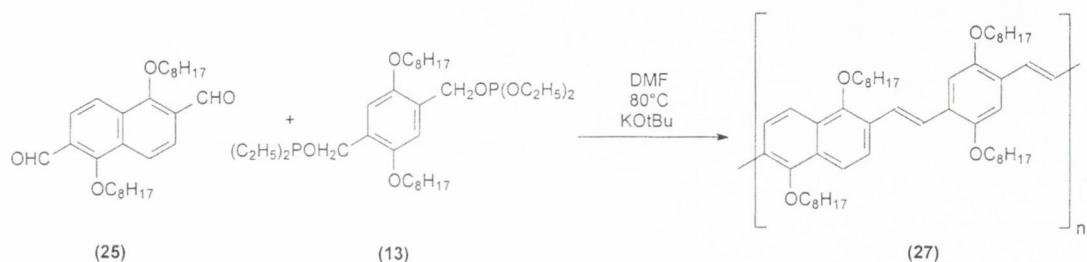
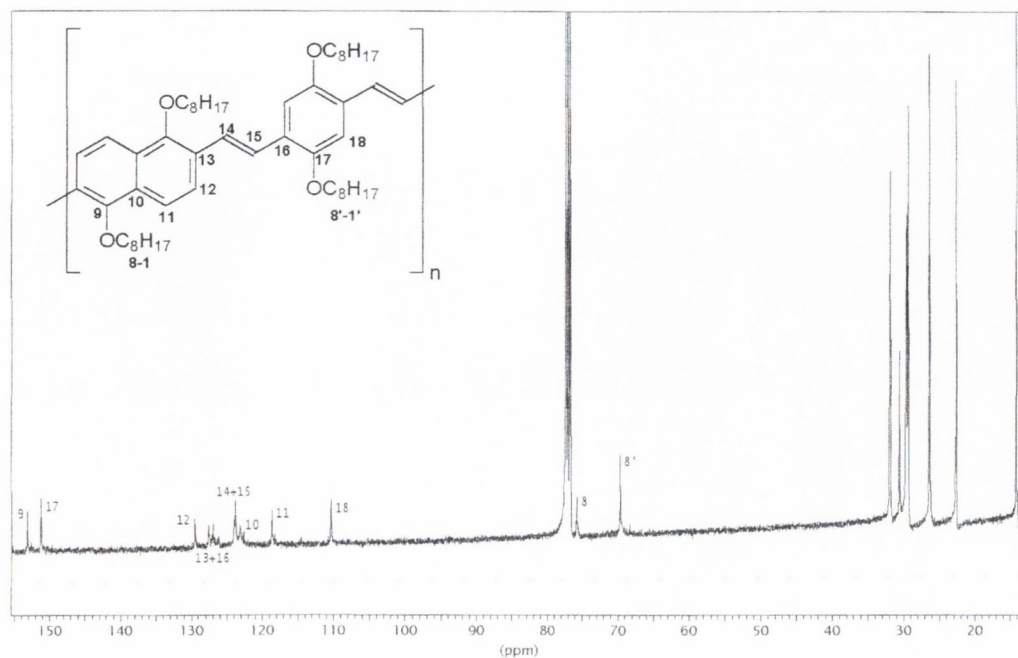


Fig. 3.15: Horner condensation polymerisation of POPV-ONV

Compared to the PPV derivatives the reaction of POPV-ONV showed a strong luminescence a short time after the KOtBu was added. Gel permeation chromatography in 1,2,4-trichlorobenzene showed a number-average molecular weight of $M_n = 5660$, a weight average molecular weight of $M_w = 13381$ and the polydispersity index $M_w/M_n = 2.35$ (polystyrene standard).

3.8.1. $^1\text{H-NMR}$

The signals of the protons in the alkyl chain appear at 0.90-1.95 ppm. The methylene groups adjacent to the oxygen of the octyloxy group show a signal at 4.12 ppm and the proton of the vinylene unit appears between 7.26 ppm. The aromatic protons of the octyloxy phenylene unit give rise to a signal at 7.65 ppm and the aromatic protons of the naphthalene unit 7.92 and 7.86.

3.8.2. ^{13}C -NMRFig. 3.17: ^{13}C -NMR of POPV-ONV

The aliphatic methylene carbons adjacent to the oxygen of the octyloxy group show two signals at 69.6 ppm for the octyloxy phenylene unit (8') and at 75.1 ppm for the octyloxy naphthalene unit (8). Also the ether substituted ring atoms give rise to two different signals at 151.2 ppm (17) and 153.2 ppm (9). The two vinylene carbons appear at 123.8 ppm. The carbons 13 and 16 ($\delta = 127.6, 127.0$ ppm) are non-protonated and were assigned using DEPT technique. No peak that indicates remaining starting material is present in the spectra. The protonated peaks of the naphthalene unit appear at 129.5 ppm (12) and 118.7 ppm (11), and the protonated carbon of the phenyl unit (18) is shifted to 110.3 ppm.

3.8.3. FTIR

The spectra show the characteristic C-H stretching vibration of aryl compounds at 3030 cm^{-1} , strong overlapping alkane C-H stretching vibrations were found at 2960, 2945, 2910 and the aryl-O-CH₂ vibration at 2858 cm^{-1} .

The alkyl-aryl ether C-O stretching vibration that was shown in the PPV spectra appears at 1045 cm^{-1} .

Six peaks were found indicating a mixture of *trans* and *cis* configuration of the vinylene unit: (i) two C=C stretching vibration modes at 1666 cm^{-1} (*trans*) and 1659 cm^{-1} (*cis*), (ii) two C-H in plane deformation vibrations at 1430 cm^{-1} (*cis*) and 1220 cm^{-1} (*trans*) and (iii) the two C-H out of plane deformation vibrations at 970 cm^{-1} (*trans*) and 685 cm^{-1} (*cis*).

A. Bleyer *et al.* ^[19] reported that the *cis-trans* ratio of poly(*m*-phenylenevinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene) can be estimated from the intensities of the C-H o.o.p deformation vibration. This was not possible for POPV-ONV due to overlapping.

Both, the *cis* and the *trans* mode were overlapped by neighbouring peaks.

The IR spectrum does not show any remaining starting material: Neither the C=O stretching vibration at 1675 cm^{-1} nor the mode at 1280 cm^{-1} (P=O), were found.

3.8.4. Raman

The spectrum shown in figure 3.18 was measured from the polymer film on a glass slide.

A broad but weak peak C-H stretching vibration mode of the alkyl chains was found at 2882 cm^{-1} . The strong aromatic C=C stretching vibration appears at 1587 cm^{-1} .

The mode at 1380 cm^{-1} was found to be the naphthalene ring stretching vibration.

The *E*- and *Z*-vinylene C-H deformation vibrations appear in two different doublets. The C-H vibration adjacent to the naphthalene unit appears at 1241 cm^{-1} and 1226 cm^{-1} and whereas the C-H vibration adjacent to the phenylene unit gives rise to signals at 1308 cm^{-1} and 1288 cm^{-1} .

Similar to the PPV derivative spectra the *p*-substituted C-H o.o.p deformation vibration was found at 885 cm^{-1} .

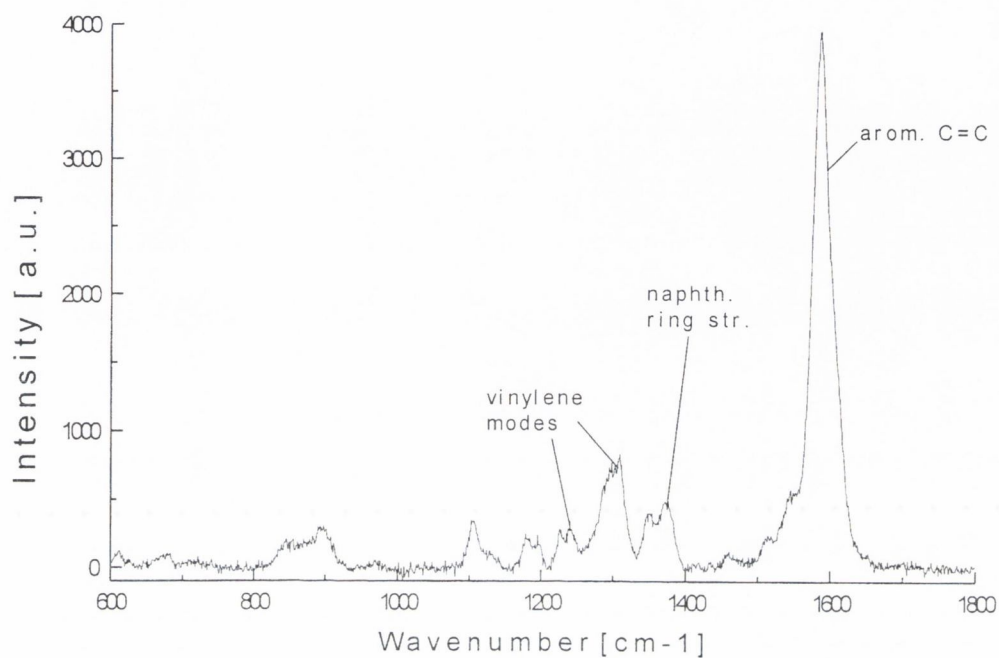


Fig. 3.18: Raman spectrum of POPV-ONV (film on glass slide)

3.9. Synthesis of 1,5-bis-n-octyloxy-2,6-dimethylnaphthalene-bis-ethylphosphonate ester

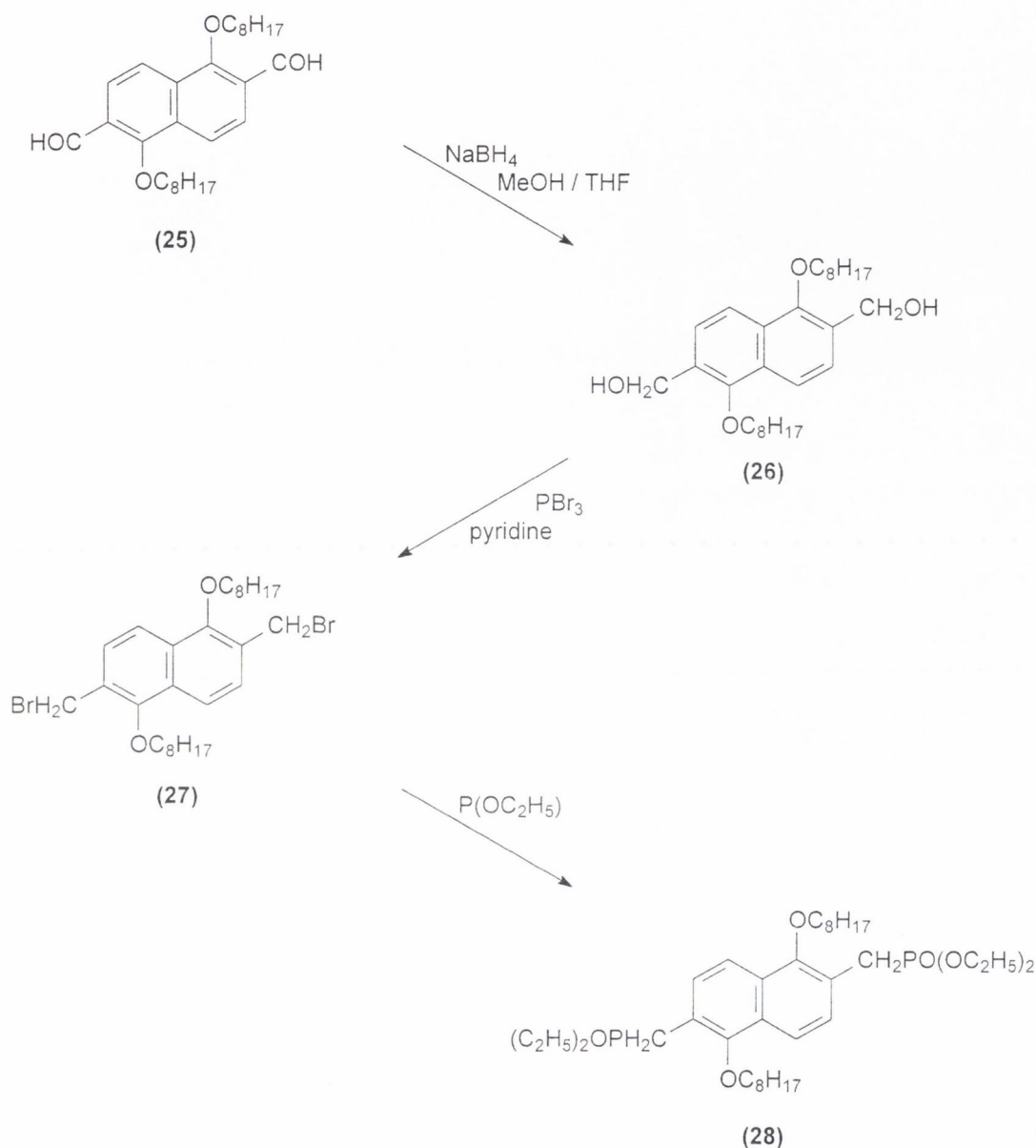


Fig. 3.19: Synthesis route of 1,5-bis-n-octyloxy-2,6-dimethylnaphthalene-bis-ethylphosphonate ester (28)

1,5-Bis(n-octyloxy)-2,6-naphthalenedialdehyde was reduced to 1,5-bis(n-octyloxy)-2,6-dihydroxymethylnaphthalene (26) followed by bromination to give 1,5-bis(n-octyloxy)-2,6-dibromomethylnaphthalene (27). These two steps were straightforward reactions without complicated purification procedures. 1,5-Bis(n-octyloxy)naphthalene-2,6-diethylphosphonate-ester (28) was obtained from

reacting 1,5-bis(n-octyloxy)-2,6-dibromomethylnaphthalene with triethylphosphite. The by-product ethyl bromide was continuously distilled off during the reaction.

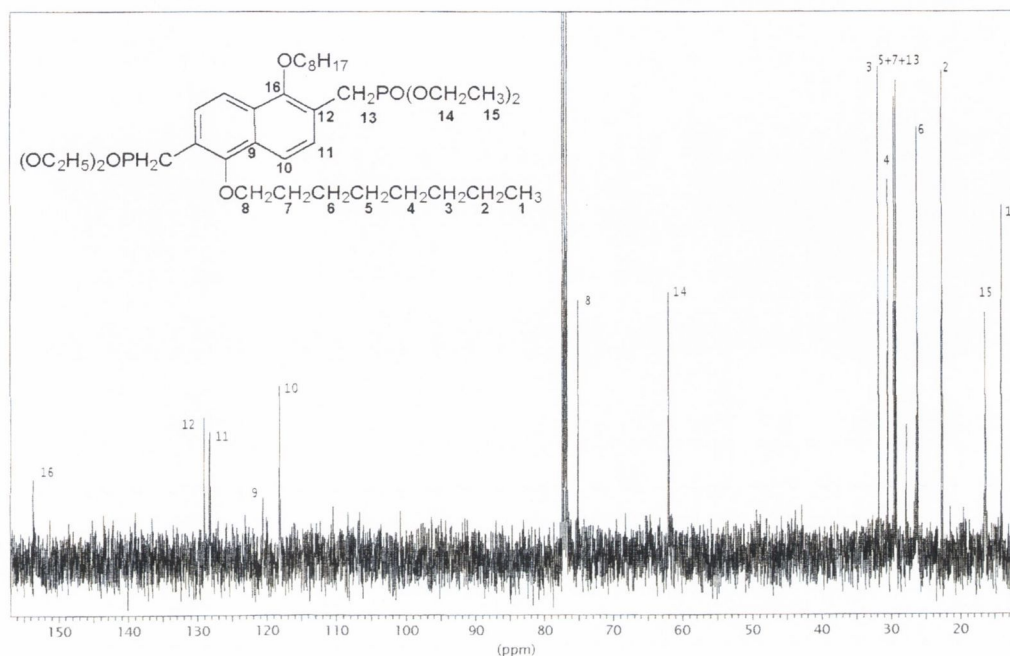


Fig. 3.20: ^{13}C -NMR spectrum of 1,5-bis-n-octyloxy-2,6-dimethylnaphthalene-bis-ethylphosphonate ester

The three peaks of the phosphonate group appear at 16.3 ppm (15), 29.9 ppm (13) and 62.1 ppm (14). In the aromatic region the protonated carbons give rise to the two signals at 118.1 ppm (10) and 128.3 ppm (11). The non-protonated peaks were assigned by DEPT 135 at 153.6 ppm (16), 129.1 (12), 120.6 ppm (9).

3.10. Polymerisation of PPV-ONV derivatives

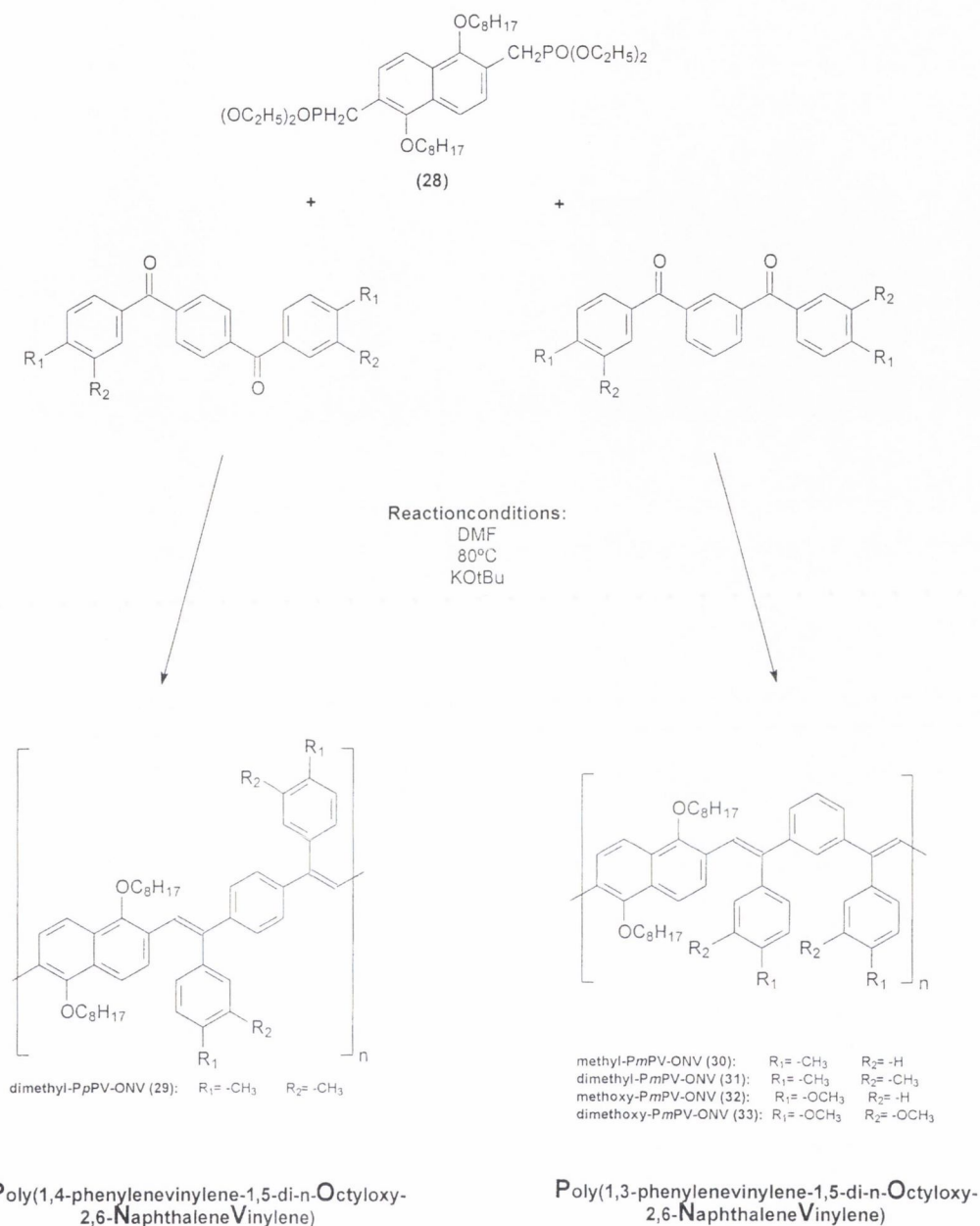


Fig. 3.21: Horner condensation polymerisation of 1,5-bis(n-octyloxy)-2,6-dimethylnaphthalene-bis-(ethylphosphonate)ester with different diketones

Compared to the PPV derivatives the PPV-ONVs are of shorter chain length. Some of the material precipitated during the reaction from the solution and therefore further chain growth was suppressed.

The purification process had to be modified since the PPV-ONVs are less soluble than the PPV derivatives. Most of the polymers were rather difficult to extract from the water suspension. Extraction with both toluene and chloroform resulted in a foamy suspension. This very fine suspension had to be centrifuged, and the crude product was redissolved in toluene and precipitated with methanol.

	M_n	M_w	M_w/M_n
dimethyl- <i>Pp</i> PV-ONV	3171	5859	1.85
methyl- <i>Pm</i> PV-ONV	2592	5759	2.22
dimethyl- <i>Pm</i> PV-ONV	2581	6793	2.63
methoxy- <i>Pm</i> PV-ONV	1717	2224	1.30
dimethoxy- <i>Pm</i> PV-ONV	1667	2366	1.42

Table 3.3: Molecular weight details of the PPV-ONV derivatives

As already mentioned these naphthalene systems are less soluble than the corresponding PPV derivatives. It was necessary to carry out the NMR-spectroscopic analysis over night. The peaks were still very undefined partially due to overlapping.

3.10.1. ^1H -NMR

The PPV-ONV spectra show very broad and overlapping peaks.

The methylene groups adjacent to the oxygen of the octyloxy group show a signal at approximately 4.00 ppm, the signals of the remaining protons of the alkyl chain appear from 1.98-0.87 ppm with additional peaks depending on the substitution pattern. The aromatic peaks appeared in the area between 7.90-670 ppm.

3.10.2. ^{13}C -NMR

The spectra of all PPV-ONV derivatives show that all starting material was removed by purification.

The seven signals of the alkyl chains of all PPV-ONV derivatives dominate between 14-32 ppm, the methylene carbon adjacent the oxygen ((1), see fig. 3.22) is shifted downfield compared to the PPV derivatives, to 75 ppm.

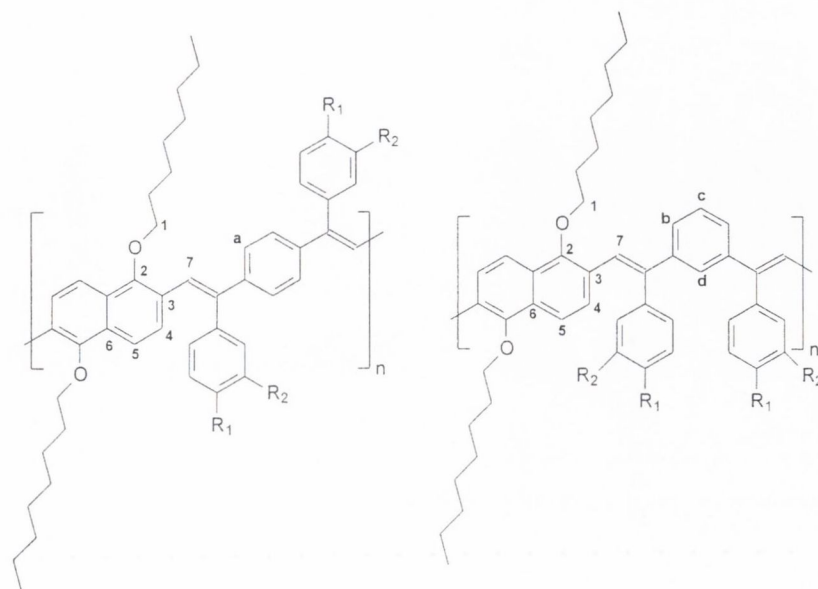


Fig. 3.22: *p*-/*m*- substituted PPV-ONV

Also the signal of the ether substituted ring atoms is shifted downfield compared to the PPV derivatives, to 154 ppm. The carbons (3, 6) are non-protonated and were assigned using DEPT technique, between 129 and 126 ppm. The protonated vinylene carbon appears at approximately 123 ppm.

The protonated peaks of the naphthalene unit appear at 125 ppm (4) and 117 ppm (5). The *p*-substituted phenyl ring only shows one strong mode for the protonated aromatic carbon (a) at 127 ppm whereas three non-equivalent aromatic carbons (b, c, d) appear for the *m*-substituted phenyl ring.

3.10.3. FTIR

Similar to the PPV derivatives very strong alkane C-H stretching vibrations were found in the region of 2920-2850 cm⁻¹. The spectra again show the C-H stretching vibration of aryl compounds at 3020 cm⁻¹ and an additional peak at 3042 cm⁻¹.

The spectra of all PPV-ONV derivatives shows C=O modes at 1659 or 1654 cm⁻¹. Due to the fact that the molecular weight was found to be rather low these peaks are expected to be C=O modes of the end-group.

The C=C stretching vibration appears at either 1598 or 1608 cm^{-1} and the alkyl-aryl ether C-O stretching vibration appears at 1040 cm^{-1} .

3.10.4. Raman

The Raman spectra of the PPV-ONV derivatives show similar modes to those that were found in the PPV spectra: (i) the C-H stretching vibrations modes of the alkyl chains at 2890 cm^{-1} , the aromatic C=C stretching vibrations at approximately 1580 cm^{-1} , the *meta* substitution modes at 885 cm^{-1} and 985 cm^{-1} and the single peak of *p*-substituted derivatives at 885 cm^{-1} .

Apart from these similarities the naphthalene substituted polymers exhibit a ring stretching vibration at 1390 cm^{-1} and also the *E/Z*-vinylene C-H deformation vibrations are shifted compared to the vinylene mode of the PPV derivatives and appears at 1250 cm^{-1} .

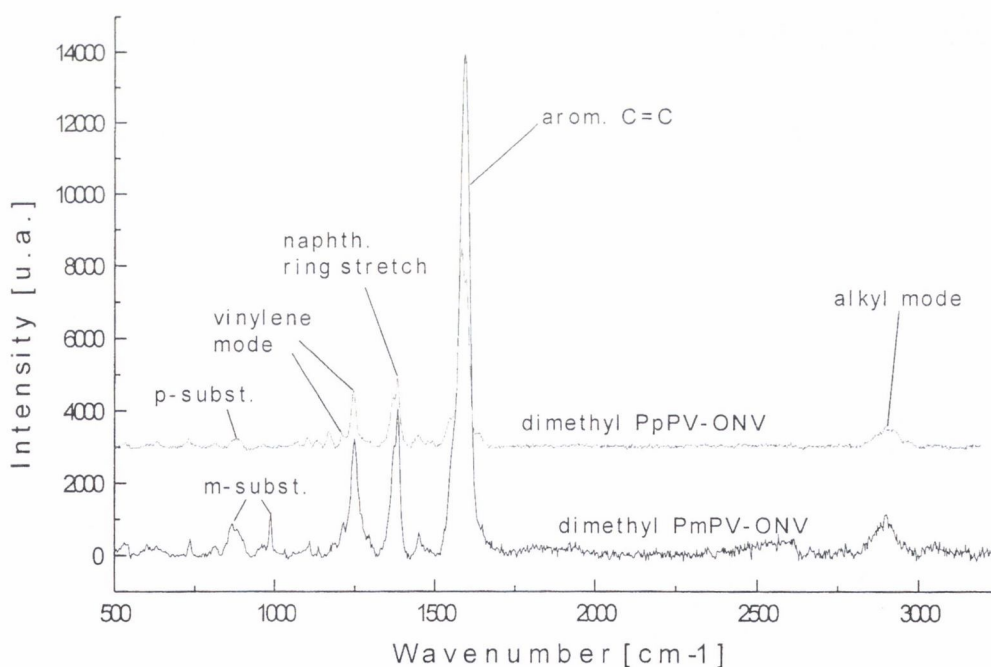
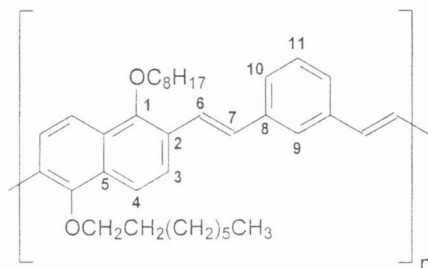


Fig. 3.23: Raman spectra of *meta* and *para* substituted dimethyl PPV-ONV

3.11. 1,3-Phenylene Vinylene-1,5-di-n-Octyloxy-2,6-Naphthylene Vinylene (PmPV-ONV)

PmPV-ONV was synthesised under the same reaction conditions as the previous polymers from molar equivalents of isophthalaldehyde and 1,5-bis(*n*-octyloxy)-2,6-dimethylnaphthalene-bis-(ethylphosphonate)ester (30).



GPC measurements gave quite low molecular weight details: $M_n = 1684$, $M_w = 3067$, $M_w/M_n = 1.82$.

The ^{13}C -NMR shows a peak at 153.4 ppm for the aromatic carbon linked with the octyloxy-group (1), the unprotonated carbon on the phenylene unit (8) at 138.3 ppm, the three protonated carbons (9, 10, 11) of the phenylene unit at 129.4 ppm, 127.6 ppm and 125.6 ppm, the two unprotonated carbons of the naphthalene unit (2, 5) at 126.4 ppm and 125.1 ppm and the protonated carbon of the naphthalene unit (3) at 118.8 ppm. The vinylene carbons (6, 7) give rise to two signals at 124.2 and 123.8 ppm.

The aliphatic peaks of the octyloxy side-chain appear in the same pattern as was shown for the substituted PPV-ONV derivatives.

3.11.1. Raman

Poly(*m*-phenylenevinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene) has found to exhibit C=C stretching vibrations at 1627 cm^{-1} . Lefrant *et al.* [130] simulated spectroscopic data of PPV. The calculations assigned a band observed at 1628 cm^{-1} to the stretching C=C of the vinyl group and the band at 1595 cm^{-1} was assigned to vibrations in aryl rings. These theoretical results of the

vinylene peak at 1628 cm^{-1} were in agreement with the observations made during measurements since the peak decreased upon doping.

The Raman spectra shown before did not contain peaks at this wavenumber which is due to the fact that the vinylene bond of these compounds is substituted.

In the graph shown below two peaks were found in this area at 1614 cm^{-1} and 1628 cm^{-1} which were assigned to *trans* and *cis* C=C stretching vibrations.

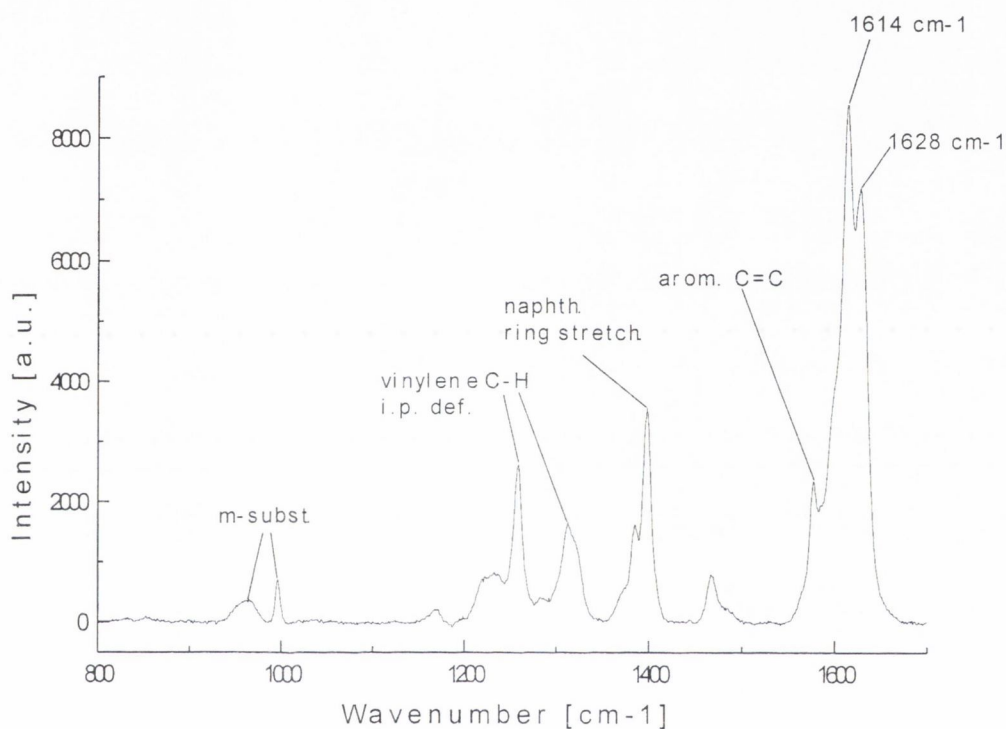


Fig. 3.24: Raman spectrum of PmPV-ONV

3.12 Synthesis of 2,6-dimethylnaphthalene-bis-(ethylphosphonate)ester

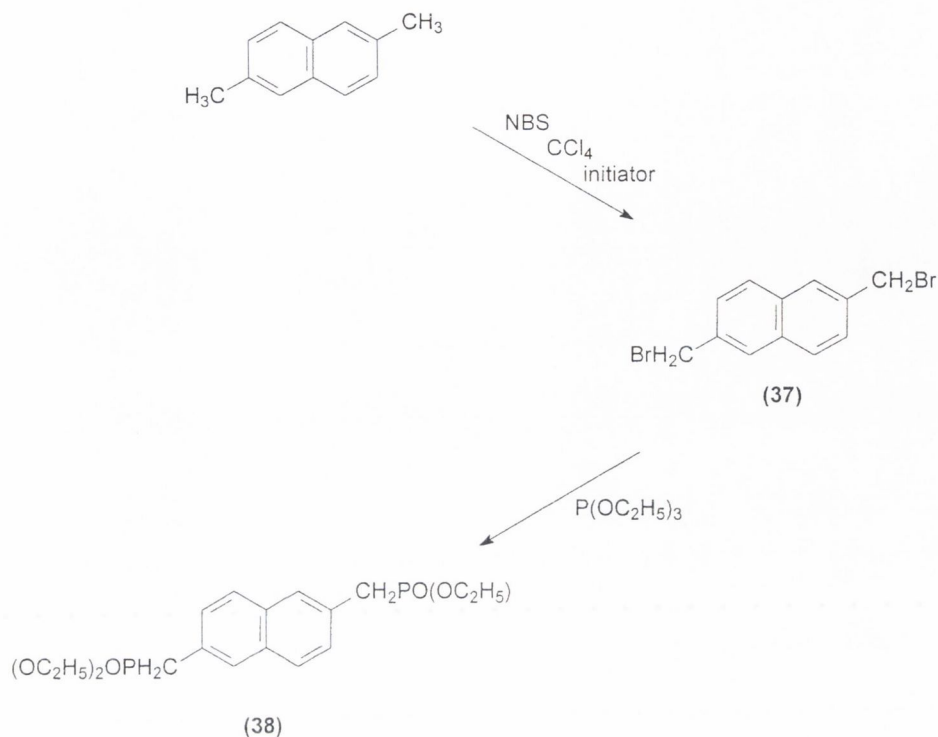


Fig. 3.25: Synthesis pathway of 2,6-dimethylnaphthalene-bis-(ethylphosphonate)ester

For the first step, the NBS-bromination of 2,6-dimethylnaphthalene, it was found that the initiator had a significant influence on the success of the reaction. Initially benzoylperoxide was employed: NMR spectra showed that the yield varied from 10-95% although the reaction conditions did not change. Since column chromatography to separate the starting material from the product was very convenient, a different initiator, AIBN, was chosen. On average employing AIBN improved the yield but there were still great variations. 1,1'-azobis(cyclohexanecarbonitrile) has shown the best yields and improved the reaction since no significant variations of starting material and product were found. The reaction of 2,6-dibromomethylnaphthalene with triethylphosphite was carried out under the same conditions as for the previous phosphonate ester derivatives. 2,6-dimethylnaphthalene-bis-(ethylphosphonate)ester is less soluble than the corresponding di-octyloxy substituted compound and the corresponding polymers.

3.13. Polymerisation of nonyl-PpPV-NV

Figure 3.26 shows the polymerisation scheme of nonyl-PpPV-NV.

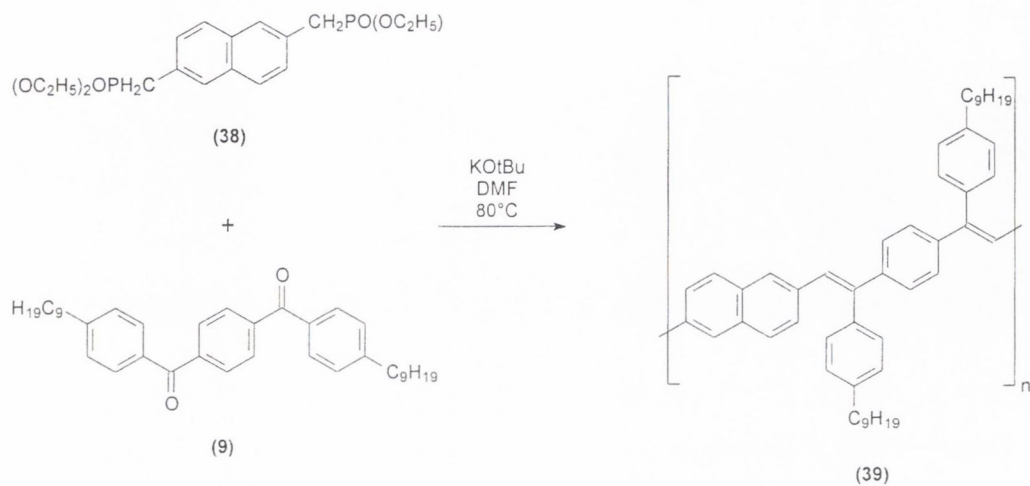


Fig. 3.26: Polymerisation of nonyl-PpPV-NV

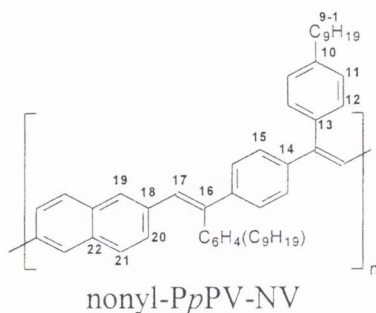
A short time after addition of KOtBu the reaction solution showed remarkable green fluorescence.

Gel permeation chromatography in 1,2,4-trichlorobenzene showed a number-average molecular weight of $M_n = 3810$, a weight average molecular weight of $M_w = 11350$ and the polydispersity index $M_w/M_n = 2.98$ (polystyrene standard).

3.13.1. $^1\text{H-NMR}$

The signals of the protons in the nonyl chains appear at 0.79-2.53 ppm. The aromatic protons of the give rise to a broad signal with four peaks at 7.36, 7.22, 7.13, 7.06 ppm.

3.13.2. ^{13}C -NMR



The carbons of the nonyl chain (1-9) gives rise to five singlets and one doublet in the region from 14.1 ppm to 35.7 ppm. The aromatic carbon connecting to the nonyl chain appears at 142.6 ppm. The non-protonated carbons (13, 14, 16, 18, 22) were assigned to four signals at 139.9, 137.4, 135.3, 132.2 and 128.1 ppm. The protonated

carbons of the naphthalene group (19, 20, 21) and also the vinylene carbon (17) show four signals at 128.7, 128.3, 127.6 and 127.2 ppm whereas the four protonated carbons of the centre benzene ring give rise to stronger peaks at 127.4 ppm (15). The two protonated carbons 11 and 12 appear at 130.8 and 130.3 ppm.

3.13.3. Raman

As was already mentioned the most intense Raman bands are usually those arising from bonds having nearly symmetrical charge distribution. Since nonyl-PpPV-NV does not contain the alkyl aryl ether group the two new peaks occurring in the spectrum shown below were assigned to C-C skeletal and C-H vibrations.

Only C-H deformation vibrations were found to give rise to the peaks in the region of 1400-1500 cm^{-1} . Therefore the three peaks at 1474-1502 cm^{-1} were assigned to the nonyl side-chains.

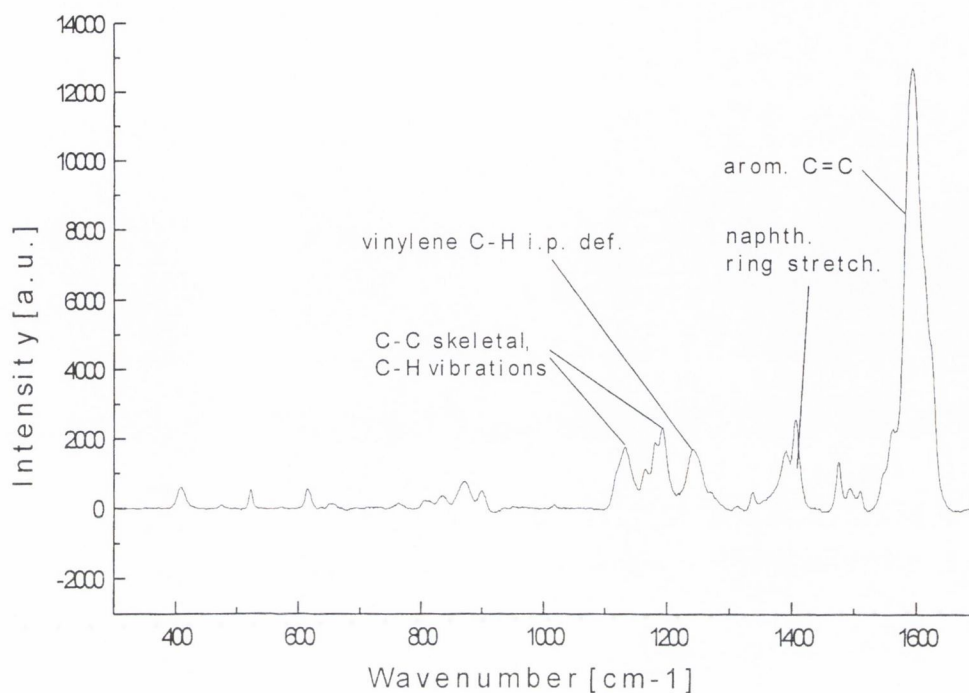


Fig. 3.27: Raman spectrum of nonyl-PpPV-NV

The usual aromatic C=C stretch vibration at 1586 cm^{-1} , the naphthalene ring stretch vibration at 1402 cm^{-1} and the in plane vinylene deformation vibration at 1242 cm^{-1} were found.

3.14. Synthesis of halogen containing PPV-NV derivatives

The synthesis of the corresponding polymers with methyl or dimethyl substitution on the phenylene unit on the vinylene bond were also attempted. They were insoluble in chloroform, toluene and other common solvents and therefore not useful for further investigations. By using a four times molar equivalent of NBS 2,6-dibromomethylnaphthalene was obtained which was then heated with triethylphosphite to give 2,6-dibromomethylnaphthalene-bis(ethyl-phosphonate) ester. Polymerisation of the phosphonate ester with isophthalaldehyde or 1,4-bis(4-nonyl-benzoyl)benzene gave yellow insoluble powders and therefore appropriate spectroscopic characterisation was impossible.

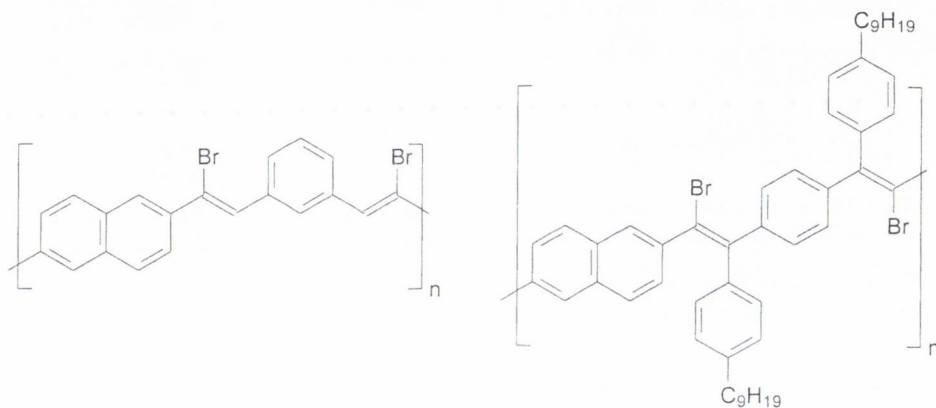


Fig. 3.27: Structure of the bromo-PPV-NV derivatives

3.15. Thermal Characterisation

3.15.1. Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis shows that all PPV derivatives are highly thermostable and do not decompose below 350°C in a nitrogen or oxygen atmosphere. Most of the phenyl substituted PPV derivatives were even stable up to 370-380°C.

The mass was reduced to 25-40% at approximately 400°C and then gradually decreased to 10-15% with increasing temperature up to 1000°C. Even in an oxygen atmosphere, decomposition or weight increase through reaction with oxygen was not recorded below 350°C. 50% of the weight was lost after approximately 450°C and 97% at approximately 800°C.

3.15.2. Differential Scanning Calorimetry (DSC)

Introductory remarks

The thermal behaviour below the decomposition temperature was investigated using a differential scanning calorimeter. Several transitions are expected for thermoplastic polymers with amorphous and crystalline segments.

There are two ways in which a polymer can pass from the solid to the liquid phase depending on the internal organisation of the chains in the sample: A polymer may be completely amorphous in the solid state, which means that the chains in the specimen are arranged in a total random fashion. After the sample is heated it passes through the glass transition temperature (T_g) beyond which it softens and becomes rubber-like. In a perfectly crystalline polymer, all the chains would be incorporated in regions of three-dimensional order and no glass transition would be observed because of the absence of disordered chains in the sample. The melting point (T_m) is the temperature of fusion of the last crystals (DSC peak temperature) [98].

Polymers usually contain varying proportions of ordered and disordered regions in the sample. These semi-crystalline polymers exhibit both T_g and T_m .

To investigate T_g , T_m and the crystallisation temperature T_c (although T_c could not be found for any of the investigated polymers) several factors e.g. chain flexibility,

molecular structure, free volume, molar mass, branching and cross-linking (though not in this case) have to be taken into consideration ^[99]. These factors have different effects on the thermal behaviour. In general the flexibility of the chain is the most important factor influencing T_g . Since the polymers investigated in this work contain a quite rigid backbone, T_g should be reasonably high already. Substitution of the vinylene unit on the backbone should increase T_g as it leads to an increase of the steric requirements about the main chain and bulky pendant groups hinder rotation about the backbone. In addition comb-like polymers have an intrinsic capacity for order through the main chain and/or the side groups ^[100]. It was also found that T_g was lowered by attaching side-groups to polymers since the increased number of end groups will increase the chain mobility and free volume ^[101].

The effect of increasing crystallinity is to decrease the intensity of the glass transition and broaden the transition temperature range as well as to shift the observed T_g to a higher temperature. Determination of T_g in semi crystalline polymers can be rather difficult if the degree of crystallinity is sufficiently high. Also, in crystalline polymers T_g increases proportionally to the amount of crystallinity because crystallites tend to reinforce or stiffen the structure. It has also been observed that T_g may decrease with increasing crystallinity ^[101].

The crystallisation temperature depends on the structure of the chain (regularity) and is decreased by structural irregularities. T_m increases with increasing of T_c . Since a sample cannot melt below its crystallisation temperature T_m is higher than T_c .

Neher *et al.* ^[20] observed that for increasing numbers of vinylene units introduced into a dialkoxy substituted PPP backbone, both T_g and T_m increase. They explain this observation with the fact that phase transition temperatures of "hairy rod" molecules are mainly determined by the gain of entropy during the transition, which is related to the number of possible conformations of the polymer. The gain of entropy in this case is determined by the density of side chains since the rigid backbone does not gain any further conformations at a solid-liquid-phase transition ^[102].

Hoerhold *et al.* ^[103] ^[104] published T_g data for the following polymers:

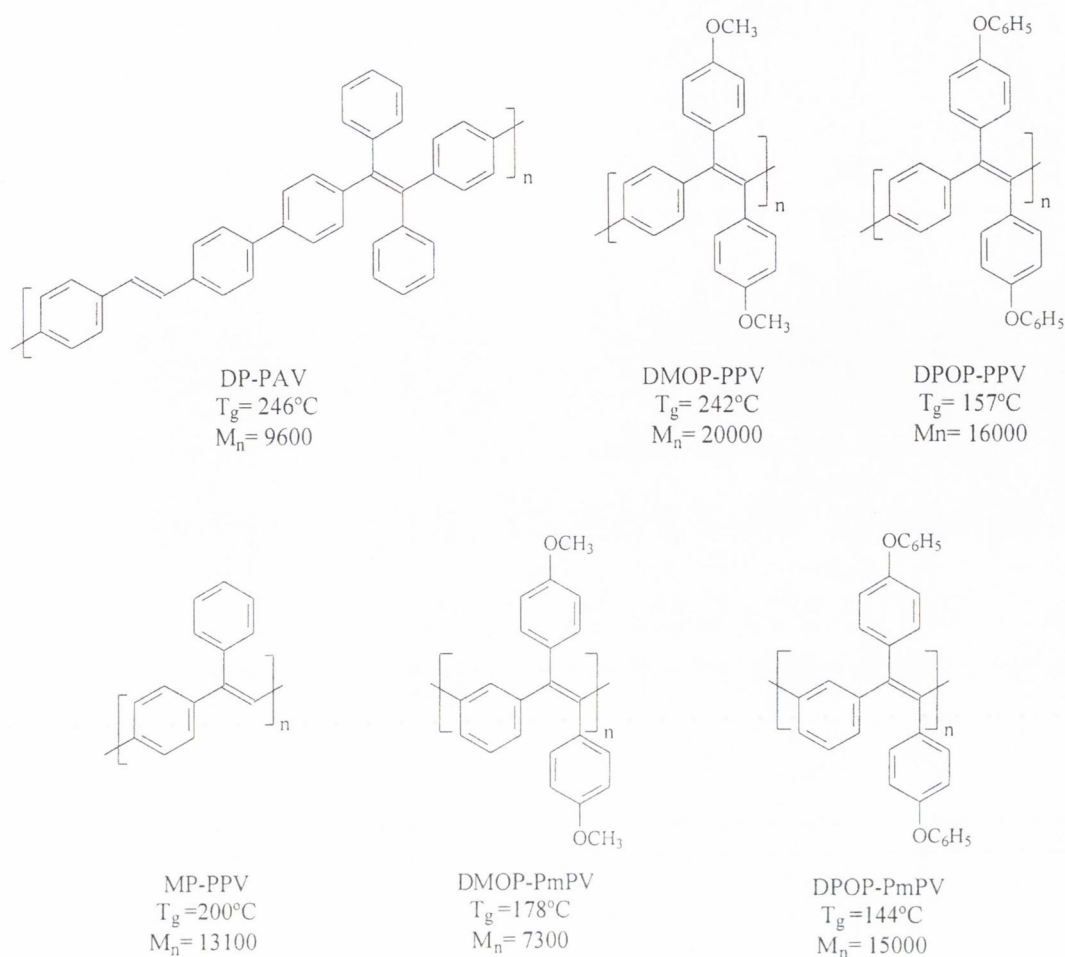


Fig. 3.28: T_g data of a selection of polymers published by Hoerhold *et al.*

The results show that T_g decreases with increasing size of the side-groups. When comparing DPOP-PPV and DPOP-PmPV, T_g seems to be slightly higher for *para* substituted than for *meta* substituted derivatives. Since the molecular weights of DMOP-PPV is almost three times as high as the molecular weight of DMOP-PmPV it is rather difficult to make any judgement as to what extent *meta*-substitution shifts T_g compared to *para* substitution.

DSC investigations on the present polymers

It should be noted that it is quite difficult to compare the influence of structure of these polymers on T_g , T_m and T_c since the molecular weight of all compounds varies and therefore must be taken into consideration as well.

The figure below shows the DSC graph of methyl-PpPV recorded at 10K/min under inert nitrogen atmosphere. The sample quantities were of the order of 10 mg.

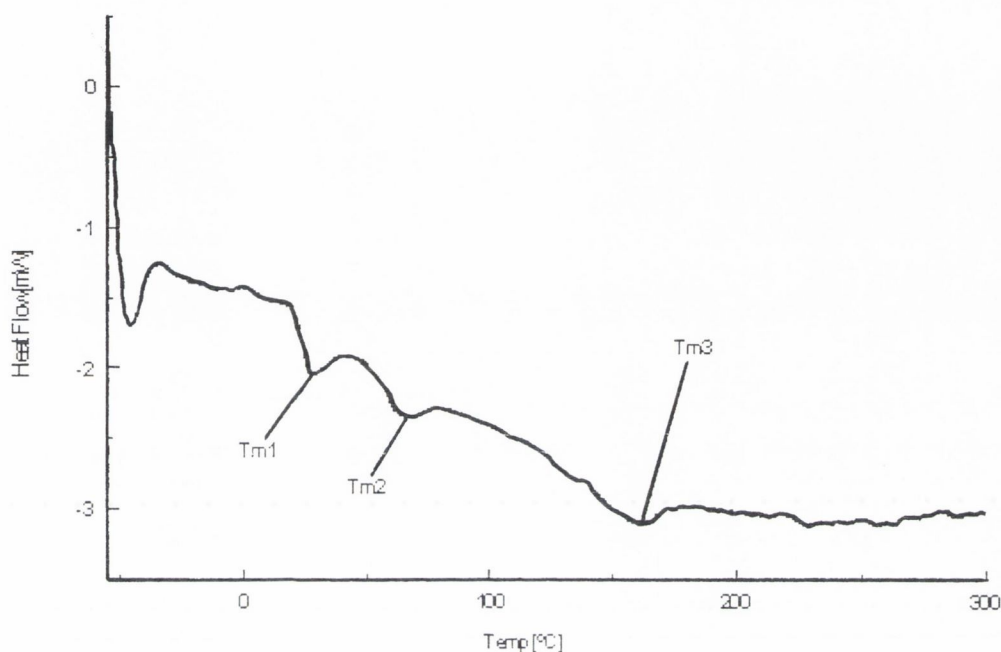


Fig. 3.29: DSC heating curve of methyl-PpPV (10K/min, N₂)

(Note, that the first endotherm peak is due to the levelling off of the apparatus and therefore no transition)

The graph of methyl-PpPV shows three melting features at $T_{m1} = 27^{\circ}\text{C}$, $T_{m2} = 66^{\circ}\text{C}$ and $T_{m3} = 160^{\circ}\text{C}$. T_{m1} and T_{m2} are melting peaks of the side groups. The melting peak of crystalline segments of the polymer chain appears at 160°C . There is no obvious glass transition found in this graph. As was already mentioned determination of T_g of semi-crystalline polymers is rather difficult. Additionally, the presented polymers are of rather low molecular weight. It has been found that the molecular weight influences the degree of crystallisation in a system. As the molecular weight increases, the level of crystallinity decreases. This reduction in crystallinity results from an increase in molecular weight dependent topological constraint, such as entanglements restrict the crystallisation process^[100].

To be able to investigate T_g , the crystallisation can be suppressed by rapid quenching, which means that the sample is heated and then rapidly cooled.

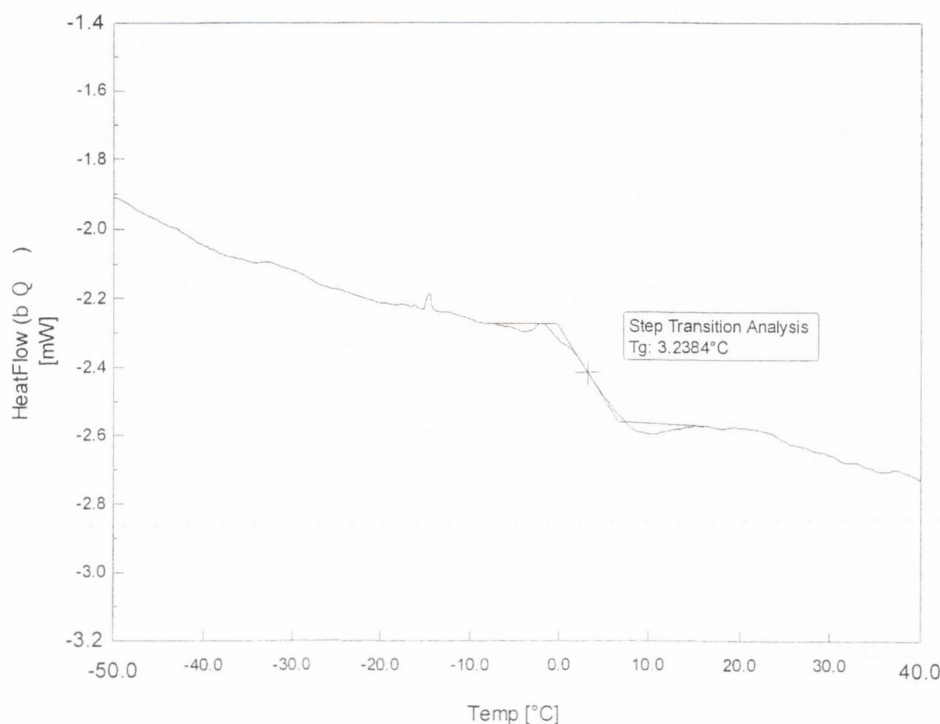


Fig. 3.30: Glass transition of the quenched methyl-PpPV

The same sample was crash-cooled at about $-30^{\circ}\text{C}/\text{min}$ from the melt to destroy the crystallinity. The second heating curve therefore does show a glass transition at 3.2°C which is surprisingly low compared to the values that were found for the PPV derivatives synthesised by Hoerhold *et al.* ^{[103] [104]}. This might be due to the fact that the present material is of lower molecular weight or that one phenylene (as opposed to two phenylene units) substitution on the vinylene bond does not stabilise the backbone and even has the opposite effect of destabilising the backbone strength. This would be in agreement with the observations made for the relative PL yield of the polymers where the unsubstituted polymers show higher yields than the substituted materials.

The melting peaks T_{m1} and T_{m2} did not appear for the reheated sample.

Relation between T_g and T_m

In linear semi-crystalline homopolymers T_g and T_m values are usually similarly raised or lowered. The ratio T_g/T_m changes from 0.5 for symmetrical polymers, e.g. poly(ethylene), to 0.75 for unsymmetrical polymers, e.g. poly(styrene) ^[99]. These ratios are calculated using absolute temperature values for T_g and T_m . The ration for methyl-PpPV in this case would be: $T_g/T_m = 0.64$.

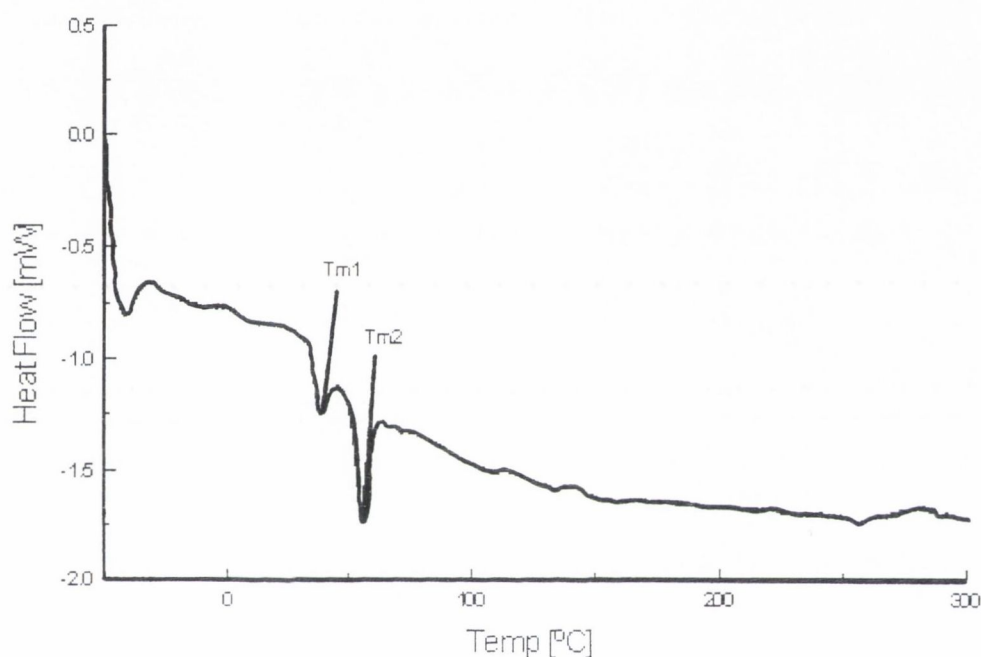


Fig. 3.31: DSC heating curve of methyl-PmPV (10K/min, N₂)

(Note, that the first endotherm peak is due to the levelling off of the apparatus and therefore no transition)

As expected, similar peaks for T_{m1} and T_{m2} (38°C and 55°C) were found for methyl-PmPV. The peaks shown above are sharper and the temperatures are slightly shifted compared to methyl-PpPV.

The melting peak is not very clear. Determination of the melting behaviour with a melting point apparatus showed that the methyl-PmPV starts melting at 95°C. At about 145°C all crystals are molten. Comparing T_m of methyl-PpPV and methyl-PmPV it was found that T_m was at lower temperature for the *meta* substituted

polymer. This is in agreement with theory since for crystallite formation, close-packing of the chains in a regular three-dimensional fashion is required. *Meta* substitution encourages bending and twisting of the polymer chain and makes close-packing difficult, this disrupts the crystal lattice and lowers T_m values. T_g was again found at approximately 3°C. Obviously the substitution pattern does not influence T_g which might indicate that the backbone does not gain any further rigidity through either *meta* or *para* linkage.

Another melting trace was observed at 250°C. For some of the investigated polymers this trace was rather strong.

Characteristic of liquid crystals is the mesophase that lies between the melting peak and the peak where the polymer changes into the isotropic state. Neher *et al.* found a liquid crystalline phase between 190 and 250°C for the polymers shown above [20]. This observation will be investigated in section 3.15.3.

Table 3.4 summarises the collected melting peak data for all investigated PPV derivatives:

	T_m [°C] (side chain)	T_m [°C]	T_m [°C] (melting point apparatus)
methyl- <i>Pp</i> PV	27, 66	160	132-177
dimethyl- <i>Pp</i> PV	22, 70	260	130-165
methoxy- <i>Pp</i> PV	21, 61	260	98-140
dimethoxy- <i>Pp</i> PV	32, 66	-	105-123
nonyl- <i>Pp</i> PV	20	89	91-143
methyl- <i>Pm</i> PV	38, 55	255	95-145
dimethyl- <i>Pm</i> PV	55	260	100-139
methoxy- <i>Pm</i> PV	58	265	65-77
dimethoxy- <i>Pm</i> PV	65	-	87-132
nonyl- <i>Pm</i> PV	42	165*	83-128
H- <i>Pm</i> PV	64	255	91-143

* very broad melting peak

Table 3.4: Collected DSC characterisation data

DSC investigations were also carried out for the naphthalene substituted derivatives, nonyl-*Pp*PV-NV and the PPV-ONV derivatives. The side-chain melting peaks and the glass transition were similar to those found for the PPV derivatives.

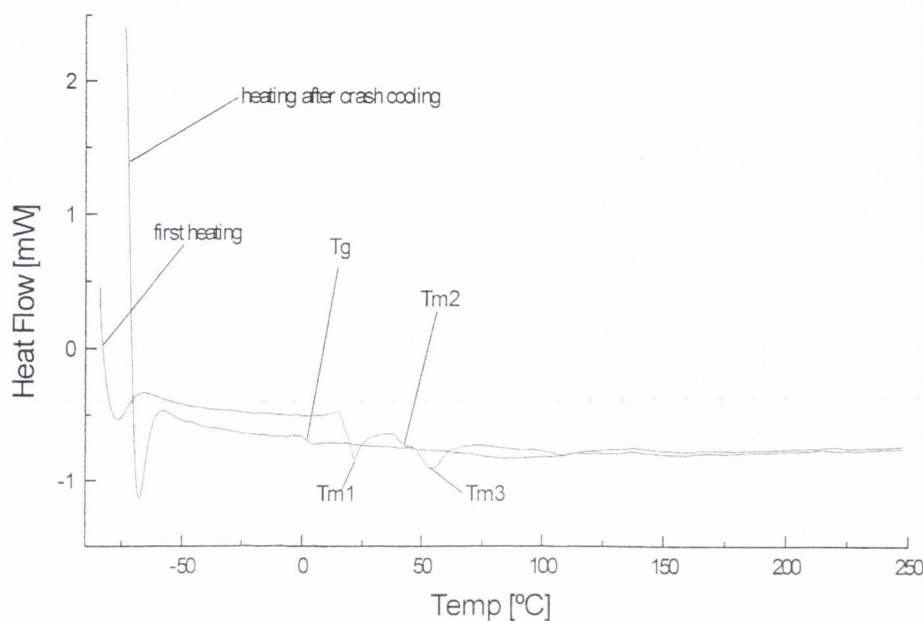


Fig. 3.32: DSC heating curve of dimethyl-*Pp*PV-ONV (10K/min, N₂)

(Note, that the first endotherm peak is due to the levelling off of the apparatus and therefore no transition)

The heating curve of dimethyl-*Pp*PV-ONV shows three melting peaks at $T_{m1} = 22^{\circ}\text{C}$, $T_{m2} = 44^{\circ}\text{C}$, $T_{m3} = 53^{\circ}\text{C}$. For all PPV-ONV derivatives it was found that the melting range was higher which is probably due to the more planar structure through introduction of a naphthalene unit. T_g appears at 3°C .

POPV-ONV only shows one melting peak at 68°C which refers to the octyloxy side chains. POPV-ONV and also the unsubstituted *Pm*PV-ONV do not melt before the decomposition temperature, which confirms the idea that the phenyl substitution on the vinylene bond increases the crystallinity.

Neither of the polymers exhibited crystallisation peaks. X-ray diffraction measurements of unsubstituted poly(*m*-phenylenevinylene-co-2,5-dicytyloxy-*p*-phenylenevinylene) showed 20% crystallinity [59].

It has been found that one has to be careful with generalising observations for a certain polymer. Investigations on poly(*m*-phenylenevinylene-co-2,5-dicytyloxy-*p*-phenylenevinylene) in our research group showed that although the chemical structure was not changed, the melting temperature and the width of the melting range changed significantly for the same polymer synthesised by different methods [84]. This shows that slight conformational differences (*cis-trans*) and probably also variations in the molecular weight in the pristine material do have quite an effect on the thermal behaviour.

3.15.3. Liquid crystalline PPV related material

Introductory remarks

Liquid crystalline behaviour is potentially important as it allows some ordering of the polymer while processing which can have significant impact on the strength, conductivity and the optical properties .

The liquid crystalline phase in polymeric materials are often difficult to identify. A liquid crystal must satisfy three basic requirements, regardless of molecular size or shape. There must be a first-order transition between the crystalline state at lower temperature leading to the liquid crystalline state and another first-order transition leading to the isotropic liquid state or another liquid crystalline state. A liquid crystalline material must display some degree of fluidity although for polymers the viscosity may be high. The preferred order of liquid crystals is one- or two-dimensional. They usually have either rigid, long shapes with a high length to breadth ratio, or disc shaped molecular structures. Chemically these may be composed of a central core comprising aromatic or cycloaliphatic units joined by rigid links, and having either polar, or flexible alkyl or alkoxy terminal groups [99]. Three-dimensional order points more towards true crystal formation. The isotropic liquid is completely disordered.

According to Hamaguchi *et al.* [105] simple dialkoxy-PPV derivatives do not appear to show thermotropic LC behaviour, although a lyotropic phase was found for

chloroform solutions of poly(1,4-dinonyl-*p*-phenylenevinylene) ^[105]. Yu and Bao ^[106] on the other hand found that a series of dialkoxy substituted (alkoxy substitutions of different lengths) PPV copolymers exhibited nematic phases often over large temperature ranges. They also observed cross-linking at temperatures over 200°C which could be suppressed by introducing very long side-chains (>C₁₆). As it was mentioned before, Neher *et al.* found a liquid crystalline phase between 190 and 250°C for the polymers mentioned in section 3.15.2. ^[20]

Hadziioannou *et al.* ^[12] have synthesised 5,6-bis(4styryl)styryl)1,4-dioctyloxybenzene and also the 5,6-bis(4styryl)-styryl)1,4-dioctylbenzene that showed a nematic liquid crystalline phase around 200°C. They observed a Schlieren texture under crossed polarisers.

Investigation on liquid crystalline properties using polarising microscopy

For the present polymers the mesophase might occur after T_g and T_m and before the very high melting peak at approximately 250°C. Geometric optimisation calculations using *hyperchem*® showed that the polymers that contain a phenylene substitutions on the vinylene bond are not planar, due to the phenylene group on the vinylene bond which is almost orthogonal to the vinylene unit and also the aromatic moieties on the backbone twist slightly.

In particular, the *m*-substitution causes a chain twist. Therefore these systems might not fulfil the requirements for liquid crystals since, as mentioned before, the preferred order of liquid crystals are one- or two-dimensional.

In some polymer liquid crystals, several mesophases can be identified. In main chain liquid crystal polymers there is usually a transition from the crystal to a mesophase, whereas in more amorphous systems when a glass transition is present, the mesophase may appear after this transition has occurred.

Liquid crystalline phases are optically anisotropic, i.e. depolarise plane-polarised light. Solutions of randomly arranged polymers are optically isotropic. Liquid crystal polymers can often be identified by observing a characteristic textures developed in thin layers of the polymer when viewed through a microscope using a linearly polarised light source.

Figure 3.33 shows the schematic arrangement of the polarising microscope employed for this work.

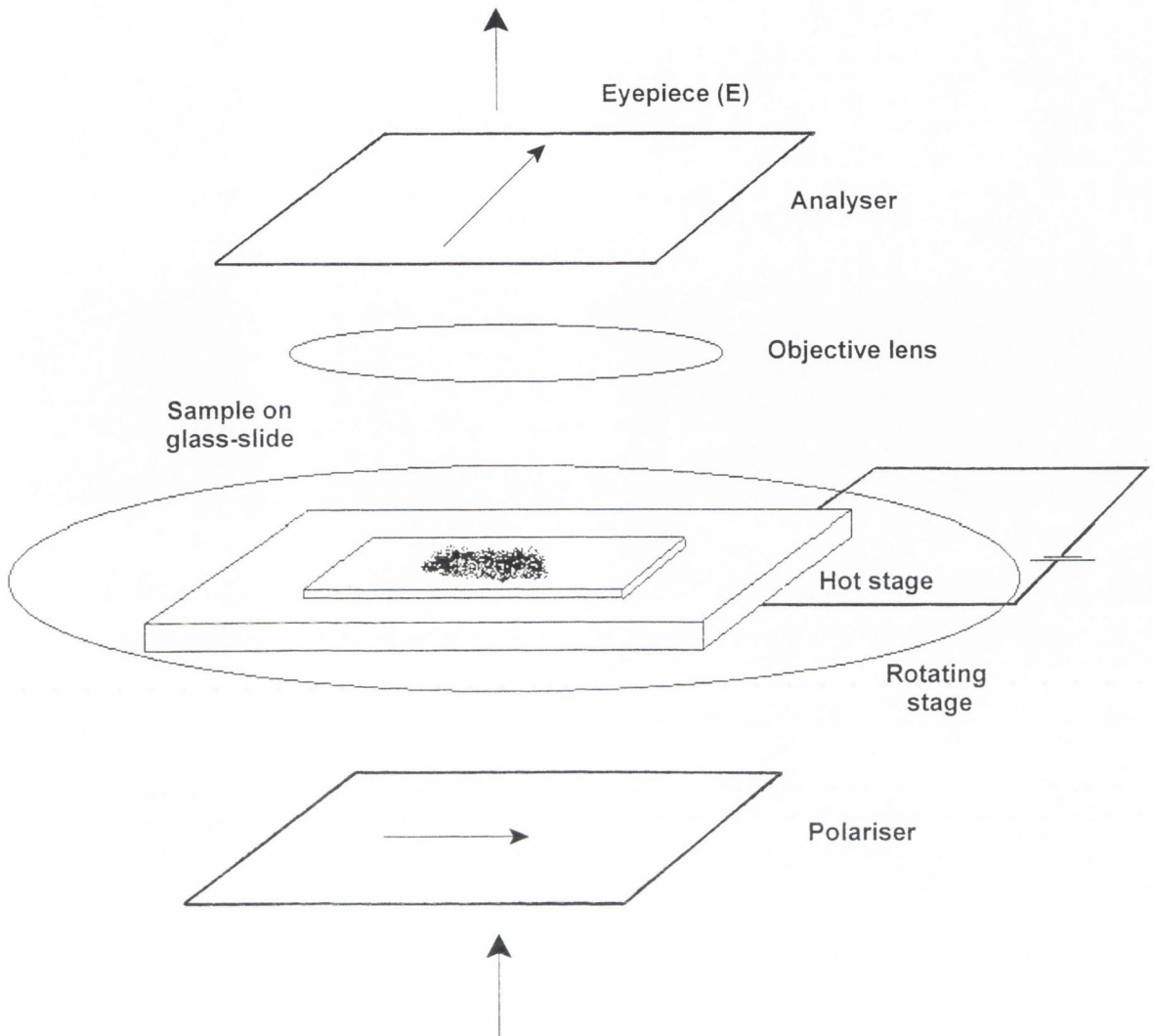


Fig. 3.33: Schematic set-up of a polarising microscopy

The incident light passes through the polariser, the sample on a temperature-controlled hot stage (with a hole in the middle) on the rotating stage, the compensator and objective lens and the analyser. When the polariser is in the 0° (or 180°) position, it is oscillation plane, i.e. the oscillation plane of the light transmitted by it is at right angles to that of the analyser, the polarisers are said to be crossed. In such arrangement light cannot reach the eyepiece, provided that the medium between them is entirely isotropic ^[107].

If a parallel beam of linearly polarised light is incident on the surface of a thin sample of an anisotropic material it encounters two refractive indices. If the propagation plane of the light is at an angle to these two principal refractive index

directions, the incident beam is resolved into two separate components propagating in these directions. The propagation direction of the incident beam is determined by the propagation direction of the polariser. Since the two components experience different refractive indices they travel through the sample at different velocities.

Methyl-PmPV, methoxy-PpPV and dimethyl-PpPV-ONV were investigated employing the polarising microscope set-up described above. They were heated from room temperature up to 300°C.

For methyl-PmPV and methoxy-PpPV no liquid crystalline texture could be observed. It should be noted that this observation does not prove that these two polymers do not contain liquid crystalline properties since the characteristic textures do not always appear^[108].

Dimethyl-PpPV-ONV exhibited liquid crystalline textures between 180°C and 230°C. The texture can be described as a mixture of marbled and Schlieren texture which indicates a nematic mesophase.

The mesophase is basically divided into three classes: the smectic, the nematic state and the cholesteric phase. The nematic phase is much less ordered than the smectic phase. While the directional ordering of the mesogen long axes is maintained, the centres of gravity are not isolated layers but are distributed randomly in the phase. The nematic state is much more fluid than the smectic phase but still exhibits birefringence. The cholesteric phase is observed in systems containing molecules with a chiral centre.

3.16. Electrochemical characterisation

3.16.1. Redox behaviour of PPV related material

Like polyacetylene and polyphenylene, PPV and its derivatives are redox polymers. The the electrochemical oxidation and reduction potential Bredas *et al.* ^[109] calculated for the following conjugated polymers is shown in table 3.5:

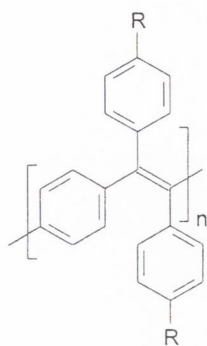
Polyacetylene	$E_{\text{ox}} = 0.4$	$E_{\text{red}} = -1.1$	$E_{\text{g}} = 1.5$
Poly(1,4-phenylene)	$E_{\text{ox}} = 1.2$	$E_{\text{red}} = -2.1$	$E_{\text{g}} = 3.2$
Poly(1,4-phenylene-vinylene)	$E_{\text{ox}} = 0.7$	$E_{\text{red}} = -1.8$	$E_{\text{g}} = 2.5$

Table 3.5: Oxidation and reduction potentials published by Bredas *et al.* ^[109]

In the past twenty years the electrochemistry of conjugated phenylene-vinylene systems has mainly been studied by Hoerhold *et al.* ^{[93] [103] [110]}. To describe the redox properties of these polymers they postulate the principle of effectively conjugated segments (ECS). This ECS concept contains the idea that the reaction sites of a conjugated polymeric chain (having a polymerisation degree n) are segments with a limited number k of repeating units. This implies that a polymeric chain consists of weakly interacting conjugated segments. They base this concept on the facts, that multiple ionisation of conjugated polymers is possible and leads to ionic centres of the same quality. The redox reactions have been found to be independent of the polymerisation degree, provided that the chain consists of more than 10 phenylene vinylene units. The length of these segments are depending on the substitution pattern of the PPV derivative, four to eight repeat units long ^[111] and can show up to three distinct, reversible oxidation stages with 0.5, 1 and 2 positive charges per repeat unit ^[112].

Hoerhold *et al.* also found that because of mesomeric effects, phenyl substitution on the vinylene bond especially, contributes to the stability of ionic states and even transmits additional electronic effects of either electron-donating or electron-accepting substituents. They demonstrate that *p*-methoxy substitution of DP-PPV (diphenyl substituted PPV) shifts both the oxidation and the reduction potential in a

negative direction whereas *p*-benzoyl substitution shifts both potentials in a positive direction.



R	E _{ox}	E _{red}	E _{ec}	E _{opt}
-H	1.17	-1.80	2.97	2.9
-OCH ₃	0.88	-1.90	2.78	2.8
-COC ₆ H ₅	1.44	-1.34	2.78	2.8

Table 3.6: Effect of vinylene substituents on oxidation/reduction potential and the optically and electrochemically estimated band gap^[113]

3.16.2. Cyclic voltammetry measurements of the present polymers

Cyclic voltammetry was performed in a three-electrode cell equipped with a glassy carbon working electrode tip, a Pt wire counter electrode and Ag/AgCl reference. The concentration of the polymers was 10^{-3} mol/L in 10^{-1} mol/L tetrabutylammonium hexafluorophosphate CH_2Cl_2 solution.

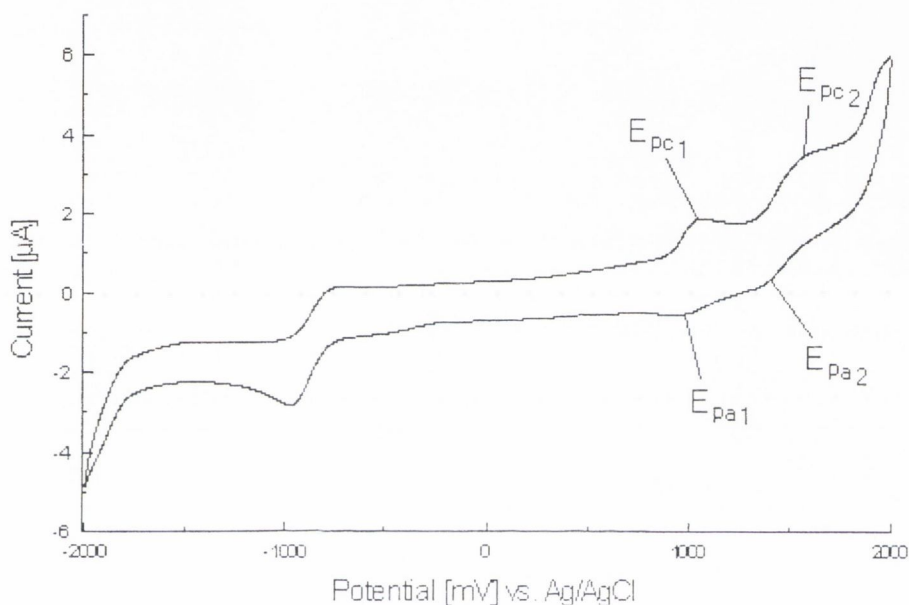


Fig. 3.34: Cyclic voltammetry graph of methyl-PmPV

(Ag/AgCl, 10^{-3} mol/L polymer in 10^{-1} mol/L tetrabutylammonium hexafluorophosphate/ CH_2Cl_2)

(Note that the peaks around -1 V are due to either the solvent electrolyte systems or apparatus features since they appeared also for the solution without polymer)

Fig. 3.34 shows that methyl-PmPV exhibits two quasi-reversible oxidation stages at 1.03 V and 1.5 V. For the first step the anodic and cathodic current peaks appear at $E_{pc1} = 1.05$ V and $E_{pa1} = 1.00$ V. The half-wave potential $E_{1/2ox1} = 1.03$ V was estimated according to Eq.3.1.

$$E_{1/2} = \frac{E_{pa} + E_{pc}}{2} \quad (3.1)$$

For the second step $E_{pa2} = 1.60$ V and $E_{pc2} = 1.40$ V the half-wave potential was estimated to be $E_{1/2ox2} = 1.50$ V although the difference of the two peak potentials ($\Delta E_p = E_{pa} - E_{pc} = 100$ mV) is higher than expected for a reversible reaction^[114]. Similar and even larger peak potential separations were found in cyclic voltammograms of polyacetylenes^[115], DP-PPV^[103] and PPV related systems^[116] indicating quasi-reversible oxidations.

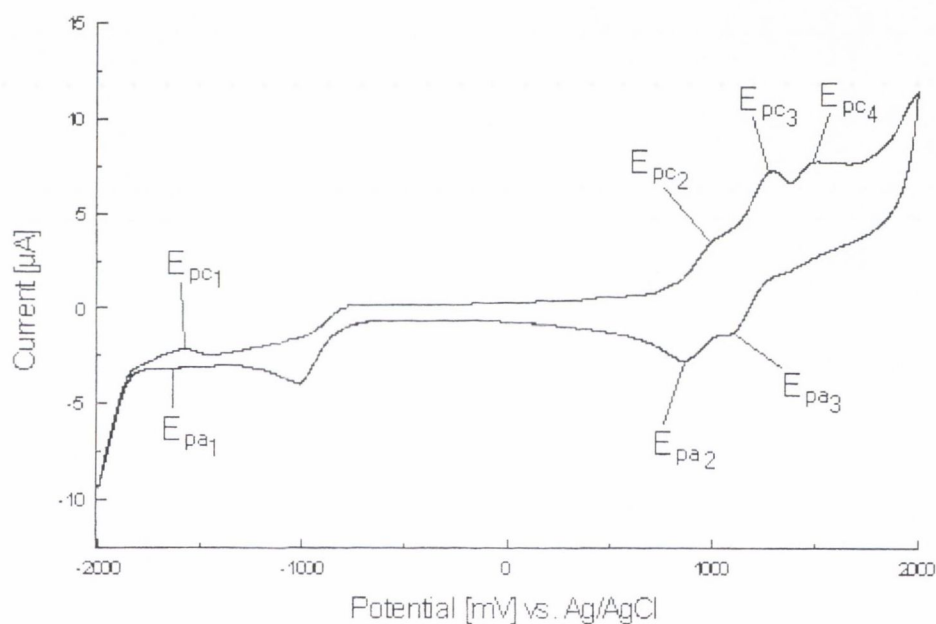


Fig. 3.35: Cyclic voltammetry graph of methoxy-PpPV

(Ag/AgCl, 10^{-3} mol/L polymer in 10^{-1} mol/L tetrabutylammonium hexafluorophosphate/ CH_2Cl_2)

(Note that the peaks around -1 V are due to either the solvent electrolyte systems or apparatus features since they appeared also for the solution without polymer)

Fig. 3.35 shows that methoxy-PpPV exhibits one quasi-reversible reduction stage at $E_{1/2red1} = -1.6$ V and two quasi-reversible oxidation stages at $E_{1/2ox2} = 0.9$ V and $E_{1/2ox3} = 1.2$. A third peak is found at $E_{pa4} = 1.5$ V but does not appear on reverse scan.

Hoerhold *et al.* ^[27] found that dimethoxy substituted distyrylbenzenes irreversibly form phenanthrene rings at 0.99 V. Anodic oxidation of tetraphenylene also leads to the formation of the radical cation at 1.36 V and an irreversible ring closure at 1.69 V to give 9,10-diphenylphenantrene. This observation will be analysed at a later stage.

If one is able to achieve both oxidation and reduction of the polymer in the same electrolyte system (which was not possible for all polymers in this case), the difference between the two onset potentials should closely correspond to the band gap and can be directly compared to the optical band gap ^[117]. Since the graph shows a reduction stage at $E_{1/2red1} = -1.6$ V and the first oxidation step at $E_{1/2ox2} = 0.9$ V the bandgap can be estimated to be $E_g = 2.5$ eV.

Table 3.7 summarises the collected CV-data of the PPV derivatives.

	$E_{1/2red}$ [V]	$E_{1/2ox1}$ [V]	$E_{1/2ox2}$ [V]	$E_{1/2ox3}$ [V]	$E_{1/2ox4}$ [V]
methoxy-PpPV	-1.6	0.9	1.2	1.5 (E_{pc3})	
nonyl-PpPV		1.0	1.3		
methyl-PmPV		1.0	1.5		
methoxy-PmPV	-1.8	0.9	1.3 (E_{pc2})	1.5	1.8
H-PmPV		1.1	1.6		

Table 3.7: Collected CV-data for PPV derivatives

(Ag/AgCl, 10^{-3} mol/L polymer in 10^{-1} mol/L tetrabutylammonium hexafluorophosphate/ CH_2Cl_2)

The oxidation potential of methoxy substituted derivatives (methoxy-PpPV, methoxy-PmPV) is lower than the oxidation potential of alkyl substituted material due to the electron donating effect of the methoxy group. Additionally, the

unsubstituted H-PmPV shows an even higher oxidation potential than the substituted material.

The observations and the structure of the polymers suggest that the oxidation takes place on the octyloxy substituted phenylene unit.

In a reversible two-step oxidation a radical cation is formed followed by the formation of a dication. This formation of the dication is attributed to the electron-donating effect of the octyloxy groups. This is emphasised by the observation that for nonyl-PpPV-NV, two irreversible peaks at $E_{pc} = 1,3$ and $1,7$ V were found.

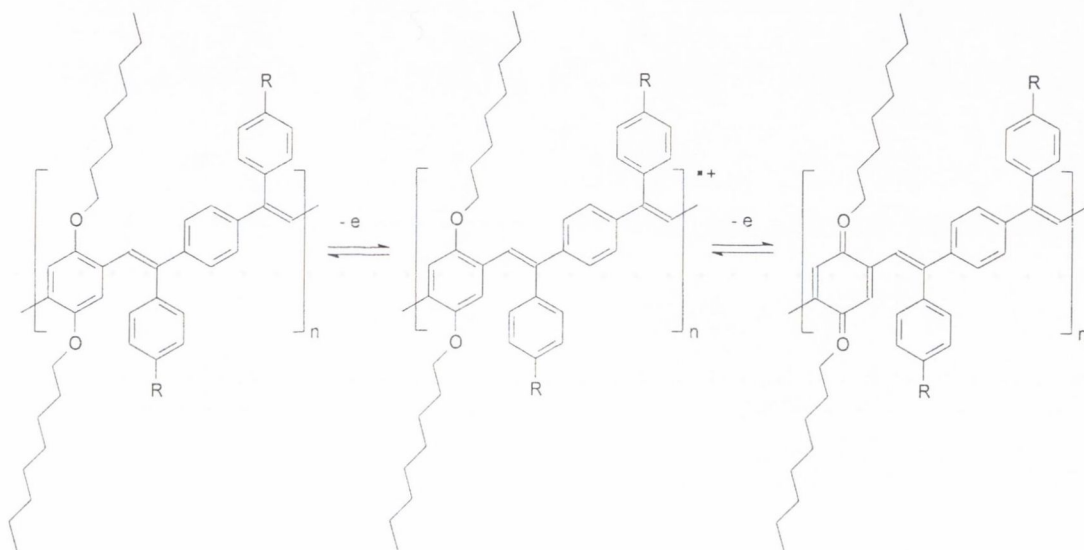


Fig. 3.36: Schematic oxidation of PPV derivatives

Two oxidation peaks at $E_{1/2ox1} = 0.9$ V, $E_{1/2ox2} = 1.6$ V were recorded for POPV-ONV. The quite low value of the first oxidation potential is probably due to the density of electron donating octyloxy groups, whereas the second oxidation potential is shifted to a rather high potential. This observation suggests that the POPV-ONV structure stabilises the radical cation state.

Comparing the *meta* and *para* substituted derivatives of methoxy-PPV shows that reduction potential of the *meta* polymers is about 0.2 V shifted to lower potential whereas the oxidation potential does not change. Therefore the bandgap of the *meta* substituted compound increases, which is in agreement with the optical results for these compounds since the optical bandgap can be estimated from the absorption onset. The same behaviour was found for the naphthalene substituted polymer shown in the table below. The reduction potential of the dimethyl-PmPV-ONV is

shifted about 0.3 V to lower potentials compared to the dimethyl *Pp*PV-ONV which therefore again increases the bandgap.

Table 3.8 summarises the electrochemical data of a selection of PPV-ONV derivatives.

	$E_{1/2\text{red}}$ [V]	$E_{1/2\text{ox1}}$ [V]	$E_{1/2\text{ox2}}$ [V]	$E_{1/2\text{ox3}}$ [V]
dimethyl- <i>Pp</i> PV-ONV	-1.3	1.2		
methyl- <i>Pm</i> PV-ONV		1.3	1.6	
dimethyl- <i>Pm</i> PV-ONV	-1.7	1.3	1.5	
dimethoxy- <i>Pm</i> PV-ONV		1.3 (E_{pc1})	1.5	1.7

Table 3.8: Collected CV-data of a selection of PPV-ONV derivatives

(Ag/AgCl, 10^{-3} mol/L polymer in 10^{-1} mol/L tetrabutylammonium hexafluorophosphate/ CH_2Cl_2)

The first and the second oxidation stages are shifted to higher potentials compared to the corresponding PPV derivatives. This is due to the larger conjugated system between the octyloxy groups.

3.16.3. Cyclisation through chemical oxidation

As was shown by voltammetric investigations some oxidation waves indicate irreversible oxidation which might be due to an intramolecular cyclisation. Hoerhold *et al.* found that there was complete ring closure of substituted and unsubstituted stilbene systems employing either FeCl_3 or $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ for milder oxidation at RT ^[27].

0.34 g methoxy-*Pp*PV (0.5 mmol) and 0.1 g FeCl_3 (0.6 mmol) were stirred for 3 h in 15 mL CH_2Cl_2 at RT. After purification a dark yellow powder was obtained. ^{13}C -NMR and dept 135 spectra showed a mixture of the cyclic phenanthrene-derivative and the starting material methoxy-*Pp*PV. Characteristic new features appear at 140.0 ppm and 137.7 ppm for the two new unprotonated carbon atoms (3,4) in the phenantrene ring, at 105.7 ppm for the protonated carbon atom (2) next to the

octyloxy side chain and at 109.8 ppm the protonated carbon of the former vinylene unit (1). Additionally for the O-CH₂-carbon atom of the octyloxy group two peaks are found at 68.8 ppm and 68.3 ppm.

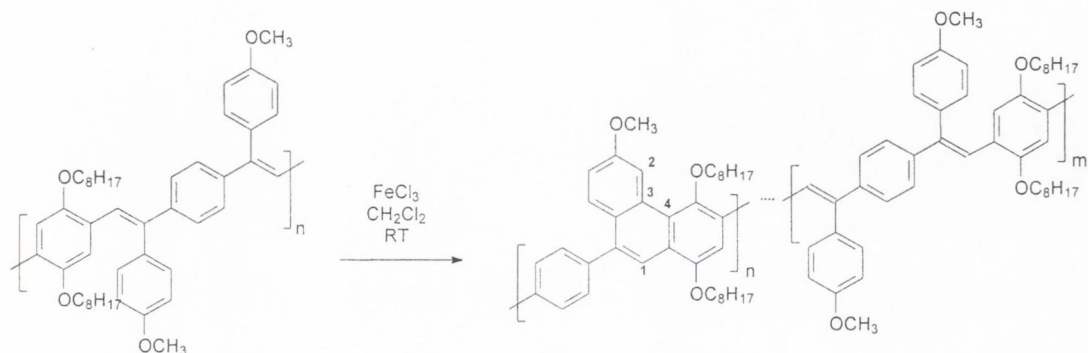


Fig. 3.37: Chemical cyclisation of methoxy-PpPV with FeCl₃

Also Raman measurements indicated the formation of a phenantrene system:

The strong aromatic C=C stretching vibrations appears at 1587 cm⁻¹ with an additional peak at 1617 cm⁻¹. The mode at 1401 cm⁻¹ was found to be the phenantrene ring stretching vibration similar to the naphthalene ring stretching vibration.

The C-H vibration adjacent to the phenantrene unit appears at 1255 cm⁻¹ and whereas the C-H vibration adjacent to the phenylene unit gives rise to signals at 1309 cm⁻¹ and 1288 cm⁻¹.

The formation of the new phenantrene system may optically be recognised by a blue shift of the absorption maximum to 415 nm and a red shift of the fluorescence maximum to 535 nm. Moreover, the fluorescence intensity has visibly increased.

The same oxidation was unsuccessfully attempted for both compounds, methyl-PmPV and dimethoxy-PmPV. ¹³C-NMR showed only starting material for the methyl-PmPV whereas dimethoxy-PmPV decomposed during the reaction and the obtained product was shown to be brown sludge. Since FeCl₃·6H₂O is a milder oxidising agent, the reaction will be repeated in future work.

3.17. Optical measurements

3.17.1. Introduction

In the following chapter the influence of different substitution patterns of the synthesised polymers on the optical properties will be investigated:

- *meta* versus *para* substitution
- unsubstituted vinylene units compared to substituted vinylene bonds
- alkyl versus alkoxy side-groups on the phenylene substitution of the vinylene bond
- exchange of the octyloxyphenylene unit with a dioctyloxynaphthalene unit
- influence of the octyloxy substitution on the naphthalene unit

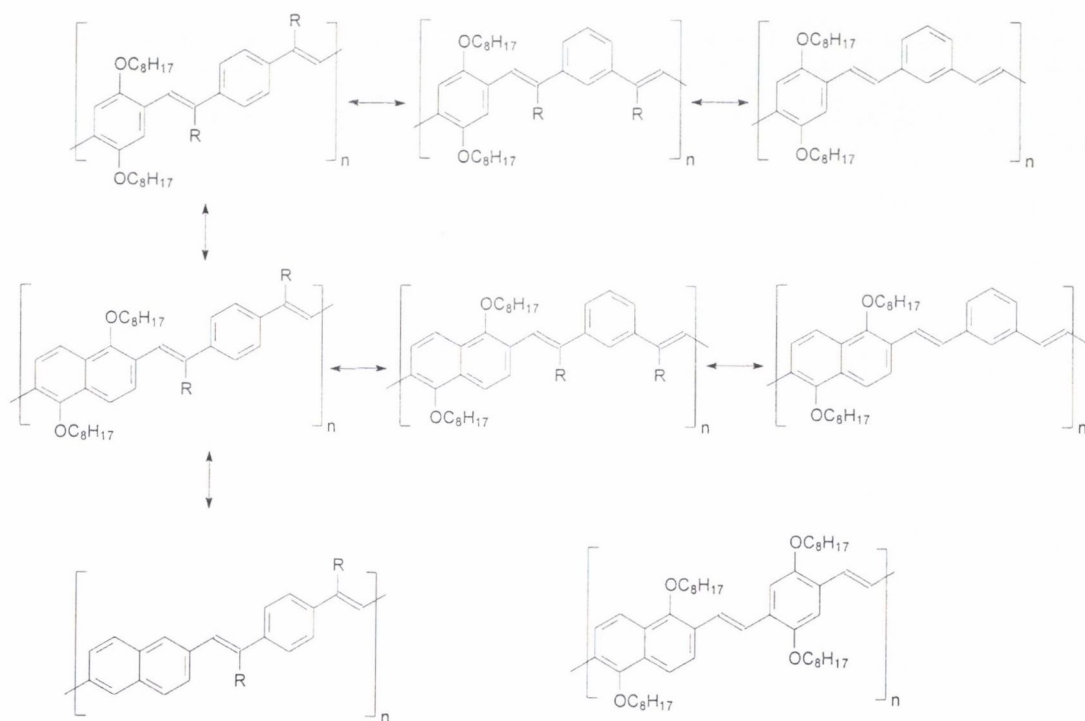


Fig. 3.38: Structures of the polymer systems that are investigated on their optical properties

3.17.2. Absorption measurements in solution

The tables 3.9 and 3.10 show three absorptions for all PPV derivatives that are shifted according to the substitution pattern (except for the dimethoxy substituted PPVs).

The absorption shoulder at lowest wavelengths appears to be mainly shifted by the substitution on the phenylene unit on the vinylene bond. Methyl and dimethyl-substituted derivatives absorb at 260 nm whereas the methoxy substituted PPVs absorb at higher wavelengths at approximately 300 nm. For dimethoxy substituted derivatives no shoulder was found in this area and the unsubstituted H-PmPV shows a blue-shifted absorption at 235 nm.

The absorption peaks at approximately 350 nm show no clear trends of either hypsochromic nor bathochromic shift varying with the substitution pattern.

The absorption around 400 nm seems to be mainly influenced by the *para* and *meta* substitution pattern. The absorption of *meta* linked derivatives shifts approximately 20-25 nm towards shorter wavelengths (390-400 nm) whereas the *para* derivatives appear around 420 nm.

The length of the substitution (methyl → nonyl) does not affect the absorption characteristics of the present polymers.

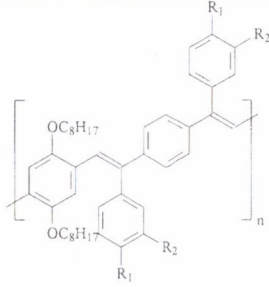
	Absorption [nm]
methyl-PpPV	418, 353, 259
dimethyl-PpPV	418, 353, 259
methoxy-PpPV	425, 350, 300
dimethoxy-PpPV	425
nonyl-PpPV	416, 338, 265

Table 3.9: Absorption data of all PpPV derivatives in 10^{-4} mol CHCl_3 solution

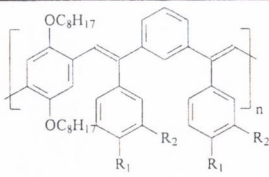
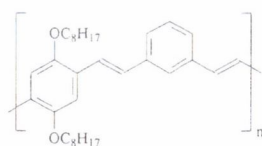
	Absorption [nm]
methyl- <i>PmPV</i>	392, 343
dimethyl- <i>PmPV</i>	401, 341
methoxy- <i>PmPV</i>	392, 350, 293
dimethoxy- <i>PmPV</i>	400
nonyl- <i>PmPV</i>	400, 339
H- <i>PmPV</i>	394, 338, 235

Table 3.10: Absorption data of all *PmPV* derivatives in 10^{-4} mol CHCl_3 solution

The phenyl substitution on the vinylene bond induces a blue-shift of approximately 60 nm as can be seen when comparing the *PmPV* derivatives with the unsubstituted *PmPV*. This can be explained by the steric requirements causing the chain to twist when phenyl units are attached to the vinylene moiety.



PmPV

λ [nm]: 460, 405, 327

Introduction of a naphthalene unit shifts the absorption towards lower wavelengths compared to the corresponding phenylene derivatives.

A hypsochromic shift of the absorption at longest wavelength of about 20 nm is induced by the introduction of the *meta* linkage.

The methoxy substituted derivative shows a slight bathochromic shift of the absorption at low wavelength compared to the methyl substituted polymers.

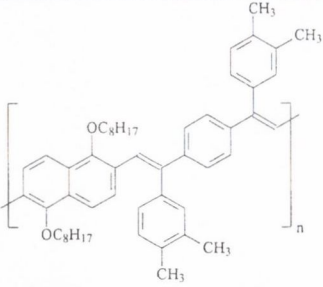
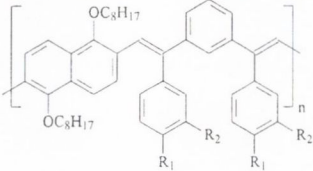
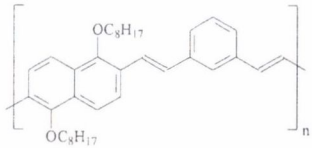
	Absorption [nm]
dimethyl-PpPV-ONV	373, 298, 267
	Absorption [nm]
methyl-PmPV-ONV	355, 295, 257
dimethyl-PmPV-ONV	354, 297, 260
methoxy-PmPV-ONV	360, 293, 270
dimethoxy-PmPV-ONV	361, 288, 259

Table 3.11: Absorption data of all PPV-ONV derivatives in 10^{-4} mol CHCl_3 solution

The unsubstituted PmPV-ONV also shows a bathochromic shift of the four absorptions. As was already explained for the corresponding PPV derivatives this is due to the steric requirements caused by the substitution.

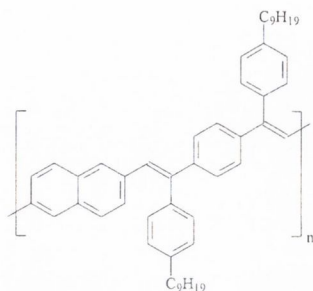


PmPV-ONV

λ [nm]: 400, 363, 303, 253

As it was mentioned before the length of the alkyl groups on the phenylene unit on the vinylene moiety do not influence the absorption features and therefore nonyl-PpPV-NV and dimethyl-PpPV-ONV can be compared to investigate the shifts caused by an alkoxy donor group. The octyloxy group is expected to induce a bathochromic shift due to asymmetric destabilisation of the HOMO and LUMO

compared to the derivative without alkoxy substitution ^[16]. For the present polymers this is not the case since the spectrum of the nonyl-*Pp*PV-NV is shifted to higher wavelengths. This is probably due to sterical hindrance causing a twist of the polymer backbone of the dimethyl-*Pp*PV-ONV.



nonyl-*Pp*PV-NV

λ [nm]: 380, 324, 299

3.17.3. Photoluminescence measurements in solution

Table 3.12 shows the photoluminescence data of the polymers in 10^{-4} mol CHCl_3 solution. As was already observed for the absorption maxima, the emission of PPV derivatives shows hypsochromic shift by altering the *para* into the *meta* linkage. This is in agreement with the theory since introduction of the *meta* linkage reduces the extent of the conjugated π -electron system leading to a blue-shifted emission characteristic of a substituted distyryl benzene unit.

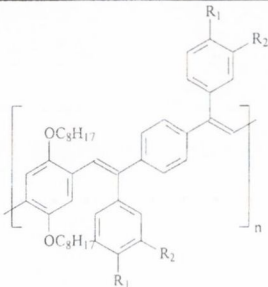
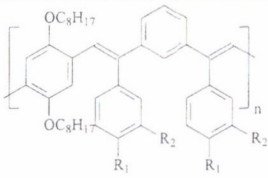
	PL [nm]
methyl-PpPV	522
dimethyl-PpPV	525
methoxy-PpPV	525
dimethoxy-PpPV	520
nonyl-PpPV	519
	PL [nm]
methyl-PmPV	494
dimethyl-PmPV	500
methoxy-PmPV	495
dimethoxy-PmPV	497
nonyl-PmPV	493
H-PmPV	497

Table 3.12: Emission data of all PPV derivatives in 10^{-4} mol CHCl_3 solution

Again, the substitution pattern on the phenylene unit on the vinylene moiety did not influence the emission wavelength to great extent which is also observed for the PPV-ONV derivatives shown in table 3.13. Replacement of the phenylene moiety by the more electron-rich naphthalene unit modifies the band structure. It has been published that linkage via the 1,4 position has a significant effect on the bandgap whereas the effect induced by incorporation through the 2,6 position is much smaller^{[23] [24]}. Theoretical calculations have shown that the energy gap of the 2,6-naphthalenevinylene-phenylenevinylene block-polymers is very similar to PPV but significantly smaller in 1,4-naphthalenevinylene-phenylenevinylene block polymers. As it can be seen from comparing the PPV derivatives with the corresponding PPV-ONV derivatives, both the emission and absorption features are blue-shifted. As already mentioned before, this might be due to the fact that the electron donating effect on the phenylene unit is much higher than on the naphthalene unit. A hypsochromic shift of around 25 nm was found comparing dimethyl-PpPV-ONV with dimethyl-PmPV-ONV.

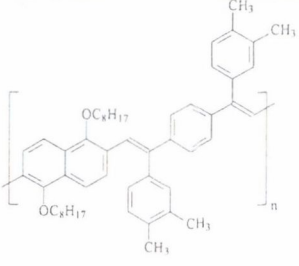
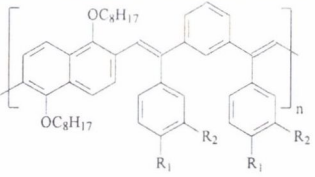
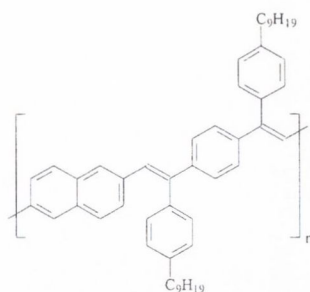
	PL [nm]
dimethyl-PpPV-ONV	490
	PL [nm]
methyl-PmPV-ONV	468
dimethyl-PmPV-ONV	470
methoxy-PmPV-ONV	465
dimethoxy-PmPV-ONV	465

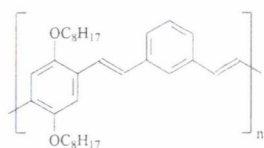
Table 3.13: Emission data of all PPV-ONV derivatives in 10⁻⁴ mol CHCl₃ solution



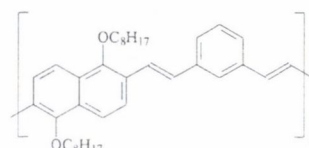
nonyl-PpPV-NV

PL, λ [nm]: 478

Comparing nonyl-PpPV-NV with dimethyl-PpPV-ONV shows that the emission of the octyloxy substituted derivative is shifted to higher wavelengths. This is in agreement with the literature. Introduction of alkoxy donor groups was found to induce an asymmetric destabilisation of the HOMO and LUMO compared to the unsubstituted derivative ^[16]. This was studied by theoretical calculations on phenylene vinylene pentamers compared to 2,5-dimethoxy-1,4 phenylene vinylene pentamers. The HOMO is more affected than the LUMO thus producing a decrease of the bandgap and subsequently shift of the colour of the emission to higher wavelengths.



PmPV

PL, λ [nm]: 480

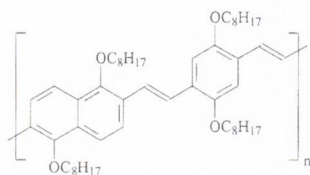
PmPV-ONV

PL, λ [nm]: 440

As can be seen from comparison of PmPV and PmPV-ONV with the corresponding phenyl substituted polymers, the absorption of the unsubstituted derivatives is 20 nm shifted towards lower wavelengths. In general, additional phenyl substitution on the vinylene bond is responsible for both a hypsochromic shift of the absorption maximum and a bathochromic shift of the luminescence emission maximum compared to the corresponding unsubstituted derivative. That means the Stokes shift is significantly enlarged by phenyl substitution ^[118]. Basically, the Stokes shift gives information about the rigidity of a system. The more rigid the polymer backbone is the less energy will be lost through vibrational de-excitation.

3.17.4. Absorption and PL of POPV-ONV

POPV-ONV shows the widest absorption range of all polymers with four absorption peaks between 480 and 240 nm. The emission was found to be in the green region of the visible spectrum at 517 nm.



POPV-ONV

Absorption, λ [nm]: 480, 457, 310, 240

Pl, λ [nm]: 517

3.17.5. Photoluminescence in films

The maximum emission of all polymers in film is shifted to higher wavelengths compared to emission of the polymer in solution. This is due to polymer aggregation.

Comparing emission from film to emission from solution of the POPV-ONV a shift of approximately 100 nm is observed whereas the emission of the PPVs and PPV-ONVs only shift about 50 nm. This can be explained by the fact that the backbone of POPV-ONV in the solid layer is planar whereas the substituted derivative is also twisted in film.

The figures below show the absorption and PL (of the film and from solution) graphs for methyl-*Pp*PV and POPV-ONV.

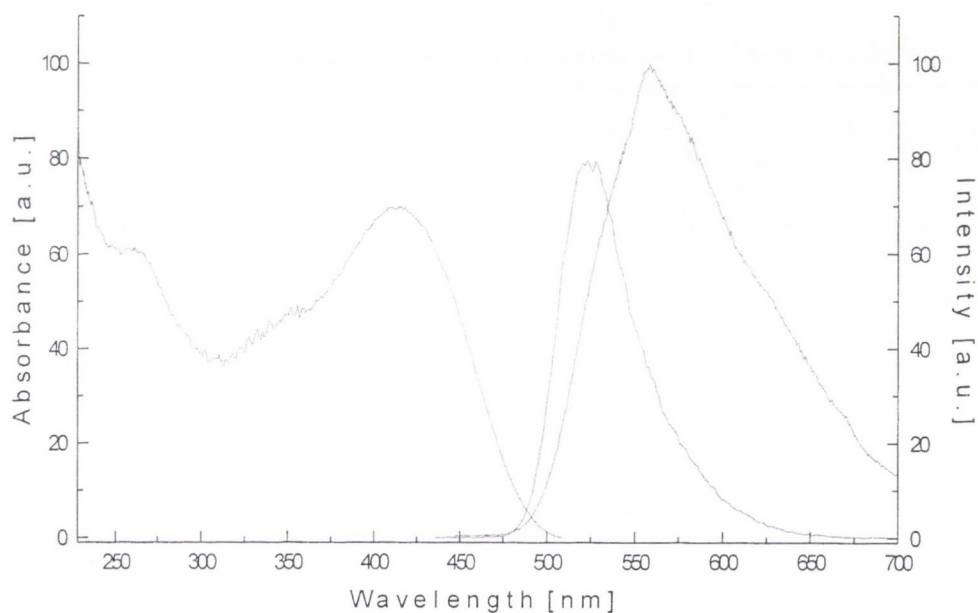


Fig. 3.38: Absorption, PL of methyl-*Pp*PV in 10^{-4} mol CHCl_3 solution and PL in film (the values of absorbance and intensities are adjusted)

The two spectra show the differences between PL_{film} and $\text{PL}_{\text{solution}}$ very well. While the two PL graphs of methyl-*Pp*PV do overlap, the PL graph of POPV-ONV in solution is shifted into the centre between absorption and PL_{film} .

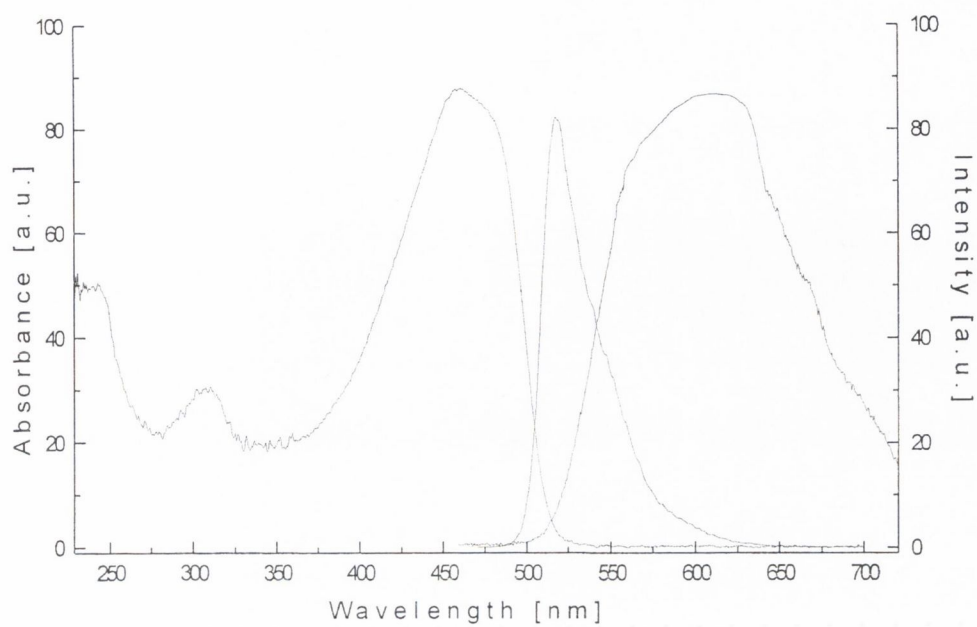


Fig. 3.39: Absorption, PL of POPV-ONV in 10^{-4} mol CHCl_3 solution and PL in film (the values of absorbance and intensities are adjusted)

	PL _{solution} [nm]	PL _{film} [nm]
methyl-PpPV	522	560
methoxy-PpPV	525	565
methyl-PmPV	494	545
POPV-ONV	517	595
dimethyl-PmPV-ONV	470	530
nonyl-PpPV-NV	480	540

Table. 3.14: PL data of a selection of polymers measured in 10^{-4} mol CHCl_3 solution and as a film on a glass-slide

3.18. Applications

3.18.1. Light emitting diodes (LEDs)

Device preparation

A typical polymer light emitting diode (LED) configuration was already shown in the introduction.

LEDs were constructed by first etching the ITO anode to pattern the electrode to prevent electrical shorting in the region of the devices where contact is made by the external test circuitry. ITO was chosen as the hole-injecting electrode in the device because it is transparent over the entire visible region and the work function is approximately 4.8 eV which is reasonably similar to the ionisation potential of most emissive conjugated polymers, thus allowing easy injection of holes into the devices ^[119]. The centre strip of ITO (9x12 mm) was painted with a resistive coating (ordinary nail varnish). This was allowed to dry in air and the substrate was then placed in a boiling 10% solution of hydrochloric acid for approximately 5 minutes to remove those regions not covered by the resist layer. Next it was washed in deionised water to remove any HCl traces and immersed in acetone in order to dissolve the resist from the surface of the ITO. Thus a strip of ITO was left only where the resist was originally painted.

After the ITO substrate had been etched it was rinsed with acetone and 2-propanol and then placed in an ultrasonic bath in a solution of Decon 90 and deionised water to remove any dust and dirt traces.

The polymer films were spin coated onto the substrate. It was found that spin coating from toluene solution gave the best results in terms of film homogeneity ^[45]. The concentration of the polymer in toluene solution was 10 g/L. The polymer after being dissolved was filtered to remove any large particulate contaminants. The substrate was placed on top of a spin coater chuck and then rotated at a speed of between 1500-7000 rpm for approximately one minute leaving a thin film of thickness between 500-15 nm.

The electron injecting metal should have a low work function as the electron affinity of most organic materials used is in the region of 2.5-3.5 eV. The metal employed for the cathode or electron injecting contact was aluminium. Aluminium

has a work function of 4.2 eV and can be easily deposited by thermal evaporation at a vacuum pressure between 6×10^{-6} and 8×10^{-7} mbar through a shadow mask. This produces six so-called metal fingers (active area: 2×2 mm) with a thickness of 100 nm. The overlap of these fingers with the bottom electrode constitutes the active area of the device.

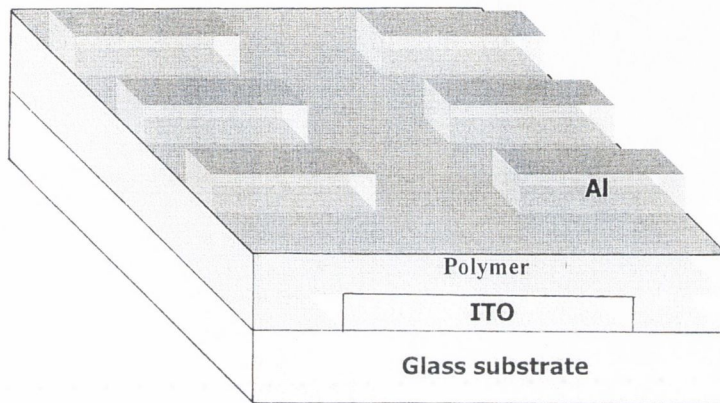


Fig. 3.40: 'Six finger' LED originally made in Sheffield ^[45] ^[46]

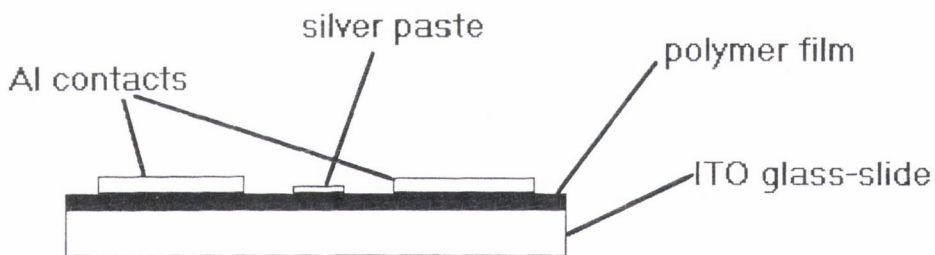


Fig 3.41: Cross section of the single layer 'six finger' LED

Electrical connections to the common anode and the six cathodes are made via spring loaded pressure contact pins set in the same pattern in a specially designed sample chamber.

Device characterisation

The following polymers were employed for LED device preparation and characterisation:

methyl-*Pp*PV
methyl-*Pm*PV
methoxy-*Pp*PV
dimethyl-*Pm*PV-ONV
POPV-ONV
nonyl-*Pp*NV

All polymers, with the exception of POPV-ONV, showed poor film forming qualities, with extensive crystalline regions present.

The low molecular weight of the materials and the packing of the polymer chains due to structural parameters cause a high degree of crystallinity. These properties are undesirable for LED's for numerous reasons. Firstly, crystallinity disrupts charge transport through the film. This can be manifested in low current densities being observed due to a reduction in the carrier mobilities of the polymer. Time of flight measurements, show a large dependence of carrier mobility on film morphology. Furthermore the presence of crystalline regions can reduce the photoluminescence quantum efficiency by quenching excitons. An improvement of this phenomenon was attempted by introducing *meta* linkages into the polymer backbone since it was found that *meta* linkage frustrate the interchain interactions that have been implicated as important for non-radiative decay in solid films ^[120].

Unlike the previous polymers with phenyl substitution on the vinylene bond, POPV-ONV has a less crystalline nature. This has been verified by DSC measurements. Furthermore the higher molecular weight of POPV-ONV is consistent with this hypothesis.

LEDs from methyl-*Pp*PV, methyl-*Pm*PV, methoxy-*Pp*PV, dimethyl-*Pm*PV-ONV, nonyl-*Pp*PV-NV gave Ohmic shorts and could therefore not be investigated. The likelihood is that the poor electrical contact was due to the high temperature of the aluminium atoms when hitting the organic surface. The poor film forming properties coupled with the low glass transition temperatures allows filamentous injection to occur, leading to short circuits at high voltages. A possible solution to this problem would be to incorporate the polymers into a polycarbonate matrix ^[116] although polycarbonate is an insulator and therefore a high drive voltage would be

required. A further possibility is to manufacture multi-layer devices. This would prevent short circuits and also provide a superior charge balance within the device. Electrical and luminance measurements were carried out on an ITO/POPV-ONV/Al device. A low turn-on voltage was observed in the region of 7 V. This corresponds to a current density of 0.06 mA/cm^2 . This is consistent with two separate scenarios. Firstly the material has a very uni-polar charge transport capability. With the injection barriers imposed by the choice of electrodes it is most likely that the polymer has a high hole mobility. This is consistent with what has been frequently observed for a range of PPV based materials. The luminance curve shows a slightly higher threshold voltage at 9 V. The luminance was measured using a photodiode which mirrors the response of the human eye, peaking at 550 nm and dropping to zero in the blue at 400 nm and in the red at 670 nm.

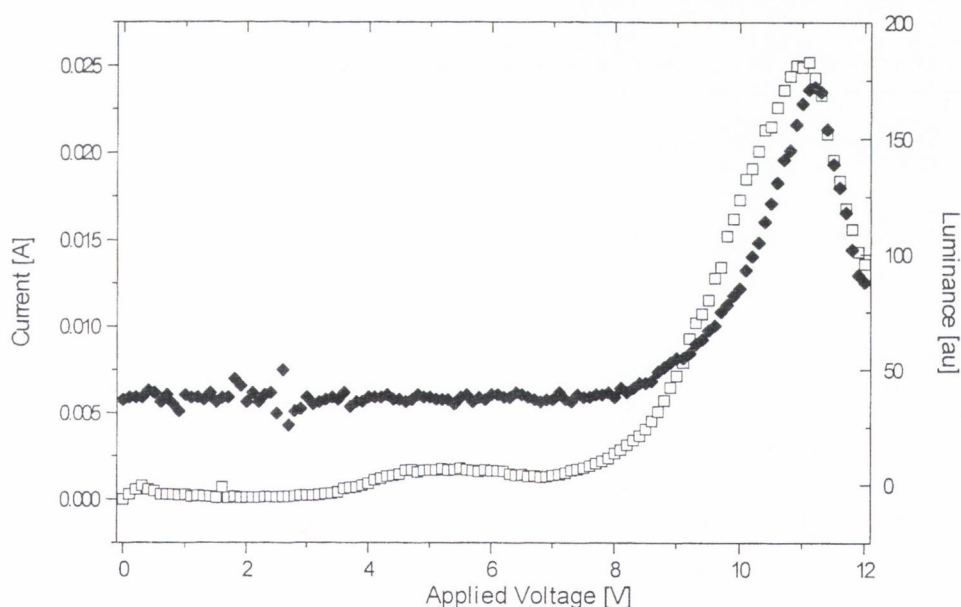


Fig. 3.42: $I(V)/L(V)$ curve of the ITO/ POPV-ONV /Al device

From figure 3.43 it can be seen that the increase in luminance is linear with current density, prior to the saturation of current. The saturation is most likely due to the movement of the exciton formation and recombination zone close to the aluminium electrode. This will allow charge carriers to leak out of the device and excitons to be quenched by the metal, consistent with a drop in both current and brightness.

The brightness is measured in arbitrary units but rough estimates would place a peak brightness in the region of 10 cd/m^2 [121]. This is poor compared to the improved brightnesses obtained in recent publications but this device is un-optimised and significant improvements could be expected with fine tuning. As a comparison brightness, the average television screen is around 100 cd/m^2 .

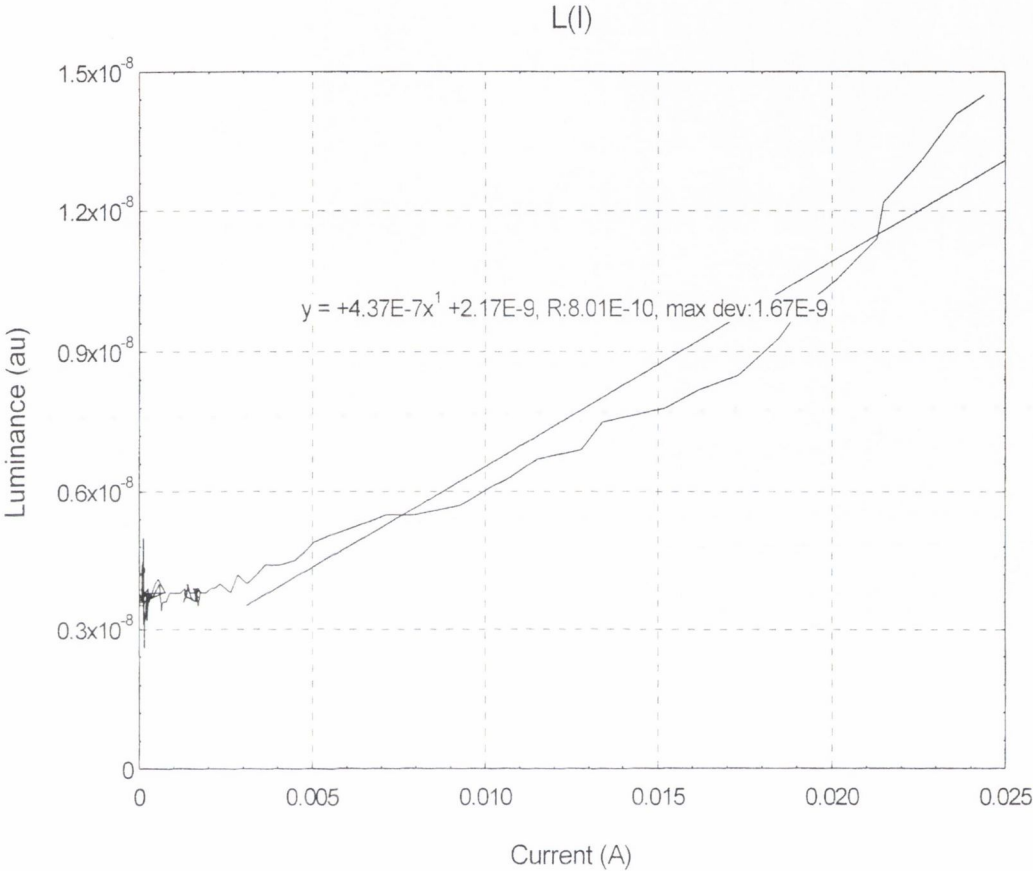


Figure 3.43: $L(I)$ curve of the ITO/POPV-ONV/Al device

3.18.2. Photovoltaic devices

Polymer based photodiodes use the photovoltaic effect, by which electrons and holes are produced, separated and subsequently collected at electrodes when a semiconductor device is illuminated.

In general, the conduction processes in a multilayer device are complicated and likely to be strongly material and also preparation dependent.

The power conversion of organic solar cells is often very low due to several factors as there are short exciton diffusion length, relatively large exciton binding energies and low charge mobility in the organic layer.

A major cause is also the recombination of excitons created by the incident light. By using a combination of materials, one having a small ionisation-potential and good hole transport properties and the other having a large electron affinity that acts as an electron transport material these excitons can be dissociated. If this combination of materials can be achieved in such way for that a percolation path for the charge carrier is created, the efficiency of the devices is increased dramatically ^[122].

Device preparation

The photovoltaic devices were prepared and measured during a visit at the Laboratory for Photonics and Interfaces at the Swiss Federal Institute of Technology, Lausanne.

Note, that the devices were prepared with a flat TiO₂ film instead of a porous, nanostructured film that is usually employed for Graetzel-type 'high surface' solar cells. These flat film devices have the advantage that they are easier to prepare (e.g. the problems of polymer penetration into the porous TiO₂ film can be avoided) but nevertheless show similar open circuit voltage and fill factor characteristics to the porous device.

The following polymers that were already employed for LEDs were also investigated for the photovoltaic device preparation and characterisation: methyl-PpPV, methyl-PmPV, methoxy-PpPV, dimethyl-PmPV-ONV, POPV-ONV and nonyl-PpPV-NV.

The photovoltaic response of cells containing these polymers as hole conductors was investigated by means of devices with a flat TiO_2 film, shown schematically in Fig. 4.44.

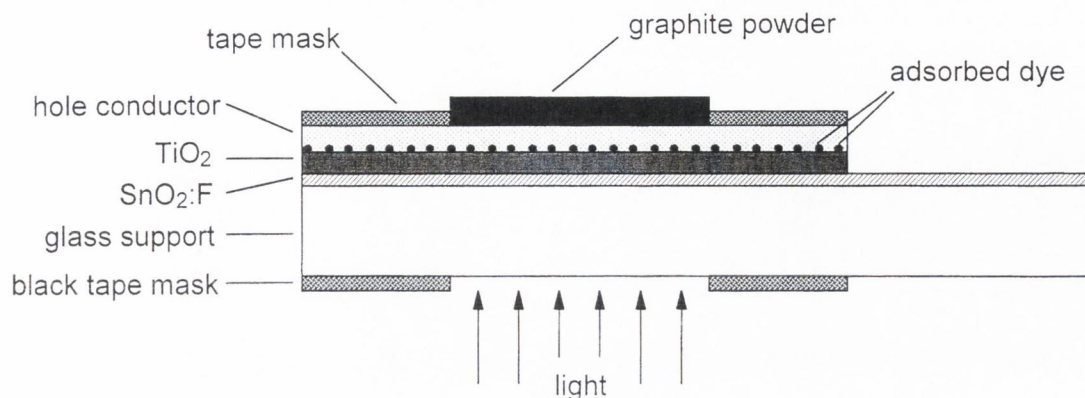


Fig. 4.44: Schematic SnO_2 /flat- TiO_2 /N3/polymer/graphite solar cell

The flat non-porous TiO_2 -films were deposited onto the conducting glass (2.3 mm thick glass support with a conducting F-doped SnO_2 layer) by spray pyrolysis^[123], to avoid direct contact (which would lead to a short circuit) between the hole transport medium layer and the SnO_2 .

A $5 \times 5 \text{ cm}^2$ glass plate was heated up to 450°C and then 4 ml of a 10% ethanolic solution of di-iso-propoxy titanium-bis(acetylacetonone) were sprayed in small portions onto (two opposite edges were covered with glass slides to avoid TiO_2 deposition to enable contact afterwards). The devices were then annealed to 450°C for two hours, cooled down and cut into electrodes ($1 \times 2.5 \text{ cm}$).

For dye adsorption the TiO_2 electrodes were heated at 450°C for 30 minutes, cooled down to $130\text{--}140^\circ\text{C}$ and put into 3 mmol/L ethanolic dye N3 ($\text{Ru}(4,4\text{-bis(carboxy)-bpy})_2(\text{NCS})_2$)^[54] solution for approximately 3 hours. After rinsing with acetonitrile, the polymer film layers were spin coated in argon atmosphere from a solution 4 mmol/L polymer/chloroform solution onto the device (for the thick film device additional drops were drop-casted onto the film). Both sides, the non-coated side and the coated side were covered with a black tape mask with a 0.25 cm^2 hole to control the area which will be exposed to light in the measurement. For the anode graphite powder was contacted with aluminium foil and both pressed with a piece of glass onto the device.]

Device characterisation

Important parameters used to assess the quality of the device are the short-circuit current I_{sc} , open circuit voltage V_{oc} , the fill factor FF and the power conversion efficiency η .

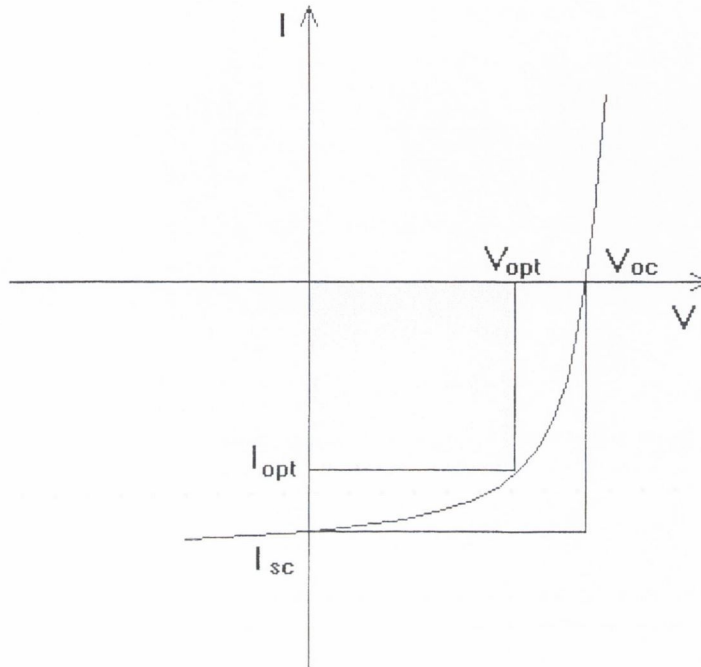


Fig. 3.45: Schematic photocurrent-voltage curve

The fill factor (FF) is a measure to compare different solar cell systems. It gives information about how the cell voltage decreases against V_{oc} when a current is applied.

It is defined as the product of current and voltage for maximum power divided by the product of short-circuit current and open-circuit voltage:

$$FF = \frac{V_{opt} I_{opt}}{V_{oc} I_{sc}} \quad (3.2)$$

where V_{opt} and I_{opt} are respectively current and voltage for maximum power output and I_{sc} and V_{oc} are the short-circuit current and open-circuit voltage^[125].

The power conversion efficiency η is the ratio of the maximum electrical power (shaded area in the schematic photocurrent-voltage curve) to the power of the radiation which produced it^[124].

$$\eta = \frac{\text{Power}_{\text{in}}}{\text{Power}_{\text{out}}} = \frac{V_{\text{opt}} I_{\text{opt}}}{\text{radiation area}} \quad (3.3)$$

As was the case for the LED device preparation all polymers, with the exception of POPV-ONV, showed poor film forming qualities. Only very small currents were obtained and therefore these devices were not investigated any further.

Two devices with different film thicknesses (due to problems with the equipment, the thicknesses could not be measured, for the thin film device it was estimated to lie between 50-100 nm) were tested. As described before for the thin film device two polymer layers were spin-coated onto the substrate whereas the thick film device had an additional layer drop-casted onto the film.

Both devices were measured at RT in the dark and under simulated sunlight of 100 mW/cm² at air mass 1.5.

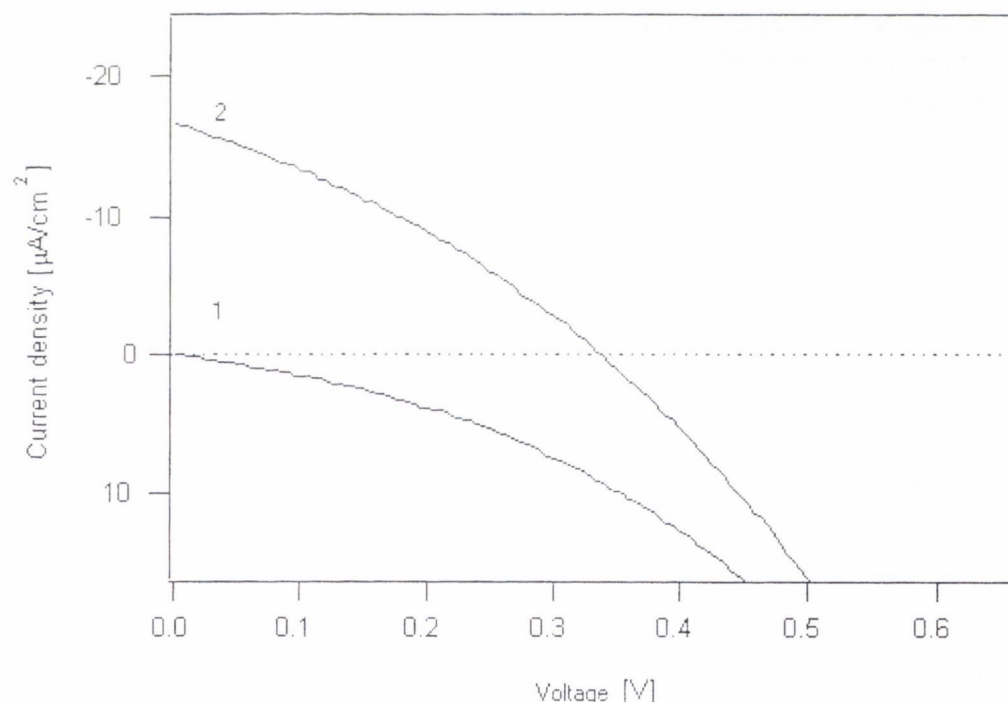


Fig. 3.46: Current/voltage characteristics, obtained from the thin film SnO₂/flat-TiO₂/N3/POPV-ONV/graphite cell (1) in the dark and (2) under white light illumination at 100 mW/cm² (AM 1.5)

The current/voltage characteristics of the thin film POPV-ONV cell shows a short-circuit current density of $J_{sc} = 16.8 \mu\text{A}/\text{cm}^2$ (J_{sc} is the short-circuit current I_{sc} per area) and the open-circuit voltage of $V_{oc} = 0.34 \text{ V}$ with an FF of 31%. Current and voltage for maximum power output are $V_{opt} = 0.19 \text{ V}$ and $J_{opt} = 9.3 \mu\text{A}/\text{cm}^2$.

The power conversion efficiency η was to be $\eta = 0.02 \%$.

The thick film cell shows an improved open circuit voltage and current density/voltage graph in the dark but therefore the graph intersects with the current density/voltage graph at illumination.

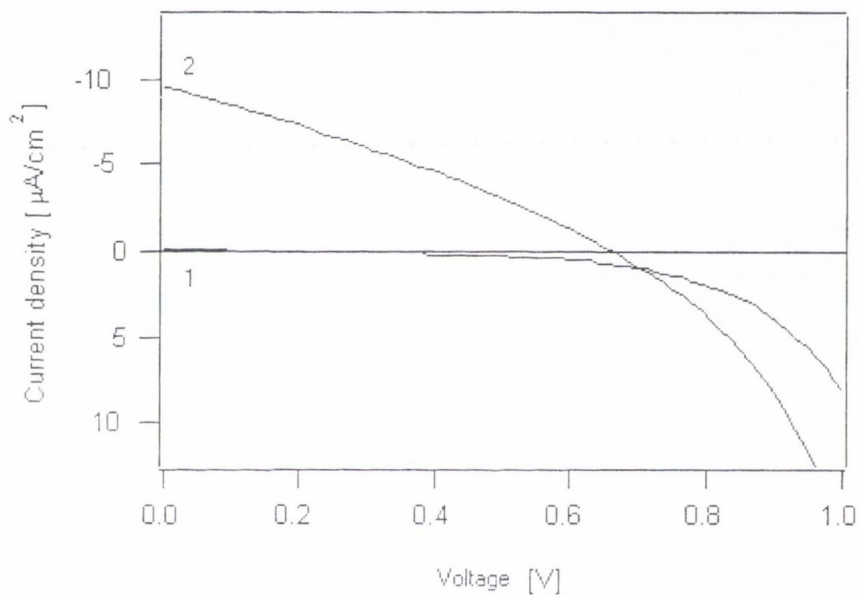


Fig. 3.47: Current/voltage characteristics, obtained from the thick film $\text{SnO}_2/\text{flat-TiO}_2/\text{N3}/\text{POPV-ONV}/\text{graphite powder}$ device (1) in the dark and (2) under white light illumination at $10 \text{ mW}/\text{cm}^2$ (AM 1.5)

The current/voltage characteristics of the thick film POPV-ONV cell short-circuit current density has found to be $I_{sc} = 9.5 \mu\text{A}/\text{cm}^2$ and the open-circuit voltage of $V_{oc} = 0.66 \text{ V}$ for the thin film device. The fill factor (FF) is 29 %.

Current and voltage for maximum power output are $V_{opt} = 0.36 \text{ V}$ and $I_{opt} = 5.1 \mu\text{A}/\text{cm}^2$. The power conversion efficiency is calculated to be $\eta = 0.02 \%$.

The graph suggests that for in the thick film device the polymer layer not only works as a hole conductor but also causes a photocurrent which will be shown by the current versus time measurements in the following.

But first another observation has to be mentioned. The thick film device also exhibited relatively strong luminescence whereas for the thin film it was almost not noticeable. Investigations made by Goossens *et al.* ^[53] on devices of MEH-PPV on both quartz and TiO₂ show that for polymer films on quartz the luminescence increases linearly whereas for the TiO₂ device at thicknesses below 20 nm the luminescence is almost completely quenched but above the luminescence increases linearly. According to this observation, the exciton diffusion length was estimated to be 20 nm ^[31]. Although the film thicknesses for the present cells were not determined, a possible effect could be that for the thick film device an amount of excitations never reach the polymer/N3-dye/TiO₂ interface where the exciton dissociation into charge carriers can occur since the film thickness is above the exciton diffusion length.

Additionally, the current/time characteristics at different incident light intensities for both cells were recorded (see figure 3.48).

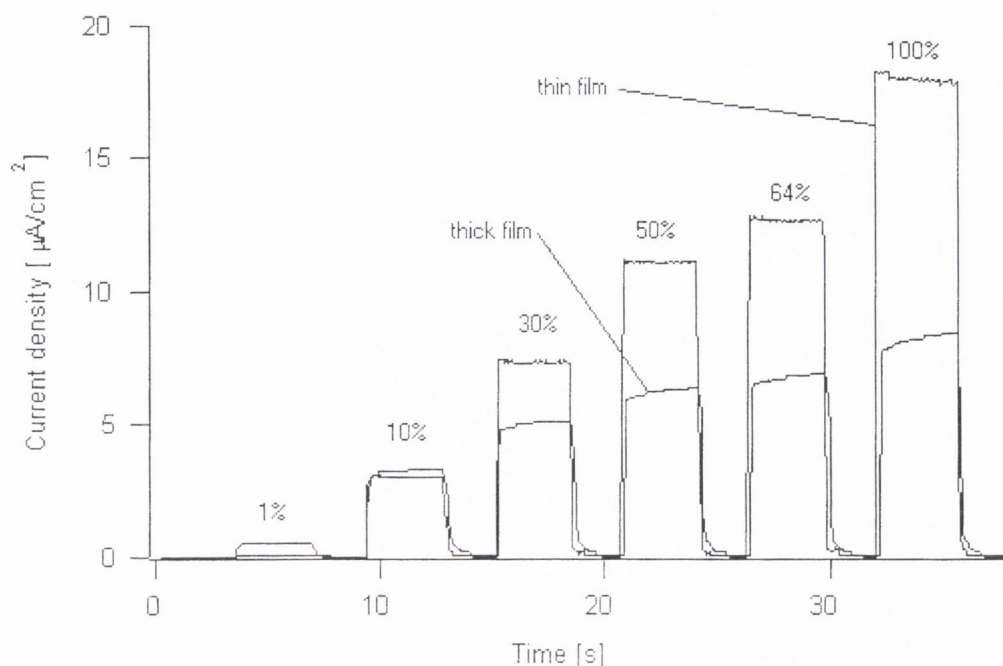


Fig. 3.48: I/t measurement with different light-intensities (1%, 10%, 30%, 50%, 64% 100% sun) where 100% sun is $10 \text{ mW}/\text{cm}^2$ (radiation distribution: AM 1.5)

The spectrum shows that the current for the thick film rises while it is exposed to light while the current of the thin film device remains constant over time. This suggests that although both devices were prepared from the same material the thick film device is photo-doped since the conduction improves while it is exposed to light.

The initial idea was to combine polymer with the ruthenium dye. These type of conjugated polymers have shown to be good hole conductors which is the requirement to regenerate the dye. So far this type of multi layer solar cell has not been published to be able to compare the results.

The same cells without the dye were rather unstable and both current and voltage decreased significantly after a few minutes of illumination. However, comparable voltages with smaller currents were initially obtained.

The recently published solid state ruthenium dye-sensitised mesoporous TiO_2 Graetzel cell with 2,2',7,7'-tetrakis(N,N-di-*p*-methoxyphenyl-amine)9,9'-spiroflourene (OMeTAD) as a hole-transport material produces a short-circuit

current density of $I_{sc} = 0.32 \text{ mA/cm}^2$ and an open-circuit voltage of $V_{oc} = 0.34 \text{ V}$. The fill factor was 62 % ^[125].

It shows that the presented devices with the polymer as a hole conducting layer are in no competition with the OMeTAD hole conductor although due to fact that these values were obtained with NC-TiO₂ layer instead of a flat TiO₂ layer.

4. Conclusions and Future Work

In this chapter the main results will be briefly reviewed and the future work resulting from these results pointed out.

Basically, the research presented in chapter three can be divided into two parts. The first part included the synthesis and chemical characterisation of all polymers. The second part dealt with the investigation of optical properties, the electrochemical behaviour and thermal behaviour. Additionally, light emitting diodes and photovoltaic devices were fabricated and characterised.

In the first section of the results and discussion chapter the complete synthesis (including starting material) of two main groups of polymers, PPV and PPV-ONV, with different *m*-/*p*-substitution and alkyl/alkoxy (R) substitution pattern was presented. All polymers were synthesised under the same conditions via Horner condensation polymerisation.

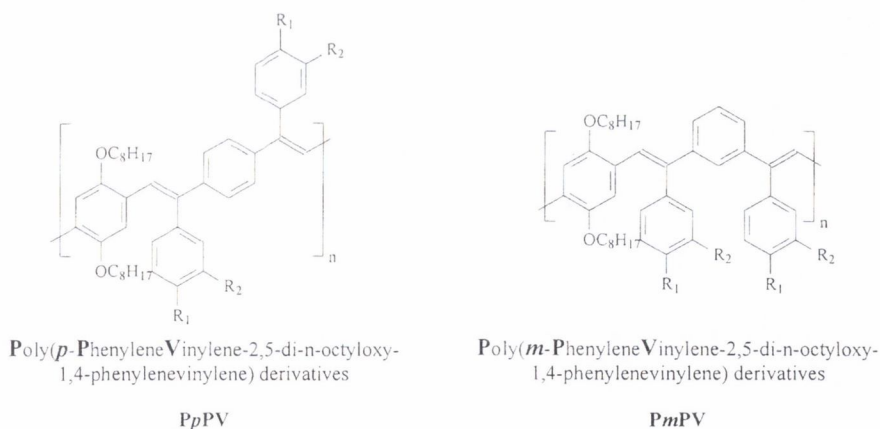


Fig. 4.1: Structure of the PPV derivatives (R = H, alkyl or alkoxy substitution)

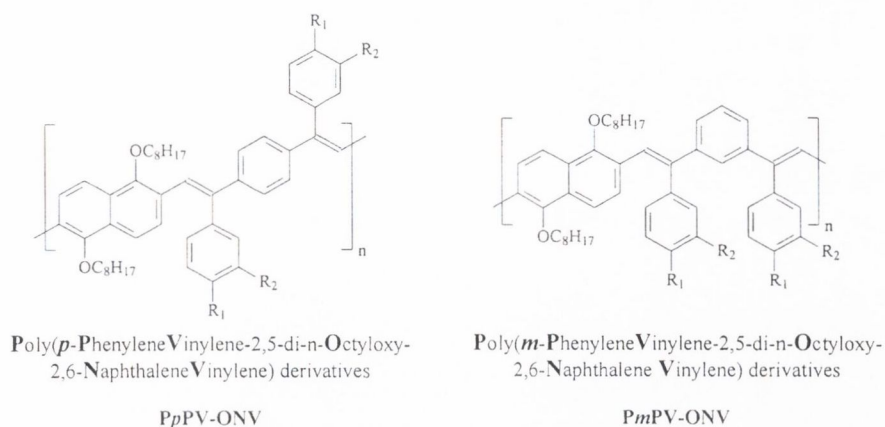


Fig. 4.2: Structure of the PPV-ONV derivatives (R = H, alkyl or alkoxy substitution)

In addition, the compounds in fig. 4.3 have been synthesised to compare their properties with the polymers of the two main groups.

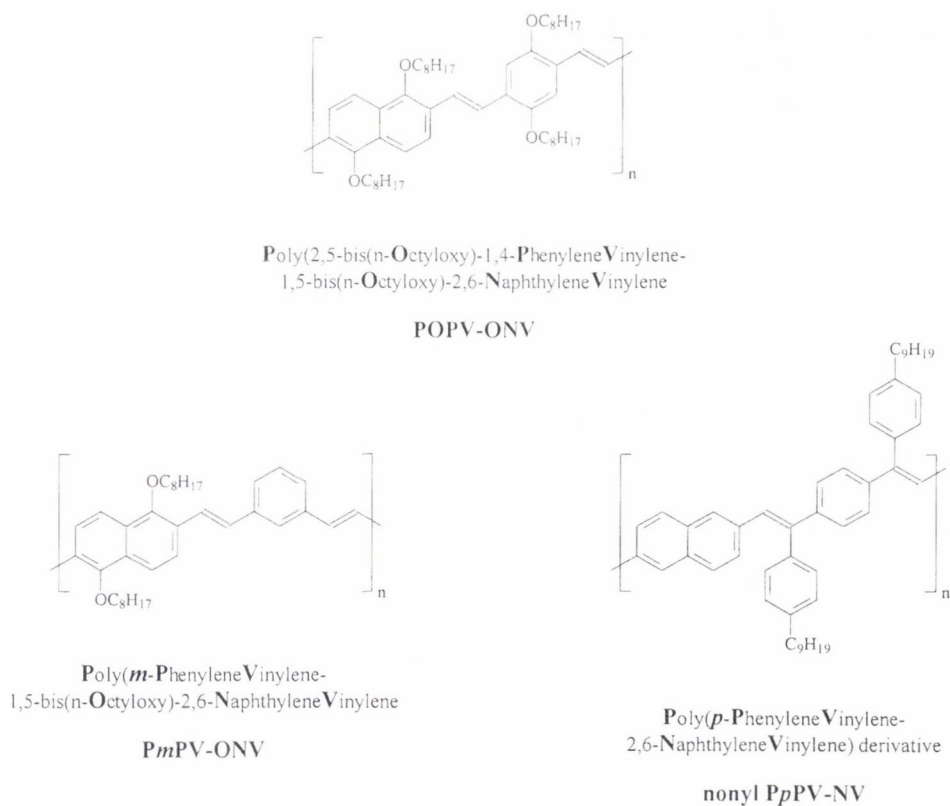


Fig. 4.3: Structures of PmPV-ONV and nonyl-PpPV-NV

The synthesised polymers were chemically characterised by NMR, GPC, IR and Raman spectroscopy.

It has been shown that the presented structures were obtained and that they were of high purity.

In general, more information could be obtained from ^{13}C -NMR than from ^1H -NMR since the proton peaks were found to be quite broad especially in the aromatic region.

The molecular weight, investigated by gel permeation chromatography, of all derivatives was found to be more in the range of oligomer molecular weight which is normal for this type of materials synthesised via the Horner polycondensation route.

The infrared spectra showed many overlapping modes due to the complex structures of the polymers and were therefore mainly employed to search for remaining starting material.

Raman investigations have found to be more useful to investigate the backbone conformation of these polymer systems. It was shown that the Raman peaks depend strongly on the substitution pattern on the backbone.

As already mentioned, the second part of the result and discussion chapter dealt with the investigation of the polymers' thermal behaviour, the optical properties and the electrochemical behaviour.

It has been shown by thermal gravimetric analysis that the polymers do not decompose in either nitrogen or air below 350°C . Most of the phenyl substituted PPV derivatives have found to be even stable up to 370°C . This is a substantial improvement as most unsubstituted PPV derivatives have been reported to decompose around 300°C .

Measurements employing differential scanning calorimetry have shown side-chain melting peaks in the area between 20°C and 70°C . The backbone melting ranges were found to be very broad and often not clearly recognisable. *Pm*PV-ONV and nonyl-*Pp*PV-NV did not melt below the decomposition temperature which indicates that the polymers containing phenyl substitution on the vinylene bond are more crystalline. Due to this high degree of crystallinity, glass transition

temperatures were not always clearly visible. For the few polymers that did exhibit T_g , it was at approximately 3°C.

A selection of polymers was tested for their liquid crystalline properties employing a polarising microscope. Dimethyl-PpPV-ONV has been shown to exhibit liquid crystalline textures between 180°C and 230°C. No liquid crystalline texture has been observed for methyl-PmPV and methoxy-PpPV. Whether this is due to the absence of a liquid crystalline phase or due to the fact that characteristic textures do not always appear, has not been investigated.

Further investigation of the liquid crystal properties of the compounds containing a phenyl substitution on the vinylene bond will be carried out since these properties could be useful for polymer alignment on devices.

Cyclic voltammetry measurements indicated that the oxidation takes place on the octyloxy substituted phenylene unit. This technique can be used to estimate the bandgap for these materials. The bandgap varied between 2.5 eV and 3 eV depending on the substitution pattern. Additional substitution on the phenylene moiety attached to the vinylene bond was shown to effect the oxidation potential. The oxidation potential of methoxy substituted derivatives was lower compared to the corresponding alkyl or hydrogen substituted derivatives. Also, methoxy substituted derivatives have been found to undergo irreversible oxidation. Chemical oxidation of methoxy-PpPV showed that this irreversible oxidation results in the formation of phenantrene units.

Some general trends of the absorption and emission properties were found. In general, these type of polymers have shown to emit light in the blue-green region.

The absorption and emission maxima of *meta* linked derivatives are blue shifted compared to the corresponding *para* derivatives. This is due to conjugation disruption of chain conjugation caused by the insertion of the *meta* linkage. Substitution of the dioctyloxy-phenylene moiety with a 2,6-linked dioctyloxy-naphthalene unit also induced a blue-shift of the absorption and the PL. Introduction of a phenyl substitution on the vinylene bond caused a hypsochromic shift of the absorption maximum and a bathochromic shift of the luminescence. As a result the Stokes shift was significantly increased. Different substitution patterns on the phenylene unit did not effect the absorption and fluorescence maxima significantly. Although the fluorescence quantum yield was not investigated, the

Stokes shift of the compounds with phenyl substitution on the vinylene bond suggests investigation of lasing properties of these compounds since a high Stokes shift is desired to prevent re-absorption.

Introduction of the electron donating octyloxy-group has been found to shift emission and luminescence towards higher wavelengths due to increased effective conjugation.

Photoluminescence measurements in film showed similar trends but in general, the emission of the investigated polymers was shifted to higher wavelengths compared to the emission maxima in solution mainly due to aggregation of the polymer chains.

Finally, the fabrication and characterisation of LEDs and solarcells has been presented. Due to poor film forming qualities caused by the high degree of crystallinity, compounds with phenylene units on the vinylene moiety have not found to be useful for both devices.

A single layer ITO/POPV-ONV/Al LED with a turn-on voltage in the region of 7 V at 0.06 mA/cm^2 has been successfully fabricated.

The photovoltaic devices were fabricated using following geometry: $\text{SnO}_2/\text{flat-TiO}_2/\text{POPV-ONV/graphite}$ or $\text{SnO}_2/\text{flat-TiO}_2/\text{N3/POPV-ONV/graphite}$. The cells without the N3-dye were unstable and both, current and voltage decreased significantly after a few minutes of illumination. Dye containing cells were stable and the thin film device exhibited a photovoltaic effect with $V_{oc}=0.34 \text{ V}$, $J_{sc}=16.8 \text{ }\mu\text{A/cm}^2$ and a fill-factor of 0.31 under AM 1.5 illumination.

5. Experimental

5.1. General Remarks

The following equipment was used:

Melting Points

Griffin melting point apparatus

NMR spectroscopy

Bruker Spectrospin DPX 400:

^1H -NMR	400.1 MHz; internal standard: TMS
^{13}C -NMR	100.6 MHz; internal standard: deuterated solvent (CDCl_3)
^{31}P -NMR	162.3 MHz;

Bruker Spectrospin MSL 300:

^1H -NMR	300.1 MHz; internal standard: TMS
^{13}C -NMR	75.3 MHz; internal standard: deuterated solvent (CDCl_3)
^{31}P -NMR	121.4 MHz;

NMR calculations

Bio-Rad Laboratories, Sadtler SuiteTM 1.0, Chem Windows Spectroscopy[®] 6.0;
Chemdraw Pro, Version 4.5

IR-spectroscopy

Nicolet 510P for the ATR-FTIR (attenuated total reflection Fourier-transform infrared set-up), using a ZnSe crystal in an overhead ATR-trough;

Nicolet continuum for FTIR-Microscopy in reflectance mode; The sample was placed onto an Al-mirror

Raman spectroscopy

Instruments S.A. Labram 1B Raman Spectrometer

All samples were measured in 10^{-4} mol chloroform solution in 10mm cells.

Absorption spectroscopy

Shimadzu UV-2101PC Absorption Spectrophotometer

All samples were measured in 10^{-4} mol chloroform solution in 1mm quartz cells.

Photoluminescence spectroscopy

For solutions: Perkin Elmer LS50B Luminescence Spectrometer

(measured in 10^{-4} mol chloroform solution in 10mm quartz cells)

For films: Light source: Roithner Lasertechnik UV LED (370 nm)

Fibre optic bundle: Oriel Bi UV 836

Spectrograph: Oriel 77406 Multispec

Detector: Andor technology CCD detector

Current-voltage-luminance characteristics

Current-voltage: Keithley 237 source measure unit

Luminance: Silicon Photodiode connected to a Blackstar 4503
Multimeter via pre amplifier

GPC measurements

The polymer solution was injected into a 60°C trichlorobenzene stream (flow rate: 1mL/min).

Calibration standard: polystyrene

Pump: Waters 600 E pump

Columns: 7.8×30mm styragel: HT3 (500 to 30000 Å)
HT5 (50000 to 4×10^6 Å)
HT6E (5000- 1×10^7 Å)

Detector: Water 410 differential spectrometer

Elemental Analysis

The samples were sent to the Microanalytical Laboratory/Department of Chemistry at University College Dublin and measured on a C440 EXITOR-Analytical Elemental Analyser.

TGA measurements

System: TA 4000; Balance: TG 50; Processor: TC 11

DSC measurements

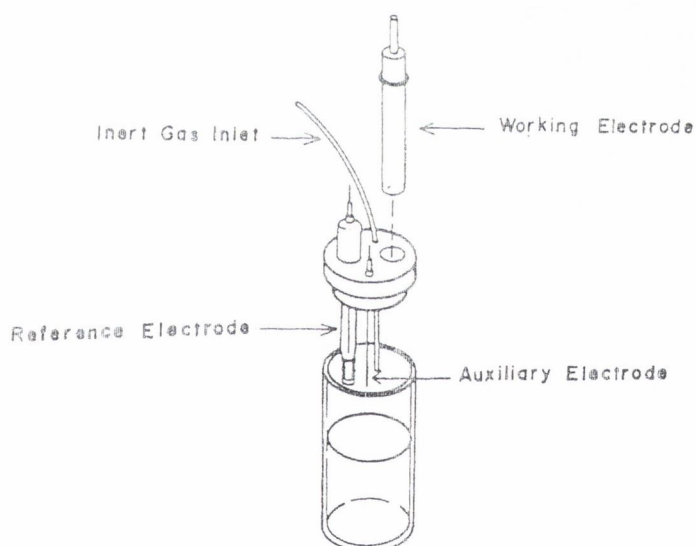
Rheometric Scientific DSC SP

Birefringence measurements

A Leitz polarising microscope with microscope hot stage with a Eurotherm temperature controller was employed.

Cyclic voltammetry

Cyclic voltammetry was performed in a three-electrode (see picture below) cell equipped with a glassy carbon working electrode tip, a Pt wire counter electrode and Ag/AgCl reference.



A BAS 100B/W electrochemical workstation/analyzer were used to generate the potential sweep and to record the current signal.

The concentration of the polymers was 10^{-3} mol/L in 10^{-1} mol/L tetrabutylammonium hexafluorophosphate in CH_2Cl_2 solution.

Solar cell measurements

The photovoltaic devices were prepared and measured during a visit at the Laboratory for Photonics and Interfaces at the Swiss Federal Institute of Technology, Lausanne (Switzerland).

Chemicals

Commercially available chemicals were used without further purification.

All solvents used in these syntheses were of laboratory grade, dried by standard methods and freshly distilled before use.

The following starting materials were synthesised according to the literature:

- 1,4-Bis(4-methyl-benzoyl)benzene **(1)** ^{[90] [126]}
1,4-Bis(3,4-dimethyl-benzoyl)benzene **(2)** ^{[90] [126]}
1,4-Bis(4-methoxy-benzoyl)benzene **(3)** ^{[90] [126]}
1,4-Bis(3,4-dimethoxy-benzoyl)benzene **(4)** ^{[90] [126]}
1,4-Bis(4-nonyl-benzoyl)benzene **(5)** ^{[90] [126]}
1,3-Bis(4-methyl-benzoyl)benzene **(6)** ^{[90] [126]}
1,3-Bis(3,4-dimethyl-benzoyl)benzene **(7)** ^{[90] [126]}
1,3-Bis(4-methoxy-benzoyl)benzene **(8)** ^{[90] [126]}
1,3-Bis(3,4-dimethoxy-benzoyl)benzene **(9)** ^{[90] [126]}
1,3-Bis(4-nonyl-benzoyl)benzene **(10)** ^{[90] [126]}
1,4-Di-n-octyloxybenzene **(11)** ^[127]
2,5-Di-n-octyloxy-1,4-bis(bromomethyl)-benzene **(12)** ^[19]
2,5-Di-n-octyloxy-1,4-xylene-diethylphosphonate-ester **(13)** ^[128]
1,5-Di-n-octyloxynaphthalene **(25)** ^[97]
1,5-Bis(n-octyloxy)-2,6-naphthalenedialdehyde **(26)** ^[129]
1,5-Bis(n-octyloxy)-2,6-dihydroxymethylnaphthalene **(28)** ^[129]
1,5-Bis(n-octyloxy)-2,6-dibromomethylnaphthalene **(29)** ^[129]
1,5-Bis(n-octyloxy)-2,6-dimethylnaphthalene-bis(ethylphosphonate)ester **(30)** ^[128]
2,6-Dibromomethylnaphthalene **(37)** ^{[90] [126]}
2,6-Dimethylnaphthalene-bis(ethylphosphonate)ester **(38)** ^[128]

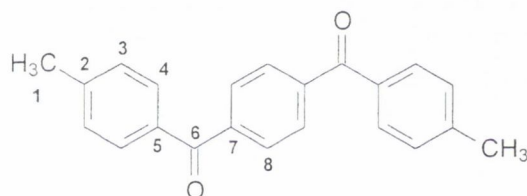
5.2. Synthesis and characterisation

5.2.1. Ketones

1,4-Bis(4-methyl-benzoyl)benzene (1)

A mixture of 7.36 g toluene (80 mmol) and 5.97 g terephthaloyl-chloride (30 mmol) was cooled down to 0°C. 9.61 g of powdered aluminium chloride (72 mmol) was added at once. The reaction was slowly warmed to RT, left stirring for 5 h and then slowly heated to 40°. After stirring for an additional 10 h, the reaction mixture was cooled down and slowly added to a 100 mL mixture of ice-water and HCl (10:1). The solid was filtered off and dissolved in toluene. The toluene solution was dried over MgSO₄ and filtered. The solvent was evaporated and the product re-crystallised in CHCl₃ to give 4.28 g white crystals (yield: 46%).

Mp.: 184-190°C



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.85 (s, 4H, H8), 7.75 (d, 4H, H4), 7.30 (d, 4H, H3), 2.45 (s, 6H, H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

195.3 (C6), 143.8 (C2), 140.8 (C7), 134.3 (C5), 130.3 (C8), 129.5 (C4), 129.1 (C3),

21.6 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

130.3 (pos. C8), 129.5 (pos. C4), 129.1 (pos. C3), 21.6 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

130.3 (C8), 129.5 (C4), 129.1 (C3)

IR (microscope set-up) ν[cm⁻¹]:

3283 w, 3021 s, 2945 s, 2663 s, 2550 m, 2294 w, 1931 w, 1700 s, 1654 s, 1598 s, 1444 m, 1403 m, 1316 s, 1244 m, 1152 w, 1116 w, 932 m, 814 w, 732 w, 686 w

1,4-Bis(3,4-dimethyl-benzoyl)benzene (2)

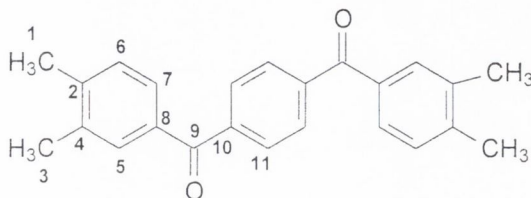
see synthesis 1,4-bis(4-methyl-benzoyl)benzene (1)

Amount: 8.48 g (80 mmol) o-xylene

5.97 g (30 mmol) terephthaloyl-chloride

Yield: 5.30 g (52%) white powder

Mp.: 165-170°C

 **$^1\text{H-NMR}$ (400 MHz, CDCl_3), δ [ppm]:**

7.86 (s, 4H, H11), 7.64 (s, 2H, H5), 7.54 (d, 2H, H7), 7.25 (d, 2H, H6), 2.36 (s, 6H, H3), 2.34 (s, 6H, H1)

 $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [ppm]:

196.0 (C9), 144.7 (C4), 142.6 (C2), 140.9 (C10), 137.0 (C8), 130.8 (C11), 129.5 (C5+7), 128.1 (C6), 20.0 (C3), 19.7 (C1)

Dept 135 (100 MHz, CDCl_3) [ppm]:

130.8 (pos. C11), 129.5 (pos. C5+7), 128.1 (pos. C6), 20.0 (pos. C3), 19.7 (pos. C1)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3283 w, 3027 w, 2980 m, 2939 s, 1654 s, 1608 m, 1449 s, 1403 m, 1301 s, 1111 m, 1024 m, 973 m, 871 m, 830 m, 737 w, 691 w

1,4-Bis(4-methoxy-benzoyl)benzene (3)

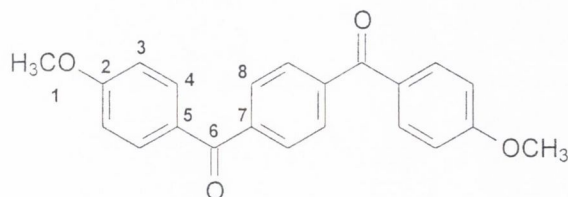
see synthesis 1,4-bis(4-methyl-benzoyl)benzene (1)

Amount: 8.46 g (80 mmol) anisole

5.97 g (30 mmol) terephthaloyl-chloride

Yield: 5.54 g (54%) white powder

Mp.: 225-227°C

 **$^1\text{H-NMR}$ (400 MHz, CDCl_3) [ppm]:**

7.86 (d, 4H, H4), 7.83 (s, 4H, H8), 6.98 (d, 4H, H3), 3.90 (s, 6H, H1)

 $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [ppm]:

195.3 (C6), 163.6 (C2), 140.7 (C7), 137.2 (C5), 132.6 (C8), 128.3 (C4), 113.7 (C3), 55.3 (C1)

Dept 135 (100 MHz, CDCl_3) [ppm]:

132.6 (pos. C8), 128.3 (pos. C4), 113.7 (pos. C3), 55.3 (pos. C1)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3001 w, 2858 m, 2709 m, 1997 m, 1874 m, 1736 m, 1654 s, 1613 m, 1526 s, 1347 m, 1326 m, 1045 s, 978 m, 942 m, 871 s, 763 s, 712 m

1,4-Bis(3,4-dimethoxy-benzoyl)benzene (4)

see synthesis 1,4-bis(4-methyl-benzoyl)benzene (1)

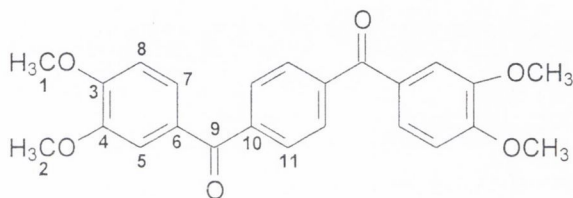
The reaction dried out while warming to RT, 10 mL of CH₂Cl₂ were added.

Amount: 11.04 g (80 mmol) veratrole

5.97 g (30 mmol) terephthaloyl-chloride

Yield: 4.58 g (38%) pale yellow crystals

Mp.: 181-183°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

7.84 (s, 4H, H10), 7.53 (s, 2H, H5), 7.40 (d, 2H, H6), 6.91 (d, 2H, H7), 3.97 (s, 6H, H2), 3.96 (s, 6H, H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

194.8 (C9), 153.5 (C4), 149.3 (C3), 141.1 (C10), 133.4 (C6), 129.3 (C11), 125.7 (C7), 112.1 (C5), 109.9 (C8), 55.68 (C2), 55.65 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

129.3 (C11), 125.7 (C7), 112.1 (C5), 109.9 (C8), 55.68 (C2), 55.65 (C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

129.3 (C11), 125.7 (C7), 112.1 (C5), 109.9 (C8)

IR (microscope set-up) ν[cm⁻¹]:

3083 w, 2945 s, 2893 s, 1833 m, 1685 s, 1644 s, 1593 s, 1511 m, 1460 s, 1413 m, 1275 s, 1132 m, 1024 m, 978 w, 876 w, 814 m, 758 w, 717 m

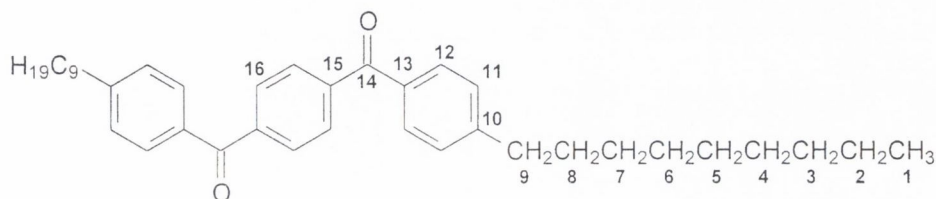
1,4-Bis(4-nonyl-benzoyl)benzene (5)

see synthesis 1,4-bis(4-methyl-benzoyl)benzene (1)

Amount: 16.32 g (80 mmol) phenylnonane
 5.97 g (30 mmol) terephthaloyl-chloride

Yield: 9.45 g (59%) white crystals

Mp.: 97-99°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

7.86 (s, 4H, H16), 7.77 (d, 4H, H12), 7.31 (d, 4H, H11), 2.70 (t, 4H, H9), 1.66 (qui, 4H, H8), 1.33-1.27 (m, 24H, H2-7), 0.88 (t, 6H, H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

195.8 (C14), 148.8 (C10), 140.3 (C15), 134.5 (C13), 130.3 (C16), 129.5 (C12), 128.5 (C11), 36.1 (C9), 31.9 (C3), 31.1 (C8), 29.9 (C6), 29.5 (C5), 29.4 (C4), 29.3 (C7), 22.6 (C2), 14.1 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

130.3 (pos. C16), 129.5 (pos. C12), 128.5 (pos. C11), 36.1 (neg. C9), 31.9 (neg. C3), 31.1 (neg. C8), 29.9 (neg. C6), 29.5 (neg. C5), 29.4 (neg. C4), 22.6 (neg. C2), 14.1 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

130.3 (C16), 129.5 (C12), 128.5 (C11)

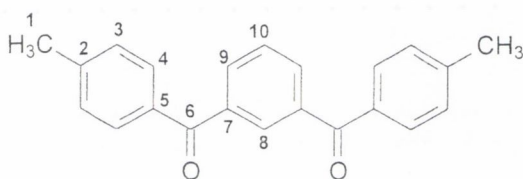
IR (microscope set-up) ν[cm⁻¹]:

3283 w, 3042 m, 2965 s, 2924 s, 2858 m, 1920 m, 1654 s, 1613 m, 1562 m, 1465 s, 1408 s, 1306 s, 1152 m, 1116 m, 932 w, 830 m, 737 s, 688 m

1,3-Bis(4-methyl-benzoyl)benzene (6)

A mixture of 7.36 g toluene (80 mmol), 5.97 g isophthaloyl dichloride (30 mmol) and 10 mL CH_2Cl_2 was cooled down to 0°C and left for stirring at that temperature for 15 min. 9.61 g of powdered aluminium chloride (72 mmol) were added at once. The reaction was very slowly warmed to RT, left stirring for 5 h and then very slowly heated to 40° . After stirring for an additional 10 h, the reaction mixture was cooled down and slowly added to a 100 mL mixture of ice-water and HCl (10:1). The solid was filtered off and dissolved in toluene. The toluene solution was dried over MgSO_4 and filtered. The solvent was evaporated and the product recrystallised in CHCl_3 to give 3.53 g white powder (yield: 38%).

Mp.: $127\text{--}129^\circ\text{C}$

 **^1H -NMR (400 MHz, CDCl_3) [ppm]:**

8.14 (s, 1H, H8), 7.99 (d, 2H, H9), 7.73 (d, 4H, H4), 7.60 (t, 1H, H10), 7.28 (d, 4H, H3), 2.44 (s, 6H, H1)

 ^{13}C -NMR (100 MHz, CDCl_3) [ppm]:

195.3 (C6), 143.7 (C2), 138.1 (C5), 137.8 (C7), 133.1 (C9), 131.0 (C8), 130.0 (C4), 129.1 (C3), 129.1 (C10), 21.7 (C1)

Dept 135 (100 MHz, CDCl_3) [ppm]:

133.1 (pos. C9), 131.0 (pos. C8), 130.0 (pos. C4), 129.1 (pos. C3), 129.1 (pos. C10), 21.7 (pos. C1)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3298 w, 2964 m, 2914 s, 1920 w, 1669 s, 1608 m, 1567 w, 1434 m, 1296 s, 1157 w, 1101 w, 1029 w, 1004 w, 898 w, 840 m, 825 m, 743 m, 699 m

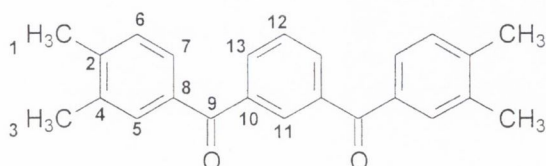
1,3-Bis(3,4-dimethyl-benzoyl)benzene (7)

see synthesis 1,3-Bis(4-methyl-benzoyl)benzene (6)

Amount: 8.48 g (80 mmol) o-xylene
 5.97 g (30 mmol) isophthaloyl dichloride

Yield: 7.95 g (78%) white powder

Mp.: 129-131°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

8.13 (s, 1H, H11), 7.99 (d, 2H, H13), 7.62 (s, 2H, H5), 7.60 (t, 1H, H12), 7.54 (d, 2H, H7), 7.23 (d, 2H, H6), 2.37 (s, 12H, H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

195.8 (C9), 143.5 (C4), 142.5 (C2), 138.2 (C8), 137.0 (C10), 133.1 (C13), 131.2 (C11), 129.6 (C5+7), 128.1 (C6+12), 19.7 (C1), 20.0 (C3)

Dept 135 (100 MHz, CDCl₃) [ppm]:

133.1 (pos. C13), 131.2 (pos. C11), 128.1 (pos. C6+12), 19.7 (pos. C1), 20.0 (pos. C3)

IR (microscope set-up) ν[cm⁻¹]:

3277 w, 3027 w, 2975 m, 2909 m, 2873 m, 1659 s, 1613 s, 1449 m, 1393 w, 1291 m, 1116 m, 1019 w, 988 m, 906 w, 814 m, 743 m, 702 m

1,3-Bis(4-methoxy-benzoyl)benzene (8)

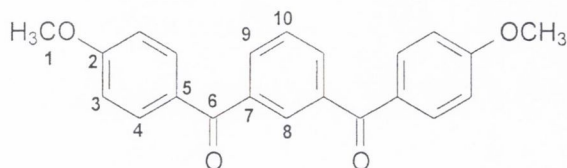
see synthesis 1,3-Bis(4-methyl-benzoyl)benzene (6):

Amount: 8.46 g (80 mmol) anisole

5.97 g (30 mmol) isophthaloyl dichloride

Yield: 6.26 g (61%) white powder

Mp.: 123-124°C

 **$^1\text{H-NMR}$ (400 MHz, CDCl_3) [ppm]:**

8.09 (s, 1H, H8), 7.95 (d, 2H, H9), 7.84 (d, 4H, H4), 7.60 (t, 1H, H10), 6.97 (d, 4H, H3), 3.89 (s, 6H, H1)

 $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [ppm]:

194.7 (C6), 163.6 (C2), 132.8 (C9), 132.6 (C5+7), 130.6 (C8), 129.7 (C4), 128.5 (C10), 113.8 (C3), 55.31 (C1)

Dept 135 (100 MHz, CDCl_3) [ppm]:

132.8 (pos. C9), 130.6 (pos. C8), 129.7 (pos. C4), 128.5 (pos. C10), 113.8 (pos. C3), 55.31 (pos. C1)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

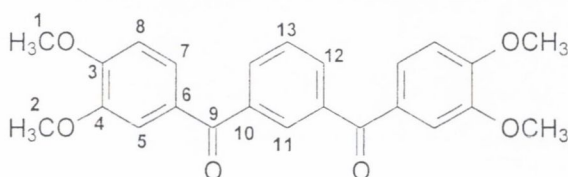
3293 m, 3027 w, 2975 m, 2929 m, 1669 s, 1608 s, 1511 m, 1449 m, 1321 s, 1285 s, 1173 m, 1024 w, 988 w, 840 w, 809 w, 748 w

1,3-Bis(3,4-dimethoxy-benzoyl)benzene (9)

see synthesis 1,3-Bis(4-methyl-benzoyl)benzene (6)

The reaction mixture was poured into H₂O/HCl 10:1. The crude product remained a viscous liquid therefore it was left stirring for 48 h until it solidified.

Amount: 11.04 g (80 mmol) veratrole
 5.97 g (30 mmol) isophthaloyl dichloride
 Yield: 3.01 g (25%) white powder
 Mp.: 173-174°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

8.11(s, 1H, H11), 7.96 (d, 2H, H12), 7.60 (t, 1H, H13), 7.51 (s, 2H, H5), 7.38 (d, 2H, H7), 6.98 (d, 2H, H8), 3.96 (s, 6H, H2), 3.95 (s, 6H, H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

1954.6 (C9), 153.4 (C3), 149.4 (C4), 139.9 (C6), 138.4 (C10), 132.5 (C12), 130.5 (C11), 128.2 (C13), 125.5 (C7), 112.0 (C5), 109.9 (C8), 56.03, 56.00 (C1+3)

Dept 135 (100 MHz, CDCl₃) [ppm]:

132.5 (pos. C12), 130.5 (pos. C11), 128.2 (pos. C13), 125.5 (pos. C7), 112.0 (pos. C5), 109.9 (pos. C8), 56.03, 56.00 (pos. C1+3)

Dept 90 (100 MHz, CDCl₃) [ppm]:

132.5 (C12), 130.5 (C11), 128.2 (C13), 125.5 (C7), 112.0 (C5), 109.9 (C8)

IR (microscope set-up) ν[cm⁻¹]:

2965 w, 2924 w, 2832 w, 1644 s, 1588 m, 1506 m, 1454 w, 1408 w, 1255 s, 1132 s, 1014 m, 871 w, 809 w, 743 w, 717 w

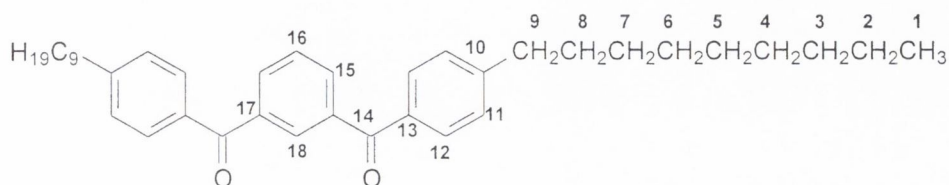
1,3-Bis(4-nonyl-benzoyl)benzene (10)

see synthesis 1,3-Bis(4-methyl-benzoyl)benzene (6)

Amount: 16.32 g (80 mmol) phenylnonane
 5.97 g (30 mmol) terephthaloyl-chloride

Yield: 7.05 g (44%) pale yellow powder

Mp.: 30-33°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

8.16 (s, 1H, H18), 7.99 d, 2H, H15), 7.75 (d, 4H, H12), 7.60 (t, 1H, H16), 7.29 (d, 4H, H11), 2.68 (t, 4H, H9), 1.65 (qui, 4H, H8), 1.32-1.27 (m, 24H, H2-7), 0.88 (t, 6H, H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

195.5 (C14), 148.7 (C10), 139.8 (C13), 138.1 (C17), 133.0 (C15), 130.9 (C18), 130.3 (C12), 128.4 (C11), 128.3 (C16), 36.0 (C9), 31.8 (C3), 31.1 (C8), 29.9 (C6), 29.5 (C5), 29.4 (C4), 29.3 (C7), 22.6 (C2), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

133.0 (pos. C15), 130.9 (pos. C18), 130.3 (pos. C12), 128.4 (pos. C11), 128.3 (pos. C16), 36.0 (neg. C9), 31.8 (neg. C3), 31.1 (neg. C8), 29.9 (neg. C6), 29.5 (neg. C5), 29.4 (neg. C4), 29.3 (neg. C7), 22.6 (neg. C2), 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

133.0 (C15), 130.9 (C18), 130.3 (C12), 128.4 (C11), 128.3 (C16)

IR (microscope set-up) ν[cm⁻¹]:

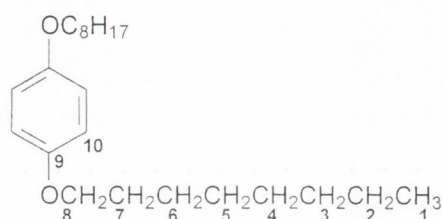
3288 w, 3032 m, 2955 s, 2924 s, 2847 s, 1654 s, 1603 m, 1470 w, 1408 w, 1311 m, 1157 w, 1127 w, 917 w, 840 w, 722 w

5.2.2. Synthesis of 2,5-Di-*n*-octyloxy-1,4-xylene-diethylphosphonate-ester

1,4-Di-*n*-octyloxybenzene (11)

To 100 ml dry DMSO was added 45.01 g (0.80 mol) powdered KOH. After stirring for 10 min, 22.12 g (0.20 mol) of *p*-hydroquinone were added, followed immediately by 77.26 g (0.40 mol) of octylbromide. After stirring for 30 min the mixture was poured into 600 ml of water and left for at least one hour. The waxy product was collected and re-crystallised in *n*-heptane. After filtration and drying 49.87 g (74.7%) white flakes of *p*-di-*n*-octyloxybenzene were obtained.

Mp.: 56-57°C



¹H-NMR (400 MHz, CDCl₃) [ppm]:

6.84 (s, 4H, H₁₀), 3.93 (t, 4H, H₈), 1.77 (qui, 4H, H₇), 1.32 - 1.49 (m, 20H, H₂₋₆), 0.92 (t, 6H, H₁)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

153.3 (C₉), 115.3 (C₁₀), 68.5 (C₈), 31.8 (C₃), 29.6 (C₄), 29.3 (C₅), 29.2 (C₇), 26.0 (C₆), 22.6 (C₂), 14.0 (C₁)

Dept 135 (100 MHz, CDCl₃) [ppm]:

115.3 (pos. C₁₀), 68.5 (neg. C₈), 31.8 (neg. C₃), 29.6 (neg. C₄), 29.3 (neg. C₅), 29.2 (neg. C₇), 26.0 (neg. C₆), 22.6 (neg. C₂), 14.0 (pos. C₁)

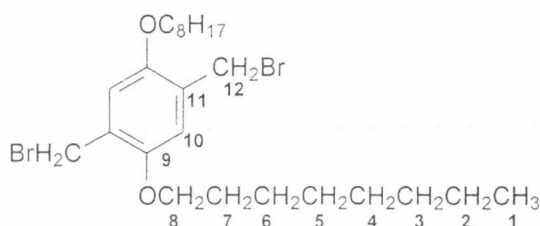
IR (microscope set-up) ν[cm⁻¹]:

2955 s, 2934 s, 2863 s, 1859 m, 1639 m, 1511 m, 1470 m, 1398 w, 1285 m, 1250 m, 1034 s, 825 m, 773 m, 717 m

2,5-Di-n-octyloxy-1,4-bis(bromomethyl)-benzene (12)

A mixture of 24.41 g (73 mmol) 1,4-di-n-octyloxybenzene, 31.52 g (1.05 mol) paraformaldehyde and 46.40 g (0.39 mol) KBr was heated in 400 mL acetic acid to 80°C. A mixture of 50 mL acetic acid and 40 mL sulphuric acid was added drop-wise over 0.5 h. After stirring for additional 5 h at 80°C the mixture was left standing overnight. The crystals were filtered off, washed with water until the acetic acid smell disappeared and re-crystallised from n-heptane to give 27.43 g (76%) pale yellow fluffy needles.

Mp.: 87-88°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

6.88 (s, 2H, H₁₀), 4.55 (s, 4H, H₁₂), 4.01 (t, 4H, H₈), 1.80-1.87 (qui, 4H, H₇), 1.33-1.56 (m, 20H, H₂₋₆), 0.92 (t, 6H, H₁)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

150.7 (C₉), 127.5 (C₁₁), 114.7 (C₁₀), 69.0 (C₈), 31.8 (C₃), 29.5 (C₄), 29.2 (C₅), 28.7 (C₇), 26.7 (C₁₂), 26.0 (C₆), 22.6 (C₂), 14.0 (C₁)

Dept 135 (100 MHz, CDCl₃) [ppm]:

114.7 (pos. C₁₀), 69.0 (neg. C₈), 31.8 (neg. C₃), 29.5 (neg. C₄), 29.2 (neg. C₅), 28.7 (neg. C₇), 26.7 (neg. C₁₂), 26.0 (neg. C₆), 22.6 (neg. C₂), 14.0 (pos. C₁)

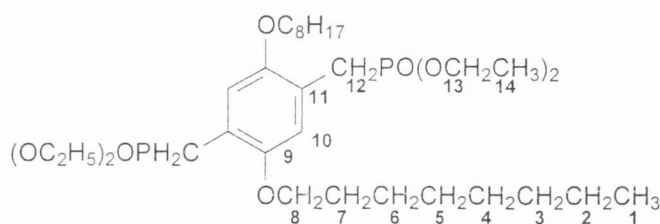
IR (microscope set-up) ν[cm⁻¹]:

3027 w, 2914 s, 2863 m, 1511 w, 1465 w, 1413 w, 1398 w, 1311 w, 1203 m, 1029 w, 702 w

2,5-Di-n-octyloxy-1,4-xylene-diethylphosphonate-ester (13)

19.11 g (110 mmol) triethylphosphite and 27.44 g (55mmol) 2,5-di-n-octyloxy-1,4-bis(bromomethyl)-benzene were heated to 150°C for 4 h while the by-product ethylbromide is continuously removed by distillation. After filtration through cotton wool and re-crystallisation from petroleum ether, 24.3 g (yield: 82.1%) of pale yellow crystals were obtained.

Mp.: 51-52°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

6.85 (s, 2H, H10), 4.04 (t, 4H, H8), 3.92 (t, 4H, H12), 1.77 (qui, 4H, H7), 1.47-1.1.22 (m, 30H, H2-6+13), 1.24 (t, 12H, H14), 0.81 (t, 6H, H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

150.0 (C9), 127.5 (C11), 114.5 (C10), 69.0 (C8), 61.6 (C13), 34.1 (C12), 32.6 (C3), 29.5 (C4), 29.2 (C5), 28.7 (C7), 26.0 (C6), 22.6 (C2), 15.9 (C14), 14.4 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

114.5 (pos. C10), 69.0 (neg. C8), 61.6 (neg. C13), 34.1 (neg. C12), 32.6 (neg. C3), 29.5 (neg. C4), 29.2 (neg. C5), 28.7 (neg. C7), 26.0 (neg. C6), 22.6 (neg. C2), 15.9 (pos. C14), 14.4 (pos. C1)

³¹P-NMR (162 MHz, CDCl₃) [ppm]:

27.12

IR (microscope set-up) ν[cm⁻¹]:

2996 s, 2868 s, 1731 w, 1499 m, 1480 s, 1419 s, 1393 m, 1280 s, 1229 s, 1065 s, 968 s, 809 m, 768 m, 722 m

5.2.3. Poly(1,4-phenylenevinylene-2,5-di-n-octyloxy-1,4-Phenylene

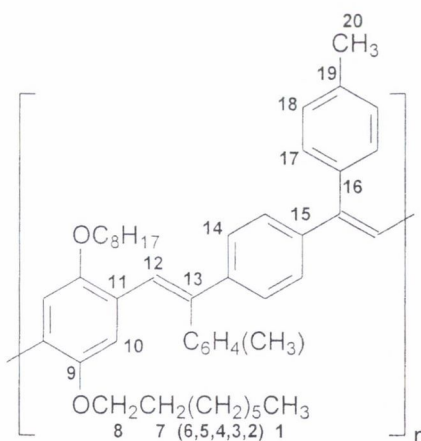
Vinylene) derivatives

methyl-PpPV (14)

A solution of 1.26 g 2,5-di-n-octyloxy-1,4-xylylene-diethylphosphonate-ester (2 mmol), 0.63 g 1,4-bis(3,4-dimethyl-benzoyl)benzene (2 mmol) and 25 mL DMF was heated to 80°C. 0.7 g potassium *tert*-butoxide (KO*t*Bu) (5.5 mmol) was added at once. The reaction mixture was left stirring at 80°C for additional 4h and then poured into 150 mL water. The suspension thus formed was extracted three times with 30 mL of toluene. The organic layer was washed with water and dried over MgSO₄. The solvent was then reduced by rotary evaporation and the product precipitated with methanol. Finally the product was soxhleted (methanol) overnight.

Yield: 0.70 g (52.0%)

Melting range: 132-177°C



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.72-7.12 (H₁₂+H₁₄+H₁₇+H₁₈), 6.25 (H₁₀), 4.01 (H₈), 2.34 (H₂₀), 1.84 (H₇), 1.51, 1.27 (H₂-H₆), 0.86 (H₁)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

150.6 (C₉), 142.4 (C₁₉), 140.9, 138.1, 136.7 (C₁₆+H₁₅+H₁₃), 130.3, 129.4, 127.6 (C₁₄+H₁₇+H₁₈), 126.0 (C₁₁), 121.8 (C₁₂), 113.8 (C₁₀), 68.5 (C₈), 31.8 (C₃), 29.3 (C₅+H₇), 26.3 (C₄), 26.1 (C₆), 22.6 (C₂), 21.2 (C₂₀), 14.1 (C₁)

Dept 135 (100 MHz, CDCl₃) [ppm]:

130.3, 129.4, 127.6 (pos. C14+17+18), 121.8 (pos. C12), 113.8 (pos. C10), 68.5 (neg. C8), 31.8 (neg. C3), 29.3 (neg. C5+7), 26.3 (neg. C4), 26.1 (neg. C6), 22.6 (neg. C2), 21.2 (pos. C20), 14.1 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

130.3, 129.4, 127.6 (C14+17+18), 121.8 (C12), 113.8 (C10)

IR (microscope set-up) ν [cm⁻¹]:

3021 s, 2955 s, 2858 s, 1900 m, 1798 m, 1603 m, 1509 m, 1478 s, 1424 s, 1210 s, 1052 s, 927 m, 840 s, 814 s, 763 m, 727 m, 686 m

Raman (10⁻⁴ CHCl₃ solution in a 10mm cell) ν [cm⁻¹]:

605 w, 721 w, 824 w, 895 w, 1092 w, 1132 w, 1177 w, 1230 m, 1289 m, 1400 w, 1575 s, 2896 w

UV/VIS, λ [nm]: 418, 353, 259 (in 10⁻⁴ mol CHCl₃ solution)

PL: 522 nm (10⁻⁴ mol CHCl₃ solution, excitation at 415 nm)

GPC: 1,2,4-Trichlorobenzene, $M_n = 5436$, $M_w = 46730$, $M_w/M_n = 8.60$

DSC: $T_m = 27, 66, 160^\circ\text{C}$, $T_g = 3.7^\circ\text{C}$

TGA: $T_d = 370\text{-}450^\circ\text{C}$

Elemental Analysis:

		Theory [%]	Found [%]
C ₄₈ H ₆₂ O ₂ (671.02 g/mol)	C	85.92	82.85
	H	9.31	8.47

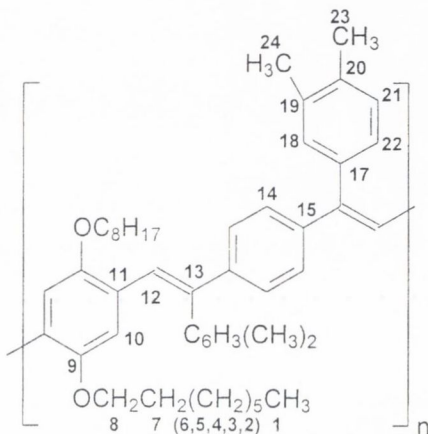
dimethyl-PpPV (15)

see synthesis methyl-PpPV (14)

Amount: 0.69 g (2 mmol) 1,4-bis(3,4-dimethyl-benzoyl)benzene
 1.26 g (2 mmol) 2,5-di-n-octyloxy-1,4-xylene-diethylphosphonate-
 ester

Yield: 0.51g (36.1%)

Melting range: 130-165°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

7.73-6.95 (H12+14+21+18+22), 6.25 (H10), 3.99 (H8), 2.24 (H23+24), 1.84 (H7),
 1.51-1.27 (H2-6), 0.87 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

150.5 (C9), 141.5, 141.1 (C19+20), 141.0, 138.5, 136.7 (C13+15+17), 131.3,
 130.4, 129.9 (C18+21+22), 127.0 (C14) 126.0 (C11), 121.8 (C12), 113.5 (C10),
 68.5 (C8), 31.8 (C3), 29.4, 29.3 (C5+7), 26.3 (C4), 26.1 (C6), 22.6 (C2), 19.6, 19.4
 (C23+24), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

131.3, 130.4, 129.9 (pos. C18+21+22), 127.0 (pos. C14), 121.8 (pos. C12), 113.5
 (pos. C10), 68.5 (neg. C8), 31.8 (neg. C3), 29.4, 29.3 (neg. C5+7), 26.3 (neg. C4),
 26.1 (neg. C6), 22.6 (neg. C2), 19.6, 19.4 (pos. C23+24), 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

131.3, 130.4, 129.9 (C18+21+22), 127.0 (C14), 121.8 (C12), 113.5 (C10)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3016 w, 2924 s, 2847 s, 1654 w, 1598 w, 1501 m, 1470 m, 1413 m, 1198 s, 1040 s, 891 w, 814 w, 712 w

Raman (10^{-4} CHCl_3 solution in a 10mm cell) $\nu[\text{cm}^{-1}]$:

609 w, 721 w, 885 m, 946 w, 1091 m, 1172 m, 1206 w, 1286 m, 1406 w, 1483 w, 1572 s, 2889 w

UV/VIS, λ [nm]: 418, 353, 259 (in 10^{-4} mol CHCl_3 solution)

PL: 525 nm (10^{-4} CHCl_3 solution, excitation at 415 nm)

GPC: 1,2,4-Trichlorobenzene, $M_n = 5025$, $M_w = 31025$, $M_w/M_n = 6.14$

DSC: $T_m = 22, 70, 260^\circ\text{C}$

TGA: $T_d = 355\text{--}450^\circ\text{C}$

Elemental Analysis:

		Theory [%]	Found [%]
$\text{C}_{50}\text{H}_{66}\text{O}_2$ (699.07 g/mol)	C	85.91	82.85
	H	9.52	8.82

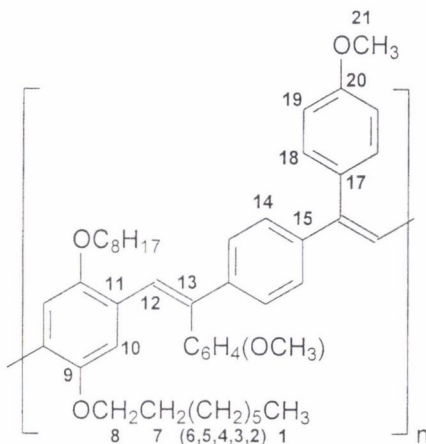
methoxy-PpPV (16)

see synthesis methyl-PpPV (14)

Amount: 0.69 g (2 mmol) 1,4-bis(4-methoxy-benzoyl)benzene
1.26 g (2 mmol) 2,5-di-n-octyloxy-1,4-xylene-diethylphosphonate-ester

Yield: 0.84 g (59.4%)

Melting range: $98\text{--}140^\circ\text{C}$



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.74-6.75 (H12+14+18+19), 6.33 (H10), 3.98 (H8), 3.88 (H20), 1.81 (H7),
1.55, 1.26 (H2-6), 0.86 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

150.6 (C9), 148.6 (C20), 141.0, 136.7 (C13+15), 133.4 (C17), 130.4 (C18), 127.2
(C14), 126.0 (C11), 122.8 (C12), 113.8 (C10), 111.0 (C19), 68.7 (C8), 55.9 (C21),
31.8 (C3), 29.3 (C5+7), 26.3 (C4), 26.0 (C6), 22.6 (C2), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

130.4 (pos. C18), 127.2 (pos. C14), 122.8 (pos. C12), 113.8 (pos. C10), 111.0 (pos.
C19), 68.7 (neg. C8), 55.9 (pos. C21), 31.8 (neg. C3), 29.3 (neg. C5+7), 26.3 (neg.
C4), 26.0 (neg. C6), 22.6 (neg. C2), 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

130.4 (18), 127.2 (C14), 122.8 (C12), 113.8 (C10), 111.0 (C19)

IR (microscope set-up) ν [cm⁻¹]:

3021 w, 2929 s, 2852 s, 1593 m, 1506 s, 1486 s, 1410 s, 1206 s, 1132 m, 1029 s,
850 s, 804 m, 758 m, 717 m

Raman (10⁻⁴ CHCl₃ solution in a 10mm cell) ν [cm⁻¹]:

598 w, 670 w, 885 m, 959 w, 1093 m, 1176 w, 1219 w, 1283 m, 1402 w, 1495 w,
1569 s, 2894 w, 3146 w

UV/VIS, λ [nm]: 425, 300 (in 10⁻⁴ mol CHCl₃ solution)

PL: 525 nm (10⁻⁴ CHCl₃ solution, excitation at 425 nm)

GPC: 1,2,4-Trichlorobenzene, M_n = 4532, M_w = 8259, M_w/M_n = 1.82

DSC: T_m = 21, 61, 260 °C

TGA: T_d = 380-440 °C

Elemental Analysis:

		Theory [%]	Found [%]
C₄₈H₆₂O₄ (703.02 g/mol)	C	82.01	75.83
	H	8.89	7.96

Cyclic Voltammetry (Ag/AgCl): $E_{1/2red1}$ = -1.6 V, $E_{1/2ox1}$ = 0.9 V, $E_{1/2ox2}$ = 1.2 V,
 E_{pc3} = 1.5 V

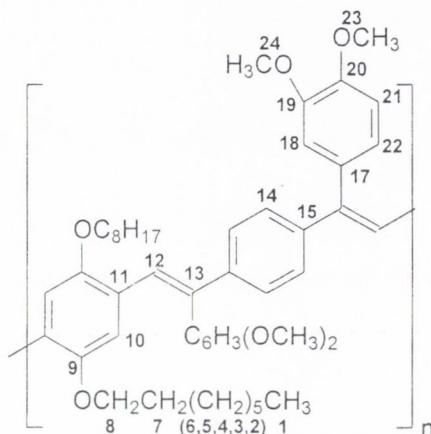
dimethoxy-PpPV (17)

see synthesis methyl-PpPV (14)

Amount: 0.69 g (2 mmol) 1,4-bis(3,4-dimethyl-benzoyl)benzene
 1.26 g (2 mmol) 2,5-di-n-octyloxy-1,4-xylylene-diethylphosphonate-
 ester

Yield: 0.97 g (63.2%)

Melting range: 105-123°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

7.75-6.75 (H12+14+18+21+22), 6.33 (H10), 3.98 (H8), 3.88, 3.83 (H23+24), 1.81 (H7), 1.55, 1.26 (H2-6), 0.86 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

150.2 (C9), 148.2, 148.0 (C19+20), 141.1, 136.7 (C13+15), 133.4 (C17), 130.1 (C22), 127.0 (C14), 126.0 (C11), 122.8 (C12), 113.4 (C10), 111.5, 110.7 (C18+21), 68.7 (C8), 56.0, 55.9 (C23+24), 31.8 (C3), 29.3 (C5+7), 26.3 (C4), 26.0 (C6), 22.6 (C2), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

130.1 (pos. C22), 127.0 (pos. C14), 122.8 (pos. C12), 113.4 pos. (C10), 111.5, 110.7 (pos. C18+21), 68.7 (pos. C8), 56.0, 55.9 (pos. C23+24), 31.8 (neg. C3), 29.3 (neg. C5+7), 26.3 (neg. C4), 26.0 (neg. C6), 22.6 (neg. C2), 14.0 (pos. C1)

IR (microscope set-up) ν[cm⁻¹]:

3019 w, 2924 s, 2852 s, 1644 w, 1598 m, 1577 m, 1511 m, 1470 m, 1413 m, 1265 m, 1198 s, 1132 m, 1024 s, 896 m, 850 m, 804 m, 763 m, 722 w

Raman (10^{-4} CHCl_3 solution in a 10mm cell) $\nu[\text{cm}^{-1}]$:

599 w, 666 w, 885 m, 955 w, 1093 m, 1176 w, 1219 w, 1283 m, 1398 w, 1495 w, 1572 s, 2892 w, 3159 w

UV/VIS, λ [nm]: 425, 300 (in 10^{-4} mol CHCl_3 solution)

PL: 520 nm (10^{-4} CHCl_3 solution, excitation at 425 nm)

GPC: 1,2,4-Trichlorobenzene, $M_n = 5499$, $M_w = 9217$, $M_w/M_n = 1.68$

DSC: $T_m = 32$, 66°C

TGA: $T_d = 380$ - 440°C

Elemental Analysis:

		Theory [%]	Found [%]
$\text{C}_{50}\text{H}_{66}\text{O}_6$ (763.07 g/mol)	C	78.70	75.82
	H	8.72	8.01

nonyl-PpPV (18)

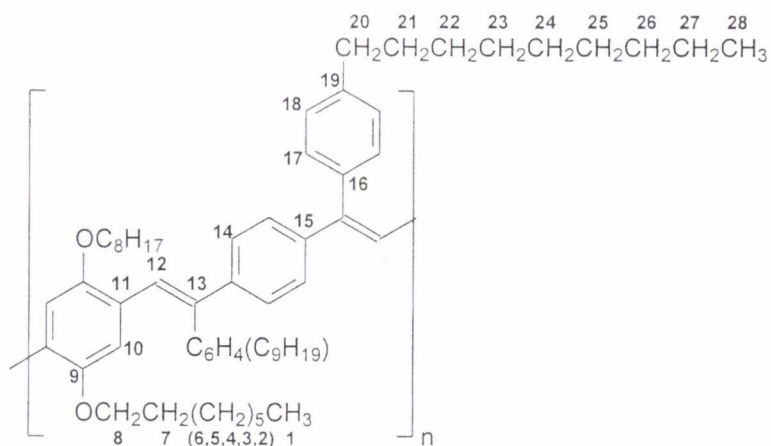
see synthesis methyl-PpPV (14)

Amount: 0.89 g (2 mmol) 1,4-bis(4-nonyl-benzoyl)benzene

1.26 g (2 mmol) 2,5-di-n-octyloxy-1,4-xylene-diethylphosphonate-
ester

Yield: 0.72 g (39.9%)

Melting range: 91 - 143°C



$^1\text{H-NMR}$ (400 MHz, CDCl_3) [ppm]:

7.76-7.12 (H12+14+17+18), 6.25 (H10), 4.01 (H8), 2.59 (H20), 1.84 (H7), 1.77-1.20 (H2-6, H21-27), 0.87 (H1+28)

^{13}C -NMR (100 MHz, CDCl_3) [ppm]:

150.6 (C9), 142.2 (C19), 140.9, 138.2, 136.3 (C13+16+15), 130.1, 128.9 (17+18), 127.5 (C14), 126.0 (C11), 122.4 (C12), 113.8 (C10), 68.4 (C8), 35.9 (C22), 31.8, 31.3, 31.0, 29.5, 29.3 (C3+5+7+23-28), 26.5 (C4), 26.0 (C6), 22.6 (C2+29), 14.0 (C1+30)

Dept 135 (100 MHz, CDCl_3) [ppm]:

130.1, 128.9 (pos. 17+18), 127.5 (pos. C14), 122.4 (pos. C12), 113.8 (pos. C10), 68.4 (neg. C8), 35.9 (C22), 31.8, 31.3, 31.0, 29.5, 29.3 (C3+5+7+23-28), 26.5 (C4), 26.0 (C6), 22.6 (C2+29), 14.0 (C1+30)

Dept 90 (100 MHz, CDCl_3) [ppm]:

130.1, 128.9 (17+18), 127.5 (C14), 122.4 (C12), 113.8 (C10)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3021 w, 2924 s, 2858 s, 1644 w, 1603 m, 1511 m, 1465 m, 1413 m, 1367, 1265 s, 1198 s, 1132 m, 1024 m, 886 m, 845 m, 804 w, 763 w, 717 w

Raman (10^{-4} CHCl_3 solution in a 10mm cell) $\nu[\text{cm}^{-1}]$:

605 w, 650 w, 885 w, 1096 m, 1136 w, 1177 w, 1226 m, 1289 m, 1400 w, 1498 w, 1575 s, 2877 w, 3152 w

UV/VIS, λ [nm]: 409, 338, 265 (in 10^{-4} mol CHCl_3 solution)**PL:** 519 nm (10^{-4} CHCl_3 solution, excitation at 410 nm)**GPC:** 1,2,4-Trichlorobenzene, $M_n = 2099$, $M_w = 5355$, $M_w/M_n = 2.55$ **DSC:** $T_m = 20$, 89°C **TGA:** $T_d = 340$ - 460°C **Elemental Analysis:**

		Theory [%]	Found [%]
$\text{C}_{64}\text{H}_{94}\text{O}_2$ (895.45 g/mol)	C	85.85	80.32
	H	10.58	9.36

Cyclic Voltammetry (Ag/AgCl): $E_{1/2ox1} = 1.0$ V, $E_{1/2ox2} = 1.3$ V, $E_{1/2ox3} = 1.9$ V

5.2.4. Poly(1,3-phenylenevinylene-2,5-di-n-octyloxy-1,4-Phenylene

Vinylene) derivatives

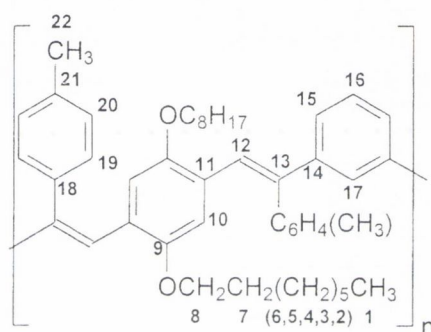
methyl-PmPV (19)

see synthesis methyl-PpPV (14)

Amount: 0.65 g (2 mmol) 1,3-bis(4-methyl-benzoyl)benzene
 1.26 g (2 mmol) 2,5-di-n-octyloxy-1,4-xylene-diethylphosphonate-
 ester

Yield: 0.32 g (47.9%)

Melting range: 95-145°C



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.71-7.08 (H12+15+16+17+19+20), 6.27 (H10), 3.96 (H8), 2.32 (H22), 1.81 (H7),
 1.48-1.24 (H2-6), 0.85 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

150.5 (C9), 143.2 (C21), 140.9, 136.8, 134.3 (C13+14+18), 130.0, 129.0 (19+20),
 128.7, 127.0 (C15+17), 126.0 (C11), 125.4 (C16), 122.0 (C12), 113.8 (C10), 68.5
 (C8), 31.8 (C3), 29.3 (C5+7), 26.5 (C4), 26.0 (C6), 22.6 (C2), 21.1 (C20), 14.0
 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

130.0, 129.0 (pos. 19+20), 128.7, 128.2, 127.0 (pos. C15+17), 125.4 (pos. C16),
 122.0 (pos. C12), 113.8 (pos. C10), 68.5 (neg. C8), 31.8 (neg. C3), 29.3 (neg.
 C5+7), 26.5 (neg. C4), 26.0 (neg. C6), 22.6 (neg. C2), 21.1 (pos. C20), 14.0 (pos.
 C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

130.0, 129.0 (19+20), 128.7, 128.2, 127.0 (C15+17), 125.4 (C16), 122.0 (C12), 113.8 (C10)

IR (microscope set-up) ν [cm⁻¹]:

3175 w, 3021 w, 2934 s, 2868 w, 1726 m, 1654 w, 1547 m, 1511 m, 1378 m, 1193 s, 1034 m, 973 w, 830 m, 753 m, 707 m

Raman (10⁻⁴ CHCl₃ solution in a 10mm cell) ν [cm⁻¹]:

602 w, 883 w, 987 w, 1095 w, 1095 w, 1159 w, 1289 m, 1491 w, 1577 s, 2894 w

UV/VIS, λ [nm]: 392, 343 (in 10⁻⁴ mol CHCl₃ solution)**PL:** 494 nm (10⁻⁴ CHCl₃ solution, excitation at 395 nm)**GPC:** 1,2,4-Trichlorobenzene, M_n = 2980, M_w = 5042, M_w/M_n = 1.69**DSC:** T_m = 38, 55, 255°C**TGA:** T_d = 355-420°C**Elemental Analysis:**

		Theory [%]	Found [%]
C ₄₈ H ₆₂ O ₂ (671.02 g/mol)	C	85.92	77.46
	H	9.31	7.86

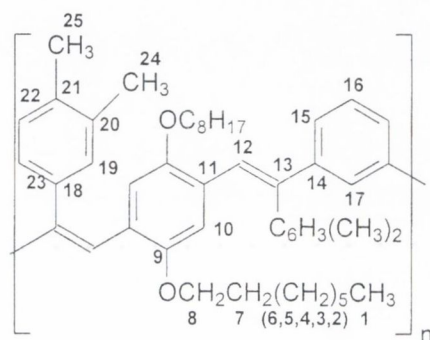
Cyclic Voltammetry (Ag/AgCl): $E_{1/2ox1}$ = 1.0 V, $E_{1/2ox2}$ = 1.5 V

dimethyl-P m PV (20)see synthesis methyl-P p PV (14)

Amount: 0.69 g (2 mmol) 1,3-bis(3,4-dimethyl-benzoyl)benzene
 1.26 g (2 mmol) 2,5-di-*n*-octyloxy-1,4-xylene-diethylphosphonate-
 ester

Yield: 1.03 g (73.4%)

Melting range: 100-139°C

 **$^1\text{H-NMR}$ (400 MHz, CDCl_3) [ppm]:**

7.76-6.85 (H12+15+16+17+19+22+23), 6.28 (H10), 3.98 (H8), 3.79 (H24+25),
 1.77 (H7), 1.49-1.26 (H2-6), 0.86 (H1)

 $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [ppm]:

150.6 (C9), 144.3, 143.7 (C20+21), 141.2, 138.3, 135.1 (C13+14+18), 132.0,
 131.3, 130.0 (C19+22+23), 129.3, 128.4, 127.8 (C15+17), 125.9 (C11), 125.2
 (C16), 122.0 (C12), 113.6 (C10), 68.5 (C8), 31.8 (C3), 29.3 (C5+7), 26.1 (C4),
 26.0 (C6), 22.6 (C2), 19.6, 19.4 (C24+25), 14.0 (C1)

Dept 135 (100 MHz, CDCl_3) [ppm]:

132.0, 131.3, 130.0 (pos. C19+22+23), 128.4, 127.8 (pos. C15+17), 125.2 (pos.
 C16), 122.0 (pos. C12), 113.6 (pos. C10), 68.5 (neg. C8), 31.8 (neg. C3), 29.3 (neg.
 C5+7), 26.1 (neg. C4), 26.0 (neg. C6), 22.6 (neg. C2), 19.6, 19.4 (pos. C24+25),
 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl_3) [ppm]:

132.0, 131.3, 130.0 (C19+22+23), 129.3, 128.4, 127.8 (C15+17), 125.2 (C16),
 122.0 (C12), 113.6 (C10)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3021 m, 2950 s, 2858 s, 1603 m, 1475 s, 1296 s, 1045 s, 983 m, 868 m, 809 m, 727 m, 702 m

Raman (10^{-4} CHCl_3 solution in a 10mm cell) $\nu[\text{cm}^{-1}]$:

609 w, 666 w, 738 w, 840 w, 885 m, 985 w, 1095 m, 1236 m, 1289 m, 1577 s, 2896 w

UV/VIS, λ [nm]: 401, 341 (in 10^{-4} mol CHCl_3 solution)

PL: 500 nm (10^{-4} CHCl_3 solution, excitation at 400 nm)

GPC: 1,2,4-Trichlorobenzene, $M_n = 4293$, $M_w = 10225$, $M_w/M_n = 2.38$

DSC: $T_m = 55$, 260°C

TGA: $T_d = 360$ - 440°C

Elemental Analysis:

		Theory [%]	Found [%]
$\text{C}_{50}\text{H}_{66}\text{O}_2$ (699.07 g/mol)	C	85.91	81.87
	H	9.52	8.53

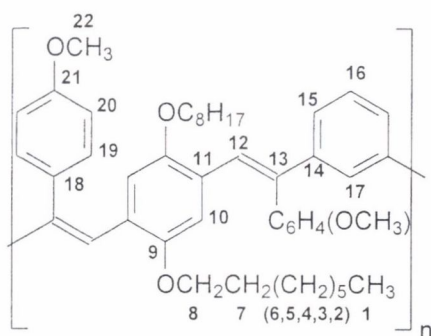
methoxy-PmPV (21)

see synthesis methyl-PpPV (14)

Amount: 0.69 g (2 mmol) 1,3-bis(4-methoxy-benzoyl)benzene
 1.26 g (2 mmol) 2,5-di-n-octyloxy-1,4-xylene-diethylphosphonate-
 ester

Yield: 0.77 g (55.1%)

Melting range: 65 - 77°C

 **^1H -NMR (400 MHz, CDCl_3) [ppm]:**

7.73-6.83 (H12+15+16+17+19+20), 6.31 (H10), 4.02 (H8), 3.79 (H22), 1.82 (H7),
 1.51-1.24 (H2-6), 0.86 (H1)

^{13}C -NMR (100 MHz, CDCl_3) [ppm]:

159.0 (C21), 150.6 (C9), 141.2, 138.3, 135.8, (C13+14+18), 131.6 (C19), 128.8, 127.9 (C15+17), 126.0 (C11), 125.3 (C16), 122.2 (C12), 114.0, 113.5 (C10+20), 68.7 (C8), 55.2 (C22), 31.7 (C3), 29.2 (C5+7), 26.5 (C4), 25.9 (C6), 22.6 (C2), 14.0 (C1)

Dept 135 (100 MHz, CDCl_3) [ppm]:

131.6 (pos. C19), 128.8, 127.9 (pos. C15+17), 125.2 (pos. C16), 122.2 (pos. C12), 114.0, 113.5 (pos. C10+20), 68.7 (neg. C8), 55.2 (pos. C22), 31.7 (neg. C3), 29.2 (neg. C5+7), 26.5 (neg. C4), 25.9 (neg. C6), 22.6 (neg. C2), 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl_3) [ppm]:

131.6 (C19), 128.8, 127.9 (C15+17), 125.2 (C16), 122.2 (C12), 114.0, 113.5 (C10+20)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3021 w, 2924 s, 2852 m, 1608 w, 1511m, 1465 m, 1419 m, 1275 m, 1209 m, 1060 m, 927 w, 840 w, 717 w

Raman (10^{-4} CHCl_3 solution in a 10mm cell) $\nu[\text{cm}^{-1}]$:

599 w, 849 w, 883 w, 985 w, 1096 w, 1159 w, 1227 w, 1289 m, 1410 w, 1577 s, 2894 w

UV/VIS, λ [nm]: 392, 350, 289 (in 10^{-4} mol CHCl_3 solution)

PL: 495 nm (10^{-4} CHCl_3 solution, excitation at 395 nm)

GPC: 1,2,4-Trichlorobenzene, $M_n = 3864$, $M_w = 9980$, $M_w/M_n = 2.58$

DSC: $T_m = 58$, 265°C

TGA: $T_d = 375$ - 430°C

Elemental Analysis:		Theory [%]	Found [%]
C₄₈H₆₂O₄ (703.02 g/mol)	C	82.01	81.87
	H	8.89	8.53

Cyclic Voltammetry (Ag/AgCl): $E_{1/2\text{red}} = -1.8$ V, $E_{1/2\text{ox1}} = 0.9$ V, $E_{\text{pc2}} = 1.3$ V,

$E_{1/2\text{ox3}} = 1.5$ V, $E_{1/2\text{ox4}} = 1.8$ V

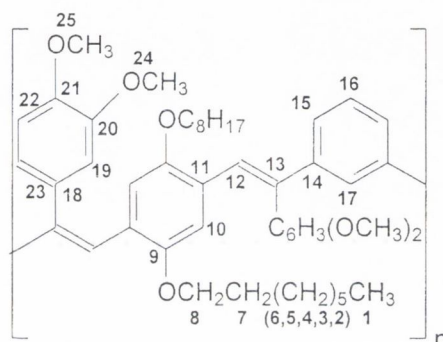
dimethoxy-PmPV (22)

see synthesis methyl-PpPV (14)

Amount: 0.69 g (2 mmol) 1,3-bis(3,4-dimethoxy-benzoyl)benzene
 1.26 g (2 mmol) 2,5-di-n-octyloxy-1,4-xylene-diethylphosphonate-
 ester

Yield: 0.94 g (61.1%)

Melting range: 87-132°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

7.72-6.67 (C12+15+16+17+19+22+23), 6.30 (H10), 4.01 (H8), 3.86, 3.84 (H24+25), 1.70-1.26 (H2-7), 0.85 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

150.5 (C9), 149.2, 148.7 (C20+21), 141.2, 136.4, 133.3 (C13+14+18), 129.4, 128.4, 127.7 (C15+17+23), 126.0 (C11), 125.4 (C16), 122.7 (C12), 113.8 (C10), 111.4, 110.8 (C22+19), 68.7 (C8), 55.8, 55.75 (C24+25), 31.7 (C3), 29.2 (C5+7), 26.0 (C4), 25.9 (C6), 22.6 (C2), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

129.4, 128.4, 127.7 (pos. C15+17+23), 125.4 (C16), 122.7 (C12), 113.8 (pos. C10), 111.4, 110.8 (pos. C22+19), 68.7 (neg. C8), 55.8, 55.75 (pos. C24+25), 31.7 (neg. C3), 29.2 (neg. C5+7), 26.0 (neg. C4), 25.9 (neg. C6), 22.6 (neg. C2), 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

129.4, 128.4, 127.7 (C15+17+23), 126.0 (C11), 125.4 (C16), 122.7 (C12), 113.8 (C10), 111.4, 110.8 (C22+19)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3021 w, 2934 s, 2863 s, 1588 s, 1526 s, 1413 s, 1270 s, 1157 s, 1050 s, 891 m, 806 m, 753 m

Raman (10^{-4} CHCl_3 solution in a 10mm cell) $\nu[\text{cm}^{-1}]$:

606 w, 671 w, 759 w, 879 m, 985 w, 1096 m, 1289 m, 1577 s, 2894 w

UV/VIS, λ [nm]: 400, 340 (in 10^{-4} mol CHCl_3 solution)

PL: 497 nm (10^{-4} CHCl_3 solution, excitation at 400 nm)

GPC: 1,2,4-Trichlorobenzene, $M_n = 3220$, $M_w = 6516$, $M_w/M_n = 2.02$

DSC: $T_m = 65^\circ\text{C}$

TGA: $T_d = 380\text{-}450^\circ\text{C}$

Elemental Analysis:

		Theory [%]	Found [%]
$\text{C}_{50}\text{H}_{66}\text{O}_6$ (763.07 g/mol)	C	78.70	76.93
	H	8.72	7.99

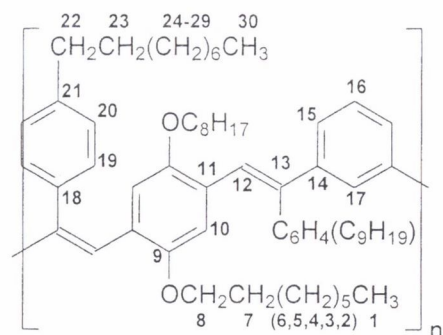
nonyl-PmPV (23)

see synthesis methyl-PpPV (14)

Amount: 0.89g (2 mmol) 1,3-bis(4-nonyl-benzoyl)benzene
1.26 g (2 mmol) 2,5-di-n-octyloxy-1,4-xylene-diethylphosphonate-ester

Yield: 1.45 g (81%)

Mp.: 83-128°C

 **$^1\text{H-NMR}$ (400 MHz, CDCl_3) [ppm]:**

7.75-7.09 (H12+15+16+17+19+20), 6.29 (H10), 3.98 (H8), 2.58 (H22), 1.60-1.24 (H2-6+24-29), 0.89 (H1+30)

^{13}C -NMR (100 MHz, CDCl_3) [ppm]:

150.6 (C9), 142.0 (C20), 140.8, 137.9, 135.0 (C13+14+18), 130.4, 129.4 (C19+20), 128.5, 127.4 (C15+17), 126.0 (C11), 125.3 (C16), 122.3 (C12), 113.6 (C10), 68.4 (C8), 35.9 (C22), 31.9, 31.4, 29.6, 29.5, 29.4 (C3+5+7+23-28), 26.5 (C4), 26.0 (C6), 22.6 (C2+29), 14.0 (C1+30)

Dept 135 (100 MHz, CDCl_3) [ppm]:

130.4, 129.4 (pos. C19+20), 128.5, 127.4 (pos. C15+17), 125.3 (pos. C16), 122.3 (pos. C12), 113.6 (pos. C10), 68.4 (neg. C8), 35.9 (neg. C22), 31.9, 31.4, 29.6, 29.5, 29.4 (neg. C3+5+7+23-28), 26.5 (neg. C4), 26.0 (neg. C6), 22.6 (neg. C2+29), 14.0 (pos. C1+30)

Dept 90 (100 MHz, CDCl_3) [ppm]:

130.4, 129.4 (C19+20), 128.5, 127.4 (C15+17), 125.3 (C16), 122.3 (C12), 113.6 (C10)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3016 w, 2924 s, 2852 s, 1654, 1608 m, 1511 m, 1465, 1419 m, 1275 m, 1209 m, 1060 m, 958 w, 840 w, 768 w, 717 w

Raman (10^{-4} CHCl_3 solution in a 10mm cell) $\nu[\text{cm}^{-1}]$:

609 w, 670 w, 879 m, 985 w, 1102 w, 1232 w, 1289 m, 1577 s, 2896 m

UV/VIS, λ [nm]: 400, 339 (in 10^{-4} mol CHCl_3 solution)

PL: 493 nm (10^{-4} CHCl_3 solution, excitation at 400 nm)

GPC: 1,2,4-Trichlorobenzene, $M_n = 4557$, $M_w = 8653$, $M_w/M_n = 1.90$

DSC: $T_m = 42$, 165°C

TGA: $T_d = 375$ - 460°C

Elemental Analysis:

		Theory [%]	Found [%]
$\text{C}_{64}\text{H}_{94}\text{O}_2$ (895.45 g/mol)	C	85.85	84.52
	H	10.58	10.08

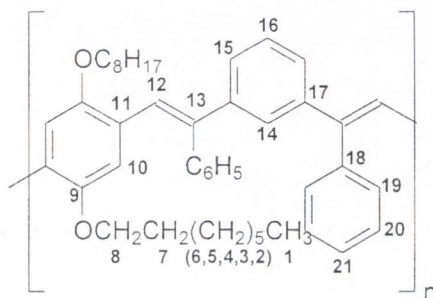
H-PmPV (24)

see synthesis methyl-PpPV (14)

Amount: 0.57 g (2 mmol) 1,3-dibenzoylbenzene
 1.26 g (2 mmol) 2,5-di-n-octyloxy-1,4-xylene-diethylphosphonate-
 ester

Yield: 0.72 g (39.9%)

Melting range: 91-143°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

7.79-7.24 (H12+14-16+19-21), 6.26 (H10), 3.92 (H8), 1.75-1.26 (H2-7), 0.85 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

150.6 (C9), 141.9, 140.9, 137.7 (C13+17+18), 130.4, 129.9, 128.6, 127.4 (C14+15+19+20+21), 126.0 (C11), 125.5 (C16), 122.4 (C12), 113.7 (C10), 68.8 (C8), 31.8 (C3), 29.2, 29.0 (C5+7), 25.9 (C4+6), 22.6 (C2), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

130.4, 129.9, 128.6, 127.4 (pos. C14+15+19+20+21), 125.5 (C16), 122.4 (pos. C12), 113.7 (pos. C10), 68.8 (neg. C8), 31.8 (neg. C3), 29.2, 29.0 (neg. C5+7), 25.9 (neg. C4+6), 22.6 (neg. C2), 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

130.4, 129.9, 128.6, 127.4 (C14+15+19+20+21), 125.5 (C16), 122.4 (C12), 113.7 (C10)

IR (microscope set-up) ν[cm⁻¹]:

3047 w, 3021 w, 2924 s, 2847 s, 1659 w, 1593 w, 1490 m, 1465 m, 1413 m, 1285 w, 1198 m, 1034 m, 896 w, 758 w, 702 m

UV/VIS, λ [nm]: 392, 340, 238 (in 10⁻⁴ mol CHCl₃ solution)

PL: 497 nm (10^{-4} CHCl₃ solution, excitation at 410 nm)

GPC: 1,2,4-Trichlorobenzene, $M_n = 1870$, $M_w = 2402$, $M_w/M_n = 1.28$

DSC: $T_m = 64$, 255°C

TGA: $T_d = 360\text{-}450^\circ\text{C}$

Elemental Analysis:

		Theory [%]	Found [%]
C₄₆H₅₈O₂ (642.97 g/mol)	C	85.93	80.32
	H	9.09	9.36

Cyclic Voltammetry

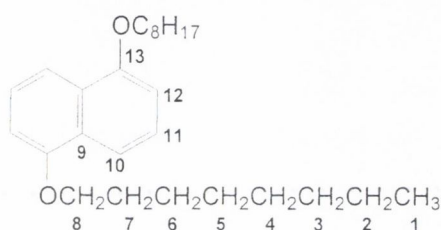
(Ag/AgCl): $E_{1/2ox1} = 1.1$ V, $E_{1/2ox2} = 1.6$ V

5.2.5. Starting material of POPV-ONV

1,5-Di-n-octyloxynaphthalene (25)

A solution of 20 g dihydroxynaphthalene (125 mmol), 58 g K_2CO_3 (420 mmol) and 96.48 g octylbromide (500 mmol) in 500 mL MEK was refluxed for 24 h. The inorganic salts were filtered off and washed with hot toluene. The solution was concentrated under reduced pressure to give a greenish solid. The crude product was re-crystallised with activated charcoal in toluene to give 41.76 g yellow crystals (87%).

Mp: 81-83°C



$^1\text{H-NMR}$ (400 MHz, CDCl_3) [ppm]:

7.84 (d, 2H, H12), 7.33 (t, 2H, H11), 6.82(d, 2H, H10), 4.11 (t, 4H, H8), 1.91 (qui, 4H, H7), 1.55 (qui, 4H, H6), 1.47-1.32 (m, 16H, H5-2), 0.89 (t, 6H, H1)

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [ppm]:

154.7 (C13), 126.9 (C9), 125.0 (C11), 114.1 (C10), 105.3 (C12), 68.2 (C8), 31.8 (C3), 29.4 (C4), 29.3 (C5), 29.27 (C7), 26.3 (C6), 22.7 (C2), 14.1 (C1)

Dept 135 (100 MHz, CDCl_3) [ppm]:

125.0 (pos. C11), 114.1 (pos. C10), 105.3 (pos. C12), 68.2 (neg. C8), 31.8 (neg. C3), 29.4 (neg. C4), 29.3 (neg. C5), 29.27 (neg. C7), 26.3 (neg. C6), 22.7 (neg. C2), 14.1 (pos. C1)

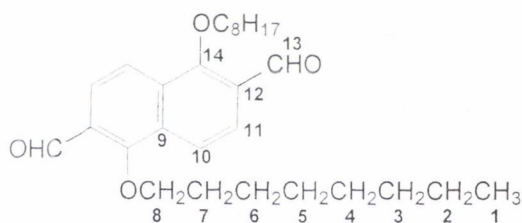
IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3052 m, 3021 m, 2939 s, 2919 s, 2858 s, 1900w, 1818 w, 1710 w, 1588 m, 1506 m, 1454 m, 1419 m, 1383 m, 1270 m, 1209 m, 1168 m, 1045 s, 1009 m, 896 m, 733 m, 727 m

1,5-Bis-n-octyloxy-2,6-naphthalenedialdehyde (26)

A solution of 11.76g 1,5-dioctyloxynaphthalene (30.6 mmol) and 24.0 mL TMEDA (159.9 mmol) in 450 mL diethyl ether was cooled to 0°C. 100 mL of a 1.6 M solution of n-BuLi in hexane (160mmol) were added drop-wise over 30 min. The mixture was stirred at 0°C for 1 h and was then slowly warmed to reflux. After being refluxed for 20 h the resulting pale orange suspension was cooled to 0°C and 20 mL DMF (260 mmol) was added drop-wise. The mixture was stirred at 0°C for 2 h and then 95 mL 4N HCl was added slowly under vigorous stirring. The resulting two-phase system was stirred for an additional 30 min. The organic layer was separated, washed with 150 mL 0.5 N HCL, 150 mL saturated NaHCO₃ solution and 150 mL brine, then dried (MgSO₄) and concentrated under reduced pressure to give a yellowish powder. The crude product was filtered over a short column (silica gel, diethyl ether) and left to crystallise out of the solution as pale yellow balls (3.24 g, 24.1%)

Mp: 61-62°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

10.60(s, 2H, H₁₃), 8.04 (d, 2H, H₁₁), 7.94 (d, 2H, H₁₀), 4.18 (t, 4H, H₈), 1.97 (qui, 4H, H₇), 1.57 (qui, 4H, H₆), 1.43-1.22 (m, 16H, H₂₋₅), 0.90 (t, 6H, H₁)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

189.5 (C₁₃), 163.1 (C₁₄), 133.2 (C₁₂), 127.5 (C₉), 123.6 (C₁₁), 119.5 (C₁₀), 68.0 (C₈), 31.8 (C₃), 29.4 (C₄), 29.4 (C₅), 29.2 (C₇), 26.0 (C₆), 22.6 (C₂), 14.1 (C₁)

Dept 135 (100 MHz, CDCl₃) [ppm]:

123.6 (pos. C₁₁), 119.5 (pos. C₁₀), 68.0 (neg. C₈), 31.8 (neg. C₃), 29.4 (neg. C₄), 29.4 (neg. C₅), 29.2 (neg. C₇), 26.0 (neg. C₆), 22.6 (neg. C₂), 14.1 (pos. C₁)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

2955 m, 2902 s, 2847 m, 1675 s, 1593 m, 1490 m, 1490 m, 1470 m, 1413 m, 1367 m, 1326 m, 1224 m, 1045 m, 1014 m, 932 m, 825 m, 758 m, 707 m

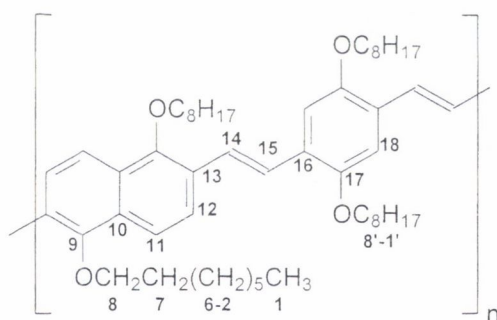
5.2.6. Poly(2,5-bis(n-Octyloxy)-1,4-Phenylene Vinylene-1,5-bis(n-Octyloxy)-2,6-Naphthylene Vinylene (POPV-ONV) (27)

see synthesis methyl-PpPV (14)

Amount: 0.44 g (1 mmol) 1,5-bis(n-octyloxy)-2,6-naphthalenedialdehyde
0.63 g (1 mmol) 1,5-bis(n-octyloxy)2,6-dimethylnaphthalene-bis-(ethylphosphonate)ester

Yield: 0.88 g (79.8%)

Mp.: $>300^{\circ}\text{C}$ (product seems to decompose since it changes the colour to dark brown while heating)

 **$^1\text{H-NMR}$ (400 MHz, CDCl_3) [ppm]:**

7.92, 7.86 (C11+12), 7.65 (C18), 7.26 (H14+15), 4.12 (H8+8'), 1.95 (H7+7'), 1.59, 1.32 (H2-6+2'-6'), 0.90 (H1+1')

 $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [ppm]:

153.2 (C9), 151.2 (C17), 129.5 (C10), 127.6, 127.0 (C13+16), 123.8 (C14+15), 123.1 (C12), 118.7 (C11), 110.3 (C18), 75.1 (C8), 69.6 (C8'), 31.9 (C3+3'), 29.7, 29.6, 29.5, 29.3 (C5+5'+7+7'), 26.4 (C4+4'+6+6'), 22.7 (C2+2'), 14.1 (C1+1')

Dept 135 (100 MHz, CDCl₃) [ppm]:

123.8 (pos. C14+15), 123.1 (pos. C12), 118.7 (pos. C11), 110.3 (pos. C18), 75.1 (neg. C8), 69.6 (neg. C8'), 31.9 (neg. C3+3'), 29.7, 29.6, 29.5, 29.3 (neg. C5+5'+7+7'), 26.4 (neg. C4+4'+6+6'), 22.7 (neg. C2+2'), 14.1 (pos. C1+1')

IR (microscope set-up) ν [cm⁻¹]:

2945 s, 2858 s, 1659 m, 1501 m, 1470 m, 1342 s, 1255 s, 1045 s, 1065 s, 953 s, 814 w, 773 m

Raman (10⁻⁴ CHCl₃ solution in a 10mm cell) ν [cm⁻¹]:

890 w, 1104 w, 1178 w, 1196 w, 1224 w, 1238 w, 1292 m, 1309 m, 1350 m, 1374 m, 1585 s, 2882 w

UV/VIS, λ [nm]: 480, 457, 310, 240 (in 10⁻⁴ mol CHCl₃ solution)

PL: 519 nm (10⁻⁴ CHCl₃ solution, excitation at 460 nm)

GPC: 1,2,4-Trichlorobenzene, M_n = 5660, M_w = 13381, M_w/M_n = 2.35

DSC: T_m = 68°C

TGA: T_{d1} = 350°C (10.6%), T_{d2} = 410°C (28.8%), T_{d3} = 700°C (65.2%), T_{end} = 950°C (85.6%)

Elemental Analysis:		Theory [%]	Found [%]
C₅₄H₈₄O₄ (797.26 g/mol)	C	81.35	77.42
	H	10.62	9.63

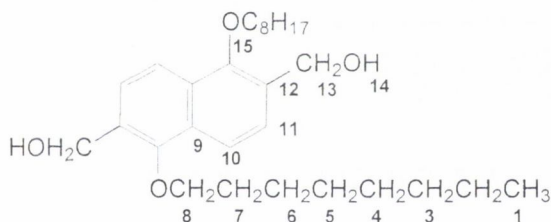
Cyclic Voltammetry (Ag/AgCl): $E_{1/2ox1}$ = 0.9 V, $E_{1/2ox2}$ = 1.6 V

5.2.7. Synthesis of 1,5-Bis-n-octyloxy-2,6-dimethylnaphthalene-bis-ethylphosphonate ester (30)

1,5-Bis-n-octyloxy-2,6-dihydroxymethylnaphthalene (28)

To a solution of 1,5-bis-n-octyloxy-2,6-naphthalenedialdehyde (2 g, 4.9 mmol), 40 mL absolute ethanol and 6 mL THF was added 0.37 g NaBH₄ (9.8 mmol) at RT. After stirring for 4h the reaction mixture was concentrated under reduced pressure. The residue was taken up in 100 mL CH₂Cl₂ and 100 mL 3 N HCl and vigorously stirred until all the solid material was dissolved. The organic layer was separated and the aqueous layer was extracted twice with 50 mL CH₂Cl₂. The combined organic layers were dried (MgSO₄) and concentrated under reduced pressure to give 1.81 g white powder (84%).

Mp: 65-67 °C



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.84 (d, 2H, H11), 7.50 (d, 2H, H10), 4.90 (s, 2H, H14), 4.00 (t, 4H, H8), 2.92 (d, 4H, H13) (J=28.60), 1.92 (qui, 4H, H7), 1.56 (qui, 4H, H6), 1.38-1.32 (m, 16H, H2-5), 0.90 (t, 6H, H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

153.3 (C15), 129.6 (C9), 129.4 (C12), 126.8 (C11), 118.5 (C10), 75.8 (C13), 61.0 (C8), 31.8 (C3), 30.4 (C4), 29.5 (C5), 29.3 (C7), 26.1 (C6), 22.7 (C2), 14.1 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

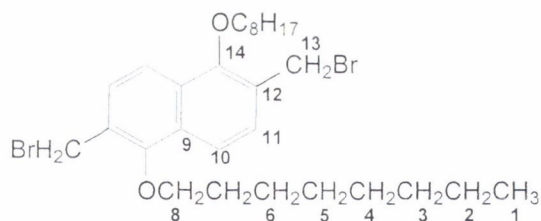
126.8 (pos. C11), 118.5 (pos. C10), 75.8 (neg. C13), 61.0 (neg. C8), 31.8 (neg. C3), 30.4 (neg. C4), 29.5 (neg. C5), 29.3 (neg. C7), 26.1 (neg. C6), 22.7 (neg. C2), 14.1 (pos. C1)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3272 s, 2945 m, 2914 s, 2852 m, 1490 m, 1470 m, 1408 w, 1372 m, 1342 m, 1219 m, 1045 s, 1009 s, 937 m, 799 s, 722 m

1,5-Bis-n-octyloxy-2,6-dibromomethylnaphthalene (29)

1.70 g 1,5-bis-n-octyloxy-2,6-dihydroxymethylnaphthalene (4.1 mmol) was dissolved in 35 mL THF. 0.15 mL pyridine was added and the reaction mixture was cooled to 0°C. 0.5 mL phosphorous tribromide (5.26 mmol) was added within 5 min giving a white precipitate. The reaction mixture was allowed to warm to RT, stirred for 20 h and then concentrated under reduced pressure. The residue was taken up in 30 mL benzene and 50 mL water. The benzene layer was separated and the water layer was extracted twice with 20 mL benzene. The combined organic layers were dried (MgSO_4) and concentrated under reduced pressure to give a brownish oil. The crude product was purified by column chromatography (silica gel, toluene) to give a yellow oil (2.08 g, 89.0%).

 **$^1\text{H-NMR}$ (400 MHz, CDCl_3) [ppm]:**

7.75 (d, 2H, H11), 7.23 (d, 2H, H10), 4.70 (s, 2H, H13), 4.00 (t, 4H, H8), 1.92 (qui, 4H, H7), 1.73 (qui, 4H, H6), 1.33-1.29 (m, 16H, H2-5), 0.90 (t, 6H, H1)

 $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [ppm]:

153.1 (C14), 126.8 (C11), 121.1 (C12), 120.3 (C9), 113.3 (C10), 60.9 (C8), 31.9 (C3), 30.6 (C4), 29.5 (C5), 29.3 (C7), 28.0 (C13), 26.2 (C6), 22.4 (C2), 14.1 (C1)

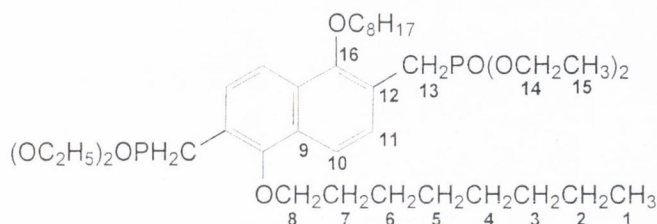
Dept 135 (100 MHz, CDCl_3) [ppm]:

126.8 (pos. C11), 113.3 (pos. C10), 60.9 (neg. C8), 31.9 (neg. C3), 30.6 (neg. C4), 29.5 (neg. C5), 29.3 (neg. C7), 28.0 (neg. C13), 26.2 (neg. C6), 22.4 (neg. C2), 14.1 (pos. C1)

1,5-Bis-n-octyloxy-2,6-dimethylnaphthalene-bis-ethylphosphonate ester (30)

A mixture of 1,5-bis-n-octyloxy-2,6-dibromomethylnaphthalene (1.90 g, 3.3 mmol) and triethylphosphite (1.26 g, 6.6 mmol) was heated for 4h at 150°C while the by-product ethyl bromide was continuously removed by distillation. After leaving the viscous liquid overnight yellow low melting crystals (2.03 g, 89.7%) formed in the flask.

Mp.: 25-26°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

7.78 (d, 2H, H11), 7.75 (d, 2H, H10), 4.05 (qui, 8H, H12), 4.03 (t, 4H, H8), 3.38 (d, 4H, 13) (J = 21.56), 1.93 (qui, 4H, H7), 1.57 (qui, 4H, H6), 1.41-1.24 (m, 16H, H2-5), 0.90 (t, 6H, H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

153.6 (C16), 129.1 (C12), 128.3 (C11), 120.6 (C9), 118.1 (C10), 75.1 (C8), 62.1 (C14), 31.8 (C3), 30.5 (C4), 29.9 (C13), 29.5 (C5), 29.3 (C7), 26.6 (C6), 22.6 (C2), 16.3 (C15) 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

128.3 (pos. C11), 118.1 (pos. C10), 62.1, 62.0 (neg. C8+14), 31.8 (neg. C3), 30.5 (neg. C4), 29.9 (neg. C13), 29.5 (neg. C5), 29.3 (neg. C7), 26.6 (neg. C6), 22.6 (neg. C2), 16.3 (pos. C15) 14.0 (pos. C1)

³¹P-NMR (162 MHz, CDCl₃) [ppm]:

27.9

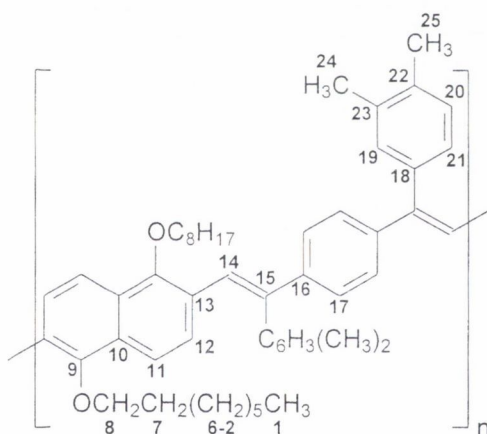
5.2.8. Poly(1,4-PhenyleneVinylene-1,5-di-n-Octyloxy-2,6-NaphthaleneVinylene)

dimethyl-PpPV-ONV (31)

0.68 g 1,5-bis(n-octyloxy)2,6-dimethylnaphthalene-bis(ethylphosphonate)ester (1 mmol) and 0.34 g 1,4-bis(3,4-dimethyl-benzoyl)benzene (1 mmol) were added to 20 mL DMF and heated under stirring to 80°C. 0.3 g (2.67 mmol) *Kt*OBu was added at once. The reaction mixture was left stirring at 80°C for additional 4h and then poured into 200 mL of water. The fine solid was centrifuged out of the suspension, dried, re-dissolved in toluene and precipitated with methanol. Finally the product was soxhleted (methanol) overnight.

Yield: 0.50 g (67%)

Melting range: 135-149°C



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.90-6.79 (H11+12+14+17+19+20+21), 4.05 (H8), 2.29, 2.23 (H24+25), 1.82 (H7), 1.45-1.26 (H2-6), 0.85 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

154.5 (C9), 142.5, 142.4 (C22+23), 139.9, 137.6, 136.2 (C15+16+18), 131.6, 130.3, 129.5 (C19+20+21), 128.8, 126.3 (C10+13), 127.6 (C17), 125.3 (C12), 122.5 (C14), 117.0 (C11), 75.1 (C8), 31.8 (C3), 30.4 (C7), 29.2 (C5), 26.4 (C4), 26.2 (C6), 22.6 (C2), 19.6, 19.4 (C24+25), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

131.6, 130.3, 129.5 (pos. C19+20+21), 127.6 (pos. C17), 125.3 (pos. C12), 122.5 (pos. C14), 117.0 (pos. C11), 75.1 (neg. C8), 31.8 (neg. C3), 30.4 (C7), 29.2 (neg. C5), 26.4 (neg. C4), 26.2 (neg. C6), 22.6 (neg. C2), 19.6, 19.4 (pos. C23+24), 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

131.6, 130.3, 129.5 (C19+20+21), 127.6 (C17), 125.3 (C12), 122.5 (C14), 117.0 (C11)

IR (microscope set-up) ν [cm⁻¹]:

3021 w, 2919 s, 2858 s, 1664 m, 1608 m, 1495 m, 1454 m, 1347 m, 1250 m, 1035 s, 963 m, 866 w, 814 m, 712 w

Raman (10⁻⁴ CHCl₃ solution in a 10mm cell) ν [cm⁻¹]:

635w, 730 w, 806 w, 879 w, 958 w, 1096 w, 1128 w, 1172 m, 1247 m, 1382 m, 1444 w, 1498 w, 1586 s, 2901 w

UV/VIS, λ [nm]: 375, 292, 262 (in 10⁻⁴ mol CHCl₃ solution)**PL:** 485 nm (10⁻⁴ CHCl₃ solution, excitation at 370 nm)**GPC:** 1,2,4-Trichlorobenzene, $M_n = 3171$, $M_w = 5859$, $M_w/M_n = 1.85$ **DSC:** $T_{cl} = 22, 44, 53^\circ\text{C}$, $T_g = 3^\circ\text{C}$ **TGA:** $T_d = 335\text{-}460^\circ\text{C}$ **Elemental Analysis:**

		Theory [%]	Found [%]
C ₅₄ H ₆₈ O ₂ (749.13 g/mol)	C	86.58	80.05
	H	9.15	7.87

Cyclic Voltammetry (Ag/AgCl): $E_{1/2red1} = -1.3\text{ V}$, $E_{1/2ox1} = 1.2\text{ V}$

5.2.9. Poly(1,3-phenylenevinylene-1,5-di-n-Octyloxy-2,6-NaphthaleneVinylene)

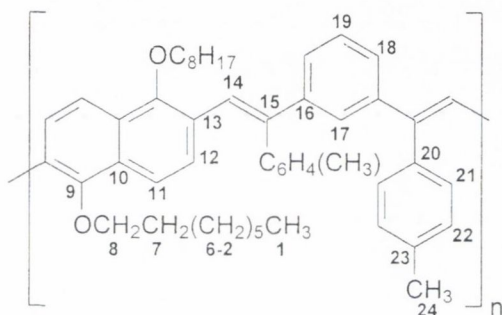
methyl-PmPV-ONV (32)

see synthesis dimethyl-PpPV-ONV (31)

Amount: 0.33 g (1 mmol) 1,3-bis(4-methyl-benzoyl)benzene
 0.68 g (1 mmol) 1,5-bis(n-octyloxy)2,6-dimethylnaphthalene-bis-(ethylphosphonate)ester

Yield: 35.5 g (49.1%)

Melting range: 151-181°C



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.85-6.80 (H11+12+14+17+18+19+21+22), 4.01 (H8), 2.36 (H24), 1.89 (H7), 1.55-1.25 (H2-6), 0.87 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

154.3 (C9), 142.6 (C23), 141.1, 138.7, 137.7 (C15+16+20), 131.6, 130.1 (C21+22), 128.8, 128.4, 126.9 (C17+18+19), 127.9, 126.3 (C10+13), 125.0 (C12), 122.8 (C14), 116.9 (C11), 75.0 (C8), 31.8 (C3), 30.4 (C7), 29.3 (C5), 26.4 (C4), 26.1 (C6), 22.6 (C2), 19.4 (C24), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

131.6, 130.1 (pos. C21+22), 128.8, 128.4, 126.9 (pos. C17+18+19), 125.0 (pos. C12), 122.8 (pos. C14), 116.9 (pos. C11), 75.0 (neg. C8), 31.8 (neg. C3), 30.4 (neg. C7), 29.3 (neg. C5), 26.4 (neg. C4), 26.1 (neg. C6), 22.6 (neg. C2), 19.4 (pos. C24), 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

131.6, 130.1 (C21+22), 128.8, 128.4, 126.9 (C17+18+19), 125.0 (C12), 122.8 (C14), 116.9 (C11)

IR (microscope set-up) ν [cm⁻¹]:

3021 w, 2924 s, 2842 s, 1659 m, 1593 m, 1501 m, 1460 m, 1403 m, 1265 m, 1050 s, 958 w, 917 w, 809 m, 768 w, 717 m, 702 m

Raman (10⁻⁴ CHCl₃ solution in a 10mm cell) ν [cm⁻¹]:

628 w, 735 w, 815 w, 885 w, 1101 w, 1132 w, 1177 w, 1247 m, 1382 m, 1449 w, 1494 w, 1586 s, 2908 w

UV/VIS, λ [nm]: 350, 296, 257 (in 10⁻⁴ mol CHCl₃ solution)**PL:** 468 nm (10⁻⁴ CHCl₃ solution, excitation at 350 nm)**GPC:** 1,2,4-Trichlorobenzene, M_n = 2592, M_w = 5759, M_w/M_n = 2.22**DSC:** T_m = 25, 81 °C**TGA:** T_d = 230-580 °C**Elemental Analysis:**

		Theory [%]	Found [%]
C ₅₂ H ₆₄ O ₂ (721.08 g/mol)	C	86.62	77.96
	H	8.95	7.77

Cyclic Voltammetry (Ag/AgCl): $E_{1/2ox1}$ = 1.3 V, $E_{1/2ox2}$ = 1.6 V

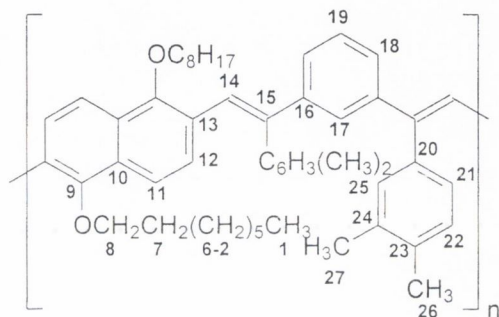
dimethyl-PmPV-ONV (33)

see synthesis dimethyl-PpPV-ONV (31)

Amount: 0.35 g (1 mmol) 1,3-bis(3,4-dimethyl-benzoyl)benzene
 0.68 g (1 mmol) 1,5-bis(n-octyloxy)2,6-dimethylnaphthalene-bis-
 (ethylphosphonate)ester

Yield: 0.23 g (30.4%)

Melting range: 159-197°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

7.83, 7.47, 7.20, 7.09 (H11+12+14+17+18+19+21+22+25), 3.90 (H8), 2.27 (H26+27), 1.83 (H7), 1.81-1.21 (H2-6), 0.84 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

154.5 (C9), 142.6, 142.4 (C23+24), 140.8, 137.8, 136.0 (C15+16+20), 131.2, 130.1, 129.5 (C21+22+25), 128.8, 128.0, 127.7 (17+18+19), 127.2, 126.2 (C10+13), 125.4 (C12), 122.7 (C14), 116.9 (C11), 75.0 (C8), 31.7 (C3), 30.4 (C7), 29.2 (C5), 26.2 (C4+6), 22.6 (C2), 19.7, 19.4 (C26+27), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

131.2, 130.1, 129.5 (pos. C21+22+25), 128.8, 128.0, 127.7 (pos. C17+18+19), 125.4 (pos. C12), 122.7 (pos. C14), 116.9 (pos. C11), 75.0 (neg. C8), 31.7 (neg. C3), 30.4 (C7), 29.2 (neg. C5), 26.2 (neg. C4+6), 22.6 (neg. C2), 19.7, 19.4 (pos. C26+27), 14.0 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

131.2, 130.1, 129.5 (C21+22+25), 128.8, 128.0, 127.7 (17+18+19), 125.4 (C12), 122.7 (C14), 116.9 (C11)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3012 w, 2934 s, 2852 s, 1649 m, 1603 m, 1501 m, 1352 m, 1250 m, 1040 m, 953 w, 825 m, 722 w

Raman (10^{-4} CHCl_3 solution in a 10mm cell) $\nu[\text{cm}^{-1}]$:

532 w, 735 w, 811 w, 860 w, 990 w, 1248 m, 1386 m, 1444 w, 1595 s, 2899 w

UV/VIS, λ [nm]: 348, 290, 250 (in 10^{-4} mol CHCl_3 solution)

PL: 464 nm (10^{-4} CHCl_3 solution, excitation at 350 nm)

GPC: 1,2,4-Trichlorobenzene, $M_n = 2581$, $M_w = 6793$, $M_w/M_n = 2.63$

DSC: $T_m = 22$, 74°C

TGA: $T_d = 300$ - 530°C (N_2)

TGA (air):	T_{d1}	T_{d2}	T_{d3}	T_{d4}	T_{end}
	390°C	450°C	570°C	725°C	800°C
	(17.1%)	(38.1%)	(60%)	(84.8%)	(98.1%)

Elemental Analysis:		Theory [%]	Found [%]
$\text{C}_{54}\text{H}_{68}\text{O}_2$ (749.13 g/mol)	C	86.58	81.52
	H	9.15	8.09

Cyclic Voltammetry (Ag/AgCl): $E_{1/2\text{red1}} = -1.7$ V, $E_{1/2\text{ox1}} = 1.3$ V, $E_{1/2\text{ox2}} = 1.5$ V

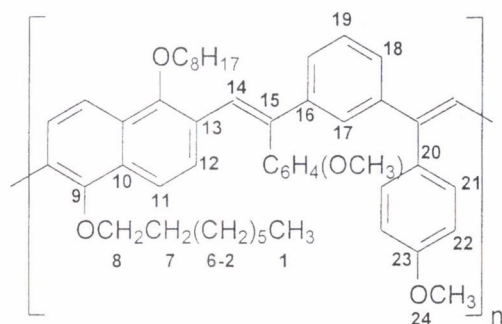
methoxy-PmPV-ONV (34)

see synthesis dimethyl-PpPV-ONV (31)

Amount: 0.35 g (1 mmol) 1,3-bis(4-methoxy-benzoyl)benzene
 0.68 g (1 mmol) 1,5-bis(n-octyloxy)-2,6-dimethylnaphthalene-bis-(ethylphosphonate)ester

Yield: 0.24 g (31.8%)

Melting range: 95 - 142°C



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.80-6.59 (H11+12+14+17+18+19+21+22), 3.96 (H8), 3.90 (H24), 1.89 (H7), 1.45-1.21 (H2-6), 0.83 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

154.5 (C9), 148.8 (C23), 141.0, 137.8, 135.7 (C15+16+20), 131.3, 129.8, 128.8, 127.3 (C17+18+19+21), 127.8, 126.0 (C10+13), 125.5 (C12), 123.1 (C14), 116.9 (C11), 110.9 (C22), 75.0 (C8), 55.9 (C24), 31.8 (C3), 30.4 (C7), 29.3 (C5), 26.3 (C4), 26.1 (C6), 22.6 (C2), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

131.3, 129.8, 128.8, 127.3 (pos. C17+18+19+21), 125.5 (pos. C12), 123.1 (pos. C14), 116.9 (pos. C11), 110.9 (pos. C22), 75.0 (neg. C8), 55.9 (pos. C24), 31.8 (neg. C3), 30.4 (neg. C7), 29.3 (neg. C5), 26.3 (neg. C4), 26.1 (neg. C6), 22.6 (neg. C2), 14.0 (pos. C1)

IR (microscope set-up) ν [cm⁻¹]:

3021 w, 2924 s, 2847 m, 1644 m, 1588 m, 1506 s, 1398 m, 1352 m, 1260 m, 1127 s, 799 m, 758 m

Raman (10⁻⁴ CHCl₃ solution in a 10mm cell) ν [cm⁻¹]:

532 w, 596 w, 686 w, 863 w, 989 w, 1123 w, 1248 m, 1386 m, 1449 w, 1598 s, 2894 m

UV/VIS, λ [nm]: 362, 287, 256 (in 10⁻⁴ mol CHCl₃ solution)

PL: 466 nm (10⁻⁴ CHCl₃ solution, excitation at 360 nm)

GPC: 1,2,4-Trichlorobenzene, M_n = 1717, M_w = 2224, M_w/M_n = 1.30

DSC: T_m = 45°C

TGA: T_d = 320-480°C

Elemental Analysis:

		Theory [%]	Found [%]
C₅₂H₆₄O₄ (753.08 g/mol)	C	82.94	74.64
	H	8.57	7.41

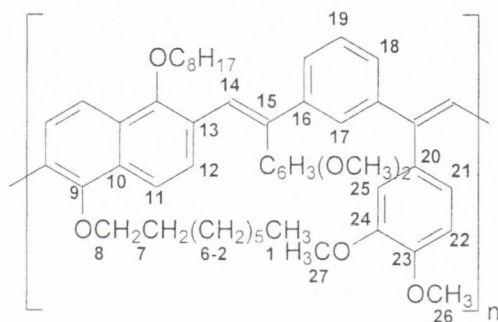
dimethoxy-PmPV-ONV (35)

see synthesis dimethyl-PpPV-ONV (31)

Amount: 0.45 g (1 mmol) 1,3-bis(3,4-dimethoxy-benzoyl)benzene
 0.68 g (1 mmol) 1,5-bis(n-octyloxy)2,6-dimethylnaphthalene-bis-
 (ethylphosphonate)ester

Yield: 0.33 g (39.9%)

Melting range: 110-131°C

**¹H-NMR (400 MHz, CDCl₃) [ppm]:**

7.96-6.80 (H11+12+14+17+18+19+21+22+25), 3.94 (H8), 3.89, 3.84 (H26+27),
 1.89 (H7), 1.52-1.23 (H2-6), 0.84 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

154.5 (C9), 149.9, 148.8 (C23+24), 138.4, 135.8, 134.2 (C15+16+20), 129.9,
 128.8, 127.2, 126.3 (C17+18+19+21), 127.8, 125.9 (C10+13), 123.3 (C14), 117.0
 (C11), 111.4, 110.9 (C22+25), 75.0 (C8), 55.9, 55.8 (C26+27), 31.7 (C3), 30.4
 (C7), 29.2 (C5), 26.1 (C4+6), 22.6 (C2), 14.0 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

129.9, 128.8, 127.2, 126.3 (pos. C17+18+19+21), 123.3 (pos. C14), 117.0 (pos.
 C11), 111.4, 110.9 (pos. C22+25), 75.0 (neg. C8), 55.9, 55.8 (pos. C26+27), 31.7
 (neg. C3), 30.4 (neg. C7), 29.2 (neg. C5), 26.1 (neg. C4+6), 22.6 (neg. C2), 14.0
 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

129.9, 128.8, 127.7, 125.9 (C17+18+19+21), 123.3 (C12), 120.8 (C25), 117.0
 (C11), 114.0 (C14), 110.9 (C22)

IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3021 w, 2924 s, 2863 s, 1644 m, 1593 s, 1516 s, 1465 m, 1413 m, 1362 w, 1250 s, 1132 m, 1024 m, 881 w, 855 w, 809 m, 768 w, 722 w

Raman (10^{-4} CHCl_3 solution in a 10mm cell) $\nu[\text{cm}^{-1}]$:

521 w, 602 w, 753 w, 869 m, 985 w, 1248 m, 1386 m, 1449 w, 1595 s, 2899 w

UV/VIS, λ [nm]: 362, 290, 258 (in 10^{-4} mol CHCl_3 solution)**PL:** 464 nm (10^{-4} CHCl_3 solution, excitation at 360 nm)**GPC:** 1,2,4-Trichlorobenzene, $M_n = 1667$, $M_w = 2366$, $M_w/M_n = 1.42$ **DSC:** $T_m = 36, 60, 133^\circ\text{C}$ **TGA:** $T_d = 290\text{-}490^\circ\text{C}$ **Elemental Analysis:**

		Theory [%]	Found [%]
$\text{C}_{54}\text{H}_{68}\text{O}_6$ (813.13 g/mol)	C	79.11	74.71
	H	8.43	7.44

Cyclic Voltammetry (Ag/AgCl): $E_{\text{pc1}} = 1.3$ V, $E_{1/2\text{ox2}} = 1.5$ V, $E_{1/2\text{ox3}} = 1.7$ V

5.2.10. 1,3-Phenylene Vinylene-1,5-di-*n*-Octyloxy-2,6-Naphthylene Vinylene (PmPV-ONV)

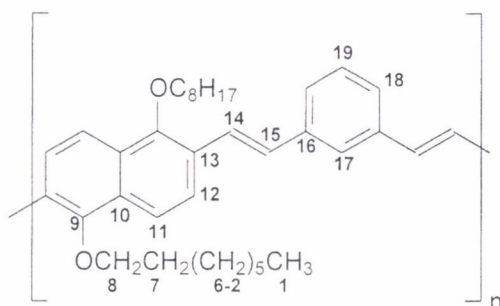
see synthesis dimethyl-PpPV-ONV (31)

Amount: 0.14 g (1 mmol) isophthalaldehyde

0.68 g (1 mmol) 1,5-bis(*n*-octyloxy)2,6-dimethylnaphthalene-bis-(ethylphosphonate)ester

Yield: 0.44 g (81.5%)

Mp.: $>300^\circ\text{C}$ (seems to decompose instead of melting)



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.92-7.29 (H11+12+14+15+17+18+19), 4.05 (H8), 1.98 (H7), 1.65 (H6), 1.38-1.29 (H2-5), 0.87 (H1)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

153.4 (C9), 138.3 (C16), 129.4, 127.6, 125.6 (C17+18+19), 126.4, 125.1 (C10+13), 124.2, 123.8 (C14+15), 118.8 (C12), 75.8 (C8), 31.9 (C3), 29.6, 29.4 (C5+7), 26.5 (C4), 26.4 (C6), 22.7 (C2), 14.1 (C1)

Dept 135 (100 MHz, CDCl₃) [ppm]:

129.4, 127.6, 125.6 (pos. C17+18+19), 124.2, 123.8 (pos. C14+15), 118.8 (pos. C12), 75.8 (neg. C8), 31.9 (neg. C3), 29.6, 29.4 (neg. C5+7), 26.5 (neg. C4), 26.4 (neg. C6), 22.7 (neg. C2), 14.1 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

129.4, 127.6, 125.6 (C17+18+19), 124.2, 123.8 (C14+15), 118.8 (C12)

IR (microscope set-up) ν [cm⁻¹]:

3042 w, 2919 s, 2852 m, 1695 w, 1598 m, 1403 m, 1367 m, 1324 w, 1265 m, 1178 w, 1034 m, 963 m, 814 w, 717 w, 681 w

Raman (10⁻⁴ CHCl₃ solution in a 10mm cell) ν [cm⁻¹]:

851 w, 961 w, 995 w, 1166 w, 1228 m, 1258 m, 1310 m, 1385 m, 1399 m, 1467 w, 1577 s, 1614 s, 1628 s

UV/VIS, λ [nm]: 400, 363, 303, 253 (in 10⁻⁴ mol CHCl₃ solution)

PL: 441 nm (10⁻⁴ CHCl₃ solution, excitation at 400 nm)

GPC: 1,2,4-Trichlorobenzene, M_n = 1684, M_w = 3067, M_w/M_n = 1.82

DSC: T_m = 67°C

TGA: T_d = 290-510°C

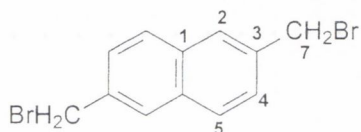
Elemental Analysis:		Theory [%]	Found [%]
C ₃₈ H ₅₂ O ₂ (540.83 g/mol)	C	84.39	76.66
	H	9.69	8.11

4.3.4. Synthesis of 2,6-Dimethylnaphthalene-bis(ethylphosphonate) ester

2,6-Dibromomethylnaphthalene (37)

A solution of 5 g 2,6-dimethylnaphthalene (32.0 mmol), 12.55 g N-bromosuccinimide (70.5 mmol), 0.04 g 1,1'-azobis(cyclohexanecarbonitrile) in 65 mL CCl_4 was allowed to stand at RT for 10 min and then slowly heated to reflux for 20 h. The solvent was evaporated and the residue was taken up in water, heated and filtered immediately in a heated funnel to remove traces of N-bromosuccinimide. The crude product was re-crystallised in toluene to give 9.35 g white, slightly reddish crystals (93.0%).

Mp: 149-151°C



^1H -NMR (400 MHz, CDCl_3) [ppm]:

7.92 (s, 2H, H2), 7.90 (d, 2H, H4), 7.57 (d, 2H, H5), 4.68 (s, 4H, H7)

^{13}C -NMR (100 MHz, CDCl_3) [ppm]:

139.2 (C3), 132.4 (C1), 129.2 (C2), 127.2 (C5), 123.8 (C4), 32.9 (C7)

Dept 135 (100 MHz, CDCl_3) [ppm]:

129.2 (pos. C2), 127.2 (pos. C5), 123.8 (pos. C4), 32.9 (neg. C7)

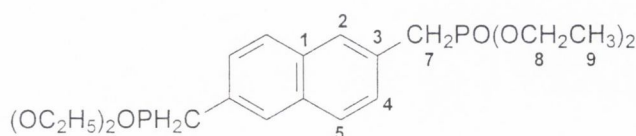
IR (microscope set-up) $\nu[\text{cm}^{-1}]$:

3001 w, 1603 w, 1511 w, 1352 m, 1203 m, 1142 s, 891 s, 799 m, 697 s

2,6-Dimethylnaphthalene-bis(ethylphosphonate) ester (38)

A mixture of 5 g 2,6-dibromomethylnaphthalene (15.9 mmol) and 5.52 g triethylphosphite (31.8 mmol) was heated for 4 hours at 140°C while the by-product ethyl bromide was continuously removed by distillation. After leaving the viscous liquid overnight 5.93 g yellow crystals (86.9%), which re-crystallisation from petroleum ether, formed in the flask.

Mp: >300°C



¹H-NMR (400 MHz, CDCl₃) [ppm]:

7.74 (d, 2H, H₄), 7.73 (s, 2H, H₂), 7.43 (d, 2H, H₅), 4.01 (m, 8H, H₈), 3.30 (d, 4H, H₇) (J = 21.56), 1.24 (t, 12H, H₉)

¹³C-NMR (100 MHz, CDCl₃) [ppm]:

139.2 (C₃), 132.3 (C₁), 129.0 (C₂), 128.1 (C₅), 127.8 (C₄), 62.2 (C₈), 33.3 (C₇), 16.4 (C₉)

Dept 135 (100 MHz, CDCl₃) [ppm]:

129.0 (pos. C₂), 128.1 (pos. C₅), 127.8 (pos. C₄), 62.2 (neg. C₈), 33.3 (neg. C₇), 16.4 (pos. C₉)

³¹P-NMR (162 MHz, CDCl₃) [ppm]:

27.5

IR (microscope set-up) ν[cm⁻¹]:

2975 w, 2806 w, 1669 s, 1403 m, 1265 s, 1193 m, 1106 m, 1019 m, 917 m, 866 m, 778 m, 727 s

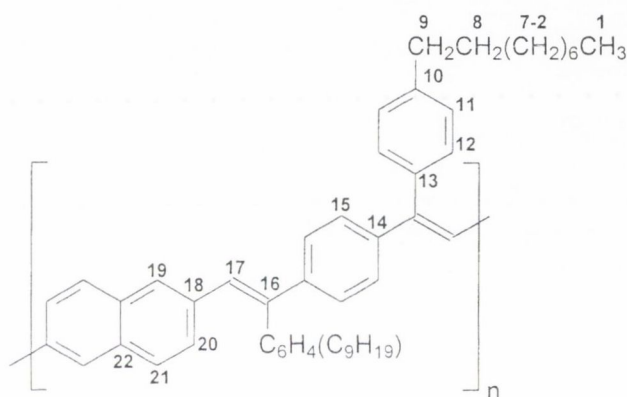
5.2.11. Poly(1,4-phenylenevinylene-2,6-NaphthyleneVinylene)

nonyl-PpPV-NV (39)

0.43 g 2,6-dimethylnaphthalene-bis(ethylphosphonate)ester (1 mmol) and 0.45 g 1,4-bis(4-nonyl-benzoyl)benzene (1 mmol) in 20 mL DMF were heated to 80°C. 0.3 g (2.67 mmol) *Kt*OBu was added at once. The reaction mixture was left stirring at 80°C for additional 4h and then poured into 200 mL of water. The fine solid was centrifuged, dried, re-dissolved in toluene and precipitated with methanol. Finally the product was soxhleted (methanol) over night.

Yield: 0.60 g (86.3%)

Mp.: 110-133°C



$^1\text{H-NMR}$ (400 MHz, CDCl_3) [ppm]:

7.36, 7.22, 7.13, 7.06 (H11+12+15+19+20+21), 2.53 (H9), 1.55 (H8), 1.18 (H2-6), 0.79 (H1)

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) [ppm]:

142.6 (C10), 139.9, 137.4, 135.3, 132.2, 128.1 (C13+14+16+18+22), 130.9, 130.3 (C11+12), 128.7, 128.3 127.6 (C19+20+21), 127.4 (C15), 127.2 (C17), 35.7 (C9), 31.9, 31.4, 29.6, 29.3 (C8-4), 22.6 (C2), 14.1 (C1)

Dept 135 (100 MHz, CDCl_3) [ppm]:

130.9, 130.3 (pos. C11+12), 128.7, 128.3 127.6 (pos. C19+20+21), 127.4 (pos. C15), 127.2 (pos. C17), 35.7 (neg. C9), 31.9, 31.4, 29.6, 29.3 (neg. C8-4), 22.6 (neg. C2), 14.1 (pos. C1)

Dept 90 (100 MHz, CDCl₃) [ppm]:

130.9, 130.3 (C11+12), 128.7, 128.3 127.6 (C19+20+21), 127.4 (C15), 127.2 (C17)

ATR-FTIR (polymer film from toluene solution) ν [cm⁻¹]:

3016 w, 2955 m, 2924 s, 2847 m, 1603 m, 1511 m, 1460 m, 1408 w, 1367 w, 1050 m, 1019 m, 895 w, 825 m, 809 m, 717 w, 666 w

Raman (10⁻⁴ CHCl₃ solution in a 10mm cell) ν [cm⁻¹]:

408 w, 521 w, 614 w, 801 w, 832 w, 870 w, 897 w, 1130 m, 1161 w, 1178 m, 1192 m, 1239 m, 1335 w, 1390 m, 1404 m, 1472 w, 1493 w, 1510 w, 1565 m, 1592 s

UV/VIS, λ [nm]: 370, 324, 290 (in 10⁻⁴ mol CHCl₃ solution)**PL:** 478 nm (10⁻⁴ CHCl₃ solution, excitation at 390 nm)**GPC:** 1,2,4-Trichlorobenzene, $M_n = 3810$, $M_w = 11350$, $M_w/M_n = 2.98$ **DSC:** $T_m = 60^\circ\text{C}$ **TGA:** $T_d = 400\text{-}590^\circ\text{C}$ **Elemental Analysis:**

		Theory [%]	Found [%]
C₅₂H₆₄ (689.08 g/mol)	C	90.64	86.15
	H	9.36	8.52

Cyclic Voltammetry (Ag/AgCl): $E_{pc1} = 1.3\text{ V}$, $E_{pc2} = 1.7\text{ V}$

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Absorption spectra

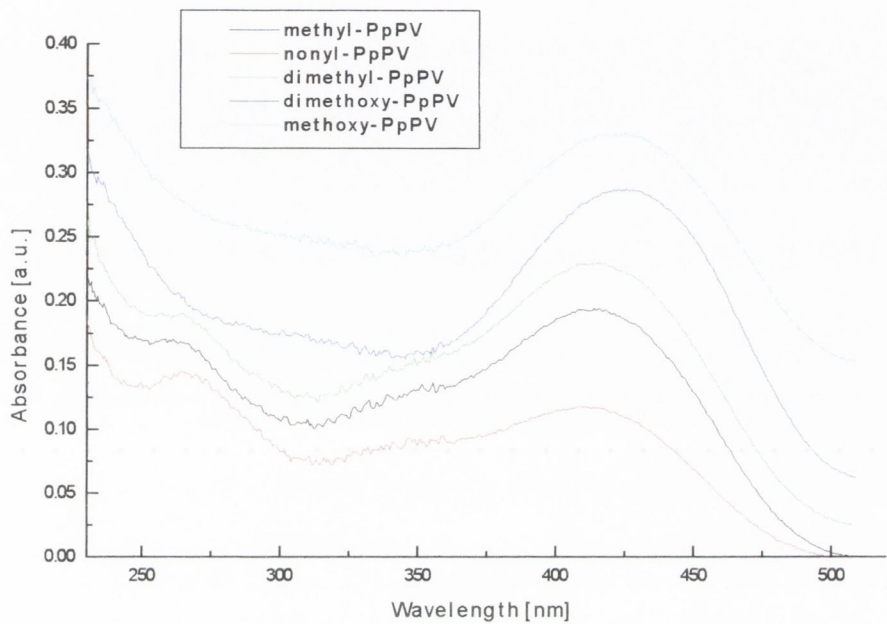


Figure A1.: Absorption spectra of *para* substituted PPV derivatives

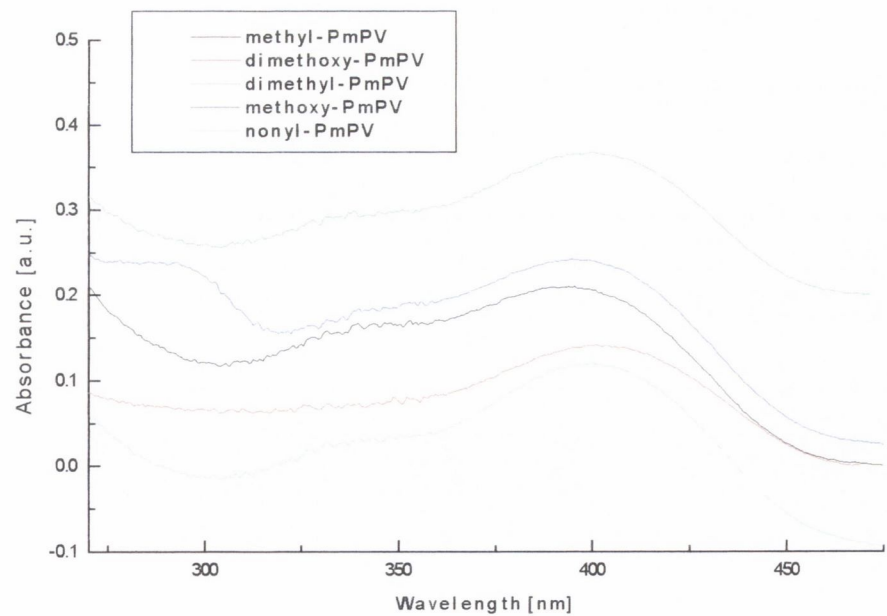


Figure A2.: Absorption spectra of *meta* substituted PPV derivatives

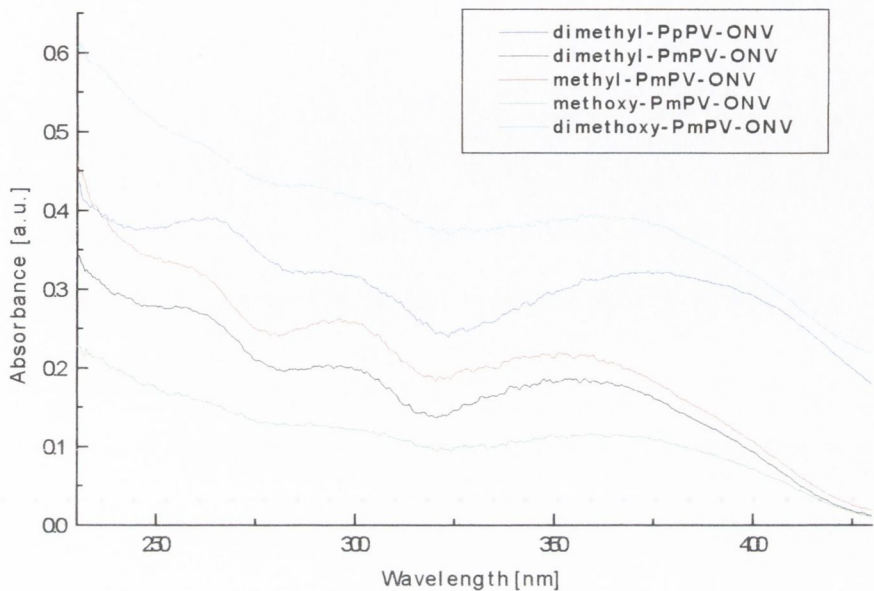


Figure A3.: Absorption spectra of PPV-ONV derivatives

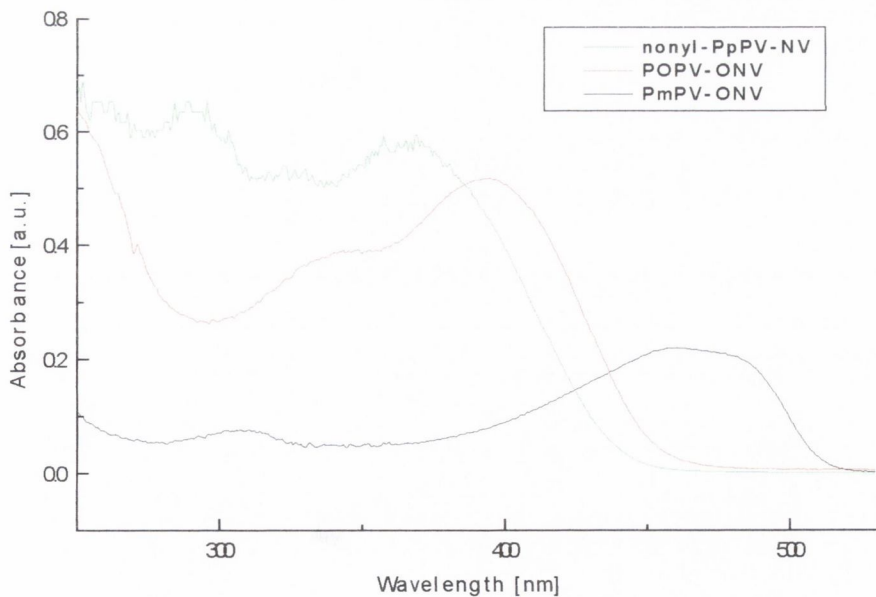


Figure A4.: Absorption spectra of nonyl-PpPV-NV, POPV-ONV and PmPV-ONV