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The effect of backbone fluorination on the carrier mobility in alkoxy and alkyl substituted conducting polymers of the poly(phenylenevinylene) type

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Summary

We report the synthesis of some new backbone fluorinated polymers of the poly(phenylenevinylene) type. The new polymers were characterised by NMR, SEC and X-ray powder diffraction. The charge carrier mobilities were determined using pulse radiolysis time resolved microwave conductivity (PR-TRMC) and the carrier mobilities were compared to the similar non-fluorinated analogues. The changes in charge carrier mobilities as a function of molecular substitution pattern is discussed in terms of other materials properties such as electronic structure and absorption properties. The major result is that it was found possible for this type of material to alter the electronic energy levels by molecular substitution without imparting significant changes in the magnitude of the charge carrier mobilities and the optical properties.

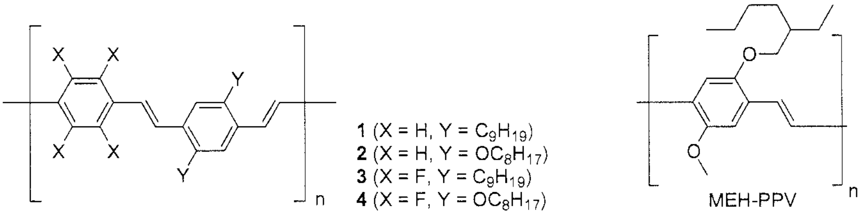
Introduction

The field of conducting polymers has received enormous attention recently due to their successful application in light emitting diodes [1] and all polymer displays [2] thus complementing their inorganic counterparts. Furthermore their potential application to all-polymer electronic circuits [3] and all-plastic solar cells [4] has become an intense field of research. There are some limitations to the widespread application, most notably the varieties of polymers that are available for studies and device fabrication are limited and also the possibility for altering and improving one particular material property while keeping others unaltered is often very difficult. As an example it is often desirable to be able to alter the absolute position of the electronic energy levels in order to make a better match between the valence band (or conduction band) edge and a metal electrode (or contact) without changing the magnitude of the charge carrier mobilities.

Chemical substitution has successfully been employed to control the photophysical and electrical properties of conjugated polymer materials. Among the chemical substitutents that have been reported one finds that fluorine has been applied in a few instances. Fluorine is a highly electron withdrawing substituent and its incorporation into conjugated materials result in an increased electron affinity [5], it has further been used to control the emission maximum of both photoluminesence and electroluminescence [6-7]. Fluorination has also been used as a probe for fluorescence quenching by exciton-exciton annihilation [8-9] and has been considered as a means to increase the stability of materials [10-11]. The carrier transport in conjugated polymers has been the subject of interest [12] as device function hinges on this issue. Carrier transport in fluorinated dendrimers has been reported in one instance [13].

In this paper we present the synthesis of a poly(phenylenevinylene) with every second benzene ring carrying four fluorine atoms and every other benzene ring carrying two alkyl or alkoxy groups (general molecular structure shown in scheme 1).

We have fully characterised these new conducting polymer materials by NMR, SEC and powder X-ray diffraction and determined the charge carrier mobilities and lifetimes using pulse-radiolysis time-resolved microwave conductivity (PR-TRMC).



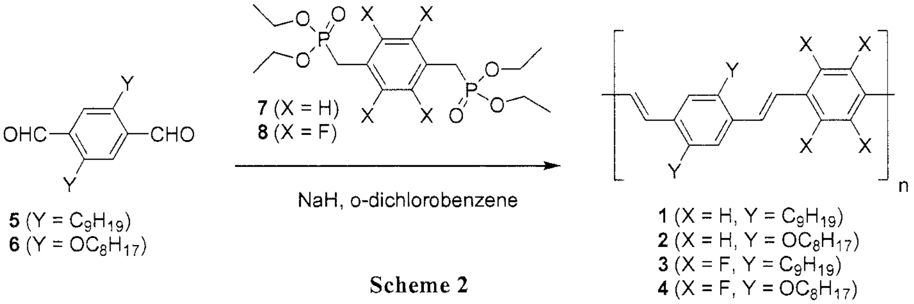
1 (X = H, Y = C_9H_{19})
2 (X = H, Y = OC_8H_{17})
3 (X = F, Y = C_9H_{19})
4 (X = F, Y = OC_8H_{17})

MEH-PPV

Scheme 1

Experimental

Methods. Commercially available compounds were purchased from Aldrich. 1,4-Diformyl-2,5-dinonylbenzene (**5**) was prepared as described in [14], 1,4-formyl-2,5-dioctyloxybenzene (**6**) was prepared as described in ref [15], bis(diethylphosphonylmethyl)benzene (**7**) was prepared as described in ref. [16], bis(diethylphosphonylmethyl)tetrafluorobenzene (**8**) was prepared as described in ref. [17]. MEH-PPV was purchased from American Dye Source Inc. and had a molecular weight of 500.000 g mol^{-1}. The general procedure for the polymerisation followed conditions given in [14]. The polymer (**1**) was obtained as described in [14] and the polymer (**2**) as described in ref. [18].



5 (Y = C_9H_{19})
6 (Y = OC_8H_{17})

7 (X = H)
8 (X = F)

NaH, o-dichlorobenzene

1 (X = H, Y = C_9H_{19})
2 (X = H, Y = OC_8H_{17})
3 (X = F, Y = C_9H_{19})
4 (X = F, Y = OC_8H_{17})

Scheme 2

General procedure for the synthesis of the polymers (1-4). The dialdehyde **5** or **6** (5 mmol) was dried at 40 °C in a vacuum oven for 24hrs and then mixed with the bis(diethylphosphonylmethyl)benzene derivative **7** or **8** (5 mmol) in a 1:1 mixture of 1,2-dichlorobenzene and diphenylether (250mL). Stoichiometric amounts were weighed out with a precision better than 0.1%. The mixture was degassed with argon.

NaH (1g) was added and the mixture was heated to reflux under argon with an air condenser. Reflux was continued for 24hrs. The mixture was cooled and methanol (200mL), containing HCl(aq) (37%, 5mL), was added and stirred for 30min. The mixture was then poured into methanol (600mL) and filtered giving a solid that was washed with ether and dried. A typical yield of ca. 95% was obtained.

Poly-1,2'''-(2,5-dinonyl-1,4-phenylene-1',2'-vinylene-1'',4''-phenylene-1''',2'''-vinylene) (1) The synthetic procedure and analytical data are in accordance with those described in ref. [14]

Poly-1,2'''-(2,5-dioctyloxy-1,4-phenylene-1',2'-vinylene-1'',4''-phenylene-1''',2'''-vinylene) (2). The analytical data conform to those described in ref. [18] ^{1}H NMR (250MHz, $CDCl_3$, 330K, TMS): δ= 0.91 (broad s, 6H, CH_3), 1.34 (broad s, 16H, CH_2), 1.56 (broad s, 4H, CH_2), 1.88 (broad s, 4H), 4.09 (m, 4H, CH_2), 6.7-7.5 (m, 10H, ArH) M_w = 3980; M_w/M_n = 1.573.

Poly-1,2'''-(2,5-dinonyl-1,4-phenylene-1',2'-vinylene-2'',3'',5'',6''-tetrafluoro-1'',4''-phenylene-1''',2'''-vinylene) (3). During the first 20 minutes of reflux a light yellow solid precipitated. The polymer was not very soluble in common solvents at room temperature. 1,2-Dichlorobenzene and chlorobenzene was found to be good solvents near the boiling point. ^{1}H NMR (250MHz, 1,2-$C_6D_4Cl_2$, 450K, TMS): δ= 1.17 (broad s, 6H, CH_3), 1.61 (broad s, 24H, CH_2), 3.15 (broad s, 4H, CH_2), 7.35 (d, 2H, J=14Hz), 7.84 (s, 2H, ArH), 8.16 (d, 2H, J=14Hz); M_w = 2530; M_w/M_n = 1.211.

Poly-1,2'''-(2,5-dioctyloxy-1,4-phenylene-1',2'-vinylene-2'',3'',5'',6''-tetrafluoro-1'',4''-phenylene-1''',2'''-vinylene) (4). During the first 20 minutes of reflux a red solid precipitated. 1,2-Dichlorobenzene was found to be a good solvent near the boiling point. ^{1}H NMR (250MHz, 1,2-$C_6D_4Cl_2$, 450K, TMS): δ= 1.18 (broad s, 6H, CH_3), 1.52 (broad s, 16H, CH_2), 1.85 (broad s, 4H, CH_2), 2.09 (broad s, 4H, CH_2), 4.31 (broad s, 4H, OCH_2), 8.19 (d, 2H) (peaks in the 7.2-7.6 range are obscured by the solvent) M_w = 3010; M_w/M_n = 1.309.

Size exclusion chromatography (SEC). SEC was performed in 1,2-dichlorobenzene at 80 °C using a polystyrene standard for molecular weight determination. Polymer 2 was slightly soluble at room temperature and polymers 3 and 4 were not very soluble. The samples for SEC were prepared by dissolving the polymers in boiling 1,2-dichlorobenzene at a concentration of 3 mg mL^{-1} and leaving them to cool to room temperature. The mixture was then filtered through a 1 μm filter and the filtrate used for SEC. While a lot of high molecular weight material was eliminated in this way this procedure was necessary in order to avoid precipitation in the SEC apparatus (inlet, pumps, columns and detector).

Differential scanning calorimetry (DSC). DSC data for **1** [14] and **2** [18] have been reported. DSC was performed at 10° min^{-1} temperature gradients in the temperature interval 50-350 °C for **3** and **4**. There were no discernible transitions. A simple melting point determination was also performed to visually check for any change coincident with the changes in the X-powder diffractograms (*vide supra*). While a darkening and gradual change in appearance was observed there were no abrupt changes that could be assigned to a particular temperature range.

Powder X-ray diffraction. The powder X-ray data collected for the thermal studies were collected at the I711 beamline at the MAXII synchrotron in Lund, Sweden. [19,20] The setup employed a HUBER G670 imaging-plate Guinier camera and an X-ray wavelength of 1.302Å which was the longest possible wavelength with the current beamline set-up.

Carrier mobility and carrier lifetime measurements. The technique employed for the determination of carrier mobilities was the well-known pulse radiolysis time resolved microwave conductivity technique (PR-TRMC). [21,22] The technique relates a measured change in reflected microwave power from the sample to the conductivity change upon passage of high-energy electrons. From the transient changes in conductivity the lifetime of the carriers can be determined as well as the sum of the mobility of the carriers. The advantage of the technique is that the magnitude of the carrier mobility obtained is the minimum average carrier mobility and it is independent of sample preparation ie. no contact resistance. This means that even higher mobilities are likely for suitably oriented samples. A disadvantage is that it is the sum of carrier mobilities that is obtained and the technique does thus not allow for distinguishing between hole and electron mobilities. The system and set-up has been described earlier [14,23]. An analysis of the conductivity transient gave the sum of charge carrier mobilities and the carrier half-life, $\tau_{\frac{1}{2}}$. The results of the carrier mobility measurements are shown in table 1. The technique relates a measured change in reflected microwave power from the sample to the conductivity change upon passage of high-energy electrons. From the transient changes in conductivity the lifetime of the carriers can be determined as well as the sum of the mobility of the carriers. The advantage of the technique is that the magnitude of the carrier mobility obtained is the minimum average carrier mobility and it is independent of sample preparation ie. no contact resistance. This means that even higher mobilities are likely for suitably oriented samples. A disadvantage is that it is the sum of carrier mobilities that is obtained and the technique does thus not allow for distinguishing between hole and electron mobilities. The system used the 10MeV electron accelerator facility at Risø National Laboratory where short pulses of electrons 10-500ns could be passed through the sample placed in an R-band waveguide (26.5-40GHz). Three microwave sources were employed. A HP8690B Sweeper with a HP8697A 26.5-40GHz module in conjunction with a broadband power amplifier. Two Gunn diode sources in the frequency range 31-35 GHz were employed when possible due to the high power (27dbm) and low noise obtained from these sources. The appropriate microwave source could be switched into the system that consisted of a 26.5-40GHz HP R532A frequency meter and a 26-40GHz HP R382A attenuator. Hereafter the microwaves were lead into the first port of a three-port circulator and from the second port to the sample holder that was placed in the path of the electron beam. The sample was evacuated to a pressure of $10^{-5} - 10^{-4}$ mBar using a turbo pump during measurements. The reflected microwave power was again entering the second port of the circulator and taken from the third port through an isolator and a circular waveguide cavity filter (TE_{111} bandpass filter with a bandwidth of 500MHz). At this point the reflected power could be switched into a power meter (HP432A with a HP R486A Thermistor Mount) for the absolute measurement of microwave power or directly to a HP R422C schottky barrier diode with a time response better than 1 ns. At this point the time response of the system is limited by the bandwidth of the cavity filter (~2ns). The fast transients were recorded in a 50Ω system on a 4Gs/s TDS784C oscilloscope from Tektronix. The electron beam was after passage through the sample picked up by a Faraday cup and used as the trigger source for the data collection. In order to extract the carrier mobility the number of carries must be known. This was obtained from dosimetry where radiochromic films were used to get the distribution around the sample holder, and inside the sample holder in four depths using polyethylene spacers (this procedure followed the ASTM E1275 standard "Practice for use of a radiochromic film dosimetry system"). A better absolute measure of the dose was obtained using alanine pellets where the dose over the whole volume of the pellet is accurately determined (this procedure followed the ASTM E1607 standard "Practice for use of the alanine-EPR dosimetry system"). The typical dose for a 100ns pulse was 25Gy and the variation in dose over the sample volume was 10%.

Results and discussion

Synthesis. The synthetic strategy simply involved condensation of an aromatic dialdehyde with a substituted aromatic disphosphonate ester in a high boiling solvent mixture making use of the Horner-Wadsworth-Emmons condensation reaction as shown in scheme 2. This reaction type has been used earlier for branched alkoxy substituted polyphenylenevinylenes [24] where much higher molecular weights were obtained. Polymer **2** has been prepared by a different route using a Heck type polymerisation using a palladium catalyst [18]. The polymers **1** and **2** were more soluble than their fluorinated counterparts **3** and **4**. The molecular weights as determined by SEC were small and we ascribe this to the general insolubility of these materials. For polymers **3** and **4** we ascribe this to more favourable interactions in the solid due to the quadrupole inversion upon fluorination of a benzene ring. This effect has been employed earlier to for the purpose of organising small molecules in the solid state [25,26]. We tried to increase the molecular weights using different high boiling solvents and the mixture of 1,2-dichlorobenzene and diphenylether gave the best results. The low molecular weights obtained and the insoluble nature of these materials may ultimately limit their applicability.

UV-vis absorption properties. The effect of backbone fluorination on the absorption spectrum is very small. The absorption maximum is virtually identical for the polymer pairs, the alkyl substituted **1** and **3** and the alkoxy substituted **2** and **4**. The UV-VIS data have been reported in the literature [27] for the polymers studied here. The effect of fluorine substitution on a given chromophore does generally not alter the absorption properties as the ground state is unaffected assuming a similar geometry between the fluorinated and non-fluorinated molecules. [28] The absolute position of the energy levels, however, is affected by the fluorination as indeed observed (vide supra). [5,27]

Molecular weight characterisation. The molecular weights of the polymers obtained in this manner were determined using size exclusion chromatography (SEC) and all the polymers were found to have a low molecular weights (M_w = 3980, 2530 and 3010 g mol^{-1} respectively for **2**, **3** and **4**). In all cases however the molecular weight determination was hampered by insolubility problems as seen by the low polydispersity obtained (< 1.600) which we interpret as being due to insolubility of the higher components. Since it is a condensation type polymerisation reaction the polydispersity should have a value around 2. It also has to be borne in mind that the measure of the molecular weight is with respect to a polystyrene standard calibration series and since these polymers are assumed to be rigid rods as opposed to polystyrene which is assumed globular in solution the molecular weights are relative. In conclusion the molecular weight of the polymers are believed to be higher than indicated by the SEC measurements since most of the material was insoluble, also supported by the weak signal.

Thermal behaviour and powder X-ray diffraction. The thermal behaviour was not easily characterised. Both DSC and simple melting point experiments did not reveal any discrete events. Temperature studies using X-ray powder diffraction however showed that changes do take place. The X-ray powder diffractograms confirm the gradual nature of the thermal behaviour as slow changes in the crystallinity with temperature as shown in figure 1.

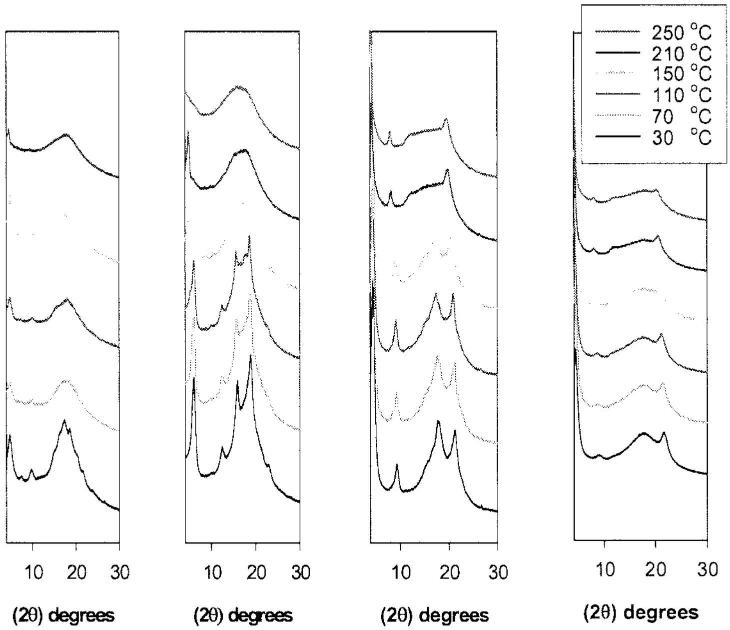


Figure 1. X-ray powder diffractograms of the polymers (**1**, **2**, **3** and **4** from left to right) as a function of temperature. All four polymers showed reversible thermal behaviour in the range 90°C-150°C. If heated to above 300°C all the peaks disappeared.

Many attempts were made at indexing the powder diffractogram to obtain information on the organisation of the molecules in the solid state by rigid body refinement and they all failed. Limited structural information on similar systems have been reported. [14] The X-ray powder diffractograms reported however showed more detail in terms of discrete Bragg peaks.

Ultraviolet photoelectron spectroscopy and energy levels. The absolute positions of the electronic energy levels was quantified using photelectron spectroscopy on films of the polymers **1-4** and on MEH-PPV as reported in [27] The differences in electronic properties between the polymers **1** and **2** and the backbone fluorinated polymers **3** and **4** confirmed a general lowering of the electronic band structure while keeping the optical bandgap properties similar.

Carrier mobility studies. The carrier mobilities and the carrier lifetimes in conducting polymers are very important issues when considering the possible performance of a given material in an application for molecular electronics. So far we have shown that the same type of polymer stays roughly invariant with respect to structural organisation and optical absorption properties upon backbone fluorination that allowed us to tune the position of the electronic energy levels. The last important point was to establish the effect of backbone fluorination upon the charge carrier mobility and lifetime. We used the PR-TRMC technique to measure this as shown in table 1. It is noteworthy that the carrier mobilities are nearly unaffected by backbone fluorination for the alkoxy substituted polymers, **2** and **4**, and that the magnitude of the carrier mobilities is similar to the reference polymer MEH-PPV. This implies that for this type of conducting polymer it is possible to tune the absolute position of the energy levels keeping all the other electronically important parameters unaffected. When compound **1** was subjected to backbone fluorination to give **3**, there was a significant decrease in the magnitude of the carrier mobility. The observed magnitude of the charge carrier mobilities for **3** is much smaller than the unusually high value observed for **1**. The observed value for **3** is however similar to the values observed for **2**, **4** and MEH-PPV.

Table 1. The minimum sum of carrier mobilities $\Sigma\mu_{min}$ (based on a carrier pair formation energy of 25 eV) and the first half life $\tau_{½}$.

Polymer	$\Sigma\mu_{min}$ ($cm^2 V^{-1} s^{-1}$)	$\tau_{½}$ (μs)
1[a]	8.90×10^{-2}	528
2	2.32×10^{-2}	4
3	1.04×10^{-2}	1
4	1.86×10^{-2}	2
MEH-PPV	2.00×10^{-2}	4

[a] data taken from ref. [14]

While the PR-TRMC method is incapable of determining which carrier type is the major contributor towards the carrier transport our results do confirm that these materials are indeed conducting polymers with high carrier mobilities and relatively long carrier lifetimes in the microsecond range. It is noteworthy that the polymer **1** aside from the significantly larger carrier mobility has a much longer lifetime than **2-4** and MEH-PPV. The values obtained by our method for MEH-PPV agree quite well with literature reports on similar systems. [29] In order to offer an explanation for the distinction of polymer **1** with respect to both the magnitude of the charge carrier mobility and the charge carrier lifetime we assume that **1** is inherently easier to purify. It was shown earlier that the purification procedure employed for **1** (recrystallisation from boiling 1,2-dichlorobenzene) increased the lifetime by orders of magnitude while leaving the magnitude of the charge carrier mobility at roughly the same level. Polymer **1** only contains hydrogen and carbon and we would like to speculate that the oxygen and fluorine atoms from the substituents are responsible for the lower values of carrier mobilities observed for **2**, **3** and **4**. Similar observations have been made for substituted phthalocyanines where the alkoxy substituted phthalocyanine exhibit much lower charge carrier mobilities in the discotic liquid crystal phase than the corresponding alkyl substituted phthalocyanine. [30]

Conclusions

We have presented the synthesis of two new polymers and have further characterised the conducting polymers using powder X-ray diffraction as a function of temperature and studied their carrier mobilities and lifetimes using the PR-TRMC technique. We provide a discussion and a comparison with known conducting polymers and show that for this series it is possible to backbone fluorinate and thus alter the position of the electronic energy levels while maintaining a high value for the charge carrier mobility. A limitiation to the applicability of the materials presented here is however a low solubility which results in a low molecular weight for the polymer product.

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