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Directional polymerisation and electronic properties of a cyanosubstituted dialkylpolyphenylenevinylene

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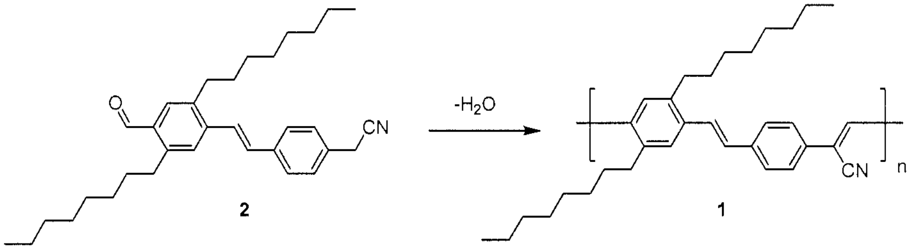
Summary

The synthesis of a monomer allowing for directional polymerisation based on the Knoevenagel condensation reaction is presented. The free running polymerisation gave a molecular weight (M_w = 24650 g mol^{-1}) polymer product. The polymerisation reaction could be followed by size exclusion chromatography (SEC) and the molecular weight of the polymer product could be controlled by termination of the polymerisation reaction at a suitable time. When terminated before completion a lower molecular weight product was obtained that could be separated into oligomers using preparative SEC. The polymer product and the oligomers were found to have very similar physical properties in terms of the optical band gaps, electronic energy levels and charge carrier mobilities as studied by UV-vis and pulse radiolysis time resolved microwave conductivity (PR-TRMC). Finally the positions of the filled energy levels were determined using ultraviolet photoelectron spectroscopy (UPS).

Introduction

Conjugated polymer materials are a class of materials that in less than three decades have gone from discovery through development to application in industrial products. Their use as the active material in light emitting devices, displays, transistors and solar cells has been demonstrated in a myriad of scientific and technical accounts. [1-4] Current efforts include the development of new materials that are obtained through rational synthesis providing stability to the polymer material or particular electronic properties.



Scheme 1. Directional synthesis of polymer **1** from monomer **2**.

In this paper I present the simple synthesis of a monomer that by condensation polymerisation provide a directional polymerisation path [5,6] (ie. Head-to-tail polymerisation) to a polyphenylenecyanovinylene type polymer [7,8]. The chemical properties of the material has been characterised using common analytical techniques and the electronic properties have been characterised with respect to the optical band gap, energy levels and carrier transport.

Experimental

Methods. Commercially available compounds were purchased from Aldrich. 4-Vinylphenylacetonitrile was obtained as described in ref. [9], 1-Bromo-2,5-dioctyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)benzene was prepared as described in ref. [5b] Four signals are missing in the ^{13}C NMR for compound **3**, and two signals for compound **2** in the region corresponding to alkyl groups. This is ascribed to accidental isochrony. Differential scanning calorimetry (DSC) on compound **1** showed no thermal transistions in the temperature interval 25-350°C.

Poly-1,2'''-(2,5-dioctyloxy-1,4-phenylene-1',2'-vinylene-1'',4''-phenylene-1'''-cyano-1''',2'''-vinylene) (1). Compound **2** (0.75g,) was dissoloved in THF (150mL) and NaOMe (0.4g, excess) dissolved in methanol (25mL) was added under argon. The colour of the solution became yellow. The mixture was heated to reflux for 24h. After cooling to room temperature methanol (200mL) was added and the mixture was acidified with HCl(aq) 37% (10mL). The orange precipitate was washed with methanol and ether before being dried in vacuum to give an orange solid. Yield: 0.6g (83%). ^{1}H NMR (250MHz, $CDCl_3$, 330K, TMS): δ= 0.89 (broad s, 6H), 1.30 (broad s, 20H), 1.68 (broad s, 4H), 2.76 (broad s, 4H), 7.09 (d, 1H, J=16Hz), 7.3-7.9 (m,8H); ^{13}C NMR (63MHz, $CDCl_3$, 293K, TMS): δ= 13.9, 22.5, 29.1, 29.4, 30.9, 31.3, 31.7, 32.9, 33.4, 112.9, 117.9, 126.3, 126.7, 127.2, 129.6, 132.1, 134.0, 137.4, 138.5, 138.9, 139.9, 140.2; SEC: $M_w = 24650$; $M_w/M_n = 3.23$.

Oligomeric-1,2'''-(2,5-dioctyloxy-1,4-phenylene-1',2'-vinylene-1'',4''-phenylene-1'''-cyano-1''',2'''-vinylene) (1). Compound 2 (15g) was dissolved in THF (200mL) and NaOMe (5g) dissolved in MeOH (100mL) was added under argon and the mixture heated to reflux. Samples were drawn and subjected to SEC analysis. The SEC trace of the oligomer product is shown in figure 1. $M_w = 3010$; $M_w/M_n = 1.309$. The crude mixture of oligomers (2.0g) was subjected to fractionation using preparative SEC and separated in five fractions. Fraction 1 was a mixture of oligomers with the heptamer being predominant as shown by MALDI-TOF. Fraction 2 was the pentamer (with presence of a little hexamer), fraction 3 was the tetramer (with a little pentamer), fraction 4 was the trimer and fraction 5 was the dimer. Fractions 1-4 were orange waxy solids and fraction 5 was a highly viscous oil. The yields of the individual fractions were: fraction 1 (0.4g), fraction 2 (0.2g), fraction 3 (0.25g), fraction 4 (0.25g), fraction 5 (0.5g).

2,5-Dioctyl-4-formyl-4'-cyanomethylstilbene (2). Compound **3** (4g, 7.2 mmol) was dissolved in TFA (100mL). The mixture has a deep yellow/red colour and was stirred while heating to near reflux temperature, water (50mL) was gradually added at such a rate that a clear solution was maintained. Water (400mL) was the added and the mixture was placed in a separating funnel and left to cool. A clear yellow oil forms at the top of the milky solution. The milky solution was discarded and the oil was washed with water. Finally the oil was taken up in a little ether that was dried using $MgSO_4$ and evaporated to give the pure product 2.7g (80%). ^{1}H NMR (250MHz,

$CDCl_3$, 293K, TMS): δ= 0.85 (s, 3H), 1.26-1.36 (m, 20H), 1.58-1.64 (m, 4H), 2.77 (t, 2H, J=8Hz), 3.01 (t, 2H, J=8Hz), 3.79 (s, 2H), 7.12 (d, 1H, J=16Hz), 7.36 (d, 2H, J=8Hz), 7.37 (d, 1H, J=16Hz), 7.48 (s, 1H), 7.56 (d, 2H, J=8Hz), 7.66 (s, 1H), 10.22 (s, 1H); ^{13}C NMR (63MHz, $CDCl_3$, 293K, TMS): δ= 14.0, 22.6, 23.4, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 30.9, 31.8, 32.2, 32.5, 32.8, 117.5, 126.0, 127.4, 128.0, 128.4, 129.6, 131.7, 132.4, 132.7, 137.0, 138.9, 141.3, 143.8, 192.7; Anal. Calcd for $C_{33}H_{45}NO\cdot H_2O$: C, 80.93; H, 9.67; N, 2.86. Found: C, 80.82; H, 9.80; N, 2.70.

2,5-Dioctyl-4-(5,5-dimethyl-,3-dioxan-2-yl)-4'-cyanomethylstilbene (3). 1-Bromo-2,5-dioctyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)benzene (71g, 143 mmol), 4-cyanomethylstyrene (22g, excess), $Pd_2(dba)_3$ (0.5g, catalyst), tributylamine (100mL) and dioxane (400mL) were mixed under argon and the mixture was degassed by rapid argon bubbling. *t*$Bu_3P\cdot HBF_4$ (0.5g, catalyst) was added and the mixture was refluxed for 3 days. After cooling the light yellow clear solution was filtered from some dark solids (Pd decomposition products etc.) and the solids were washed with ether. The combined filtrate was evaporated to give an oil and a thick caramel-like substance. Ether (1L) was added and the mixture was passed through silica leaving the caramel material on the column. Evaporation gave a light yellow solution of the product in tributylamine. Light petroleum (1L, bp:40-60°C) was added and the mixture left in the freezer overnight. A light yellow material crystallised. The product was filtered, washed with light petroleum and dried. Yield: 46g (58%). mp: 77-79°C. ^1H NMR (250MHz, $CDCl_3$, 293K, TMS): δ= 0.81 (s, 3H), 0.84-0.92 (m, 6H), 1.27-1.35 (m, 23H), 1.57-1.63 (m, 4H), 2.69 (t, 2H, J=8Hz), 2.72 (t, 2H, J=8Hz), 3.66 (d, 2H, J=11Hz), 3.76 (s, 2H), 3.79 (d, 2H, J=11Hz), 5.52 (s, 1H), 6.95 (d, 1H, J=16Hz), 7.32 (d, 2H, J=8Hz), 7.35 (d, 1H, J=16Hz), 7.38 (s, 1H), 7.45 (s, 1H), 7.52 (d, 2H, J=8Hz); ^{13}C NMR (63MHz, $CDCl_3$, 293K, TMS): δ= 14.0, 21.9, 22.6, 22.7, 23.25, 23.36, 29.2, 29.4, 29.5, 29.6, 29.7, 30.2, 31.3, 31.8, 31.9, 77.9, 99.9, 117.7, 126.7, 127.1, 127.3, 127.4, 128.2, 128.6, 128.7, 135.4, 135.7, 137.8, 138.1, 138.5; Anal. Calcd for $C_{38}H_{55}NO_2$: C, 81.62; H, 9.94; N, 2.51. Found: C, 81.83; H, 10.04; N, 2.50.

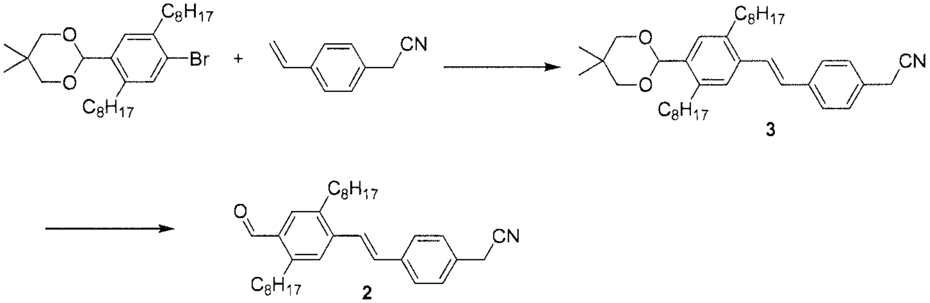
Size exclusion chromatography (SEC) and MALDI-TOF. SEC was performed in chloroform using either of two preparative Knauer systems employing a pre-column and two gel columns in succession with respectively pore diameters of 100Å and 1000Å or 500Å and 10000Å. All gel columns had dimensions of 25mmØ x 600mm. Polystyrene standards were used for molecular weight determination. The molecular weight of the purified oligomers could be accurately determined by use of MALDI-TOF employing a 2,5-dihydroxybenzoicacid matrix containing 10% wt $AgBF_4$. It was not possible to obtain MALDI-TOF data for the polymer product.

Photophysical methods. UV-vis spectra were obtained directly from the photodiodearray detector during the SEC measurements. Ultraviolet photoelectron spectroscopy was obtained on thin films of the polymer or trimer spincoated onto gold substrates from chloroform solution. The measurements employed 50eV photons from the ASTRID synchrotron at the university of Aarhus, Denmark. The experimental set-up has been described in previously. [5]

Carrier mobility and carrier lifetime measurements. Pulse radiolysis time resolved microwave conductivity (PR-TRMC) was employed for the determination of carrier mobilities. [10] The system and set-up has been described earlier [11]. An analysis of the conductivity transient gave the sum of charge carrier mobilities and the carrier half-life, $\tau_{½}$. The results of the carrier mobility measurements are shown in figure 4.

Results and discussion

Synthesis. The general synthetic procedures leading to conjugated polymers does not allow for directional synthesis where the two termini of the polymer chain have a different chemical nature. Examples in the literature where the directional approach has been employed with success are for the polythiophenes giving a highly regioregular product by either Negishi [12], Kumada [13] or stille [14] polycondensation reactions, the polyphenyleneethynylenes by Sonogashira polycondensation reactions in solution [15] or on solid support, [16] polyphenylenevinylenes by Heck polycondensation, [17] polyterphenylenevinylenes [5a] and polybiphenylenevinylenes [5b] by condensation polymerisation and polyphenylacetylenes [11b,18-20] by rhodium catalysed living polymerisation. It should be mentioned that the physical properties of conjugated polymer materials prepared by palladium catalysis can be hampered by even tiny amounts of residual catalyst in the form of metallic palladium nanoparticles.[21] The interest in a directional polymerisation are aside from the regioregularity inherent in the approach also the possibility to make multidomain molecules. This has allowed for the synthesis of dye-linked homopolymers [22a], dye-terminated polymers [22b,22c], dye-linked block copolymers [5c] and conjugated block copolymers. [11b] The synthesis of the monomer **2** is shown in scheme 2. Attempts to synthesize the monomer **2** directly from 1-bromo-2,5-dioctyl-4-formylbenzene were only partially successful as large amounts of the lower oligomers formed (mainly dimer and trimer) under the conditions of the Heck reaction. The simple protection of the aldehyde moiety as an acetal efficiently avoided the condensation problem. It was also possible to use 1-iodo-2,5-dioctyl-4-formylbenzene in the Heck reaction but this gave only a marginal improvement in the yield of **3**.



Scheme 2. Synthesis of the protected monomer **3** and deprotection to give the monomer **2**.

The deprotection of **3** could be achieved in several ways using typical acid catalysis such as THF/HCl(aq) or trifluoroacetic acid (TFA).

Table 1. The molecular weights of the fractions as determined by SEC using a polystyrene standard series and MALDI-TOF.

Fraction	**1**	**2**	**3**	**4**	**5**
***M_n*/PD (SEC)**	5056/1.37	3010/1.13	2253/1.10	1756/1.02	1314/1.00
M (MALDI)[a]	3302	2394	1941	1487	1033
λ_{max} (nm)	416	409	401	389	370

[a]The mass coresponds to the predominant molecular ion complexed with one silver ion.

The most efficient procedure was by dissolution of **3** in TFA at near reflux followed by slow addition of water. This efficiently allowed for the complete removal of neopentyl glycol. The polymerisation reaction is sufficiently slow in low boiling solvents like THF for it to be followed using SEC and stopped at a desired time (figure 1, top left). This is practical if a high yield of the short oligomers are required for preparative SEC isolation and subsequent studies.

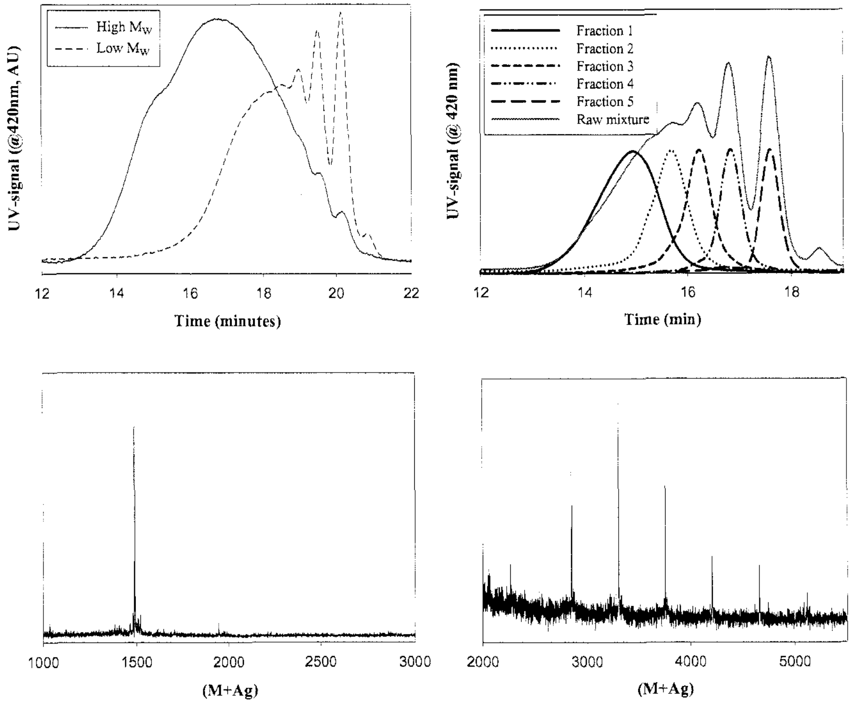


Figure 1. SEC traces of the high molecular weight product and of the oligomeric product using a column system with two columns in series with pore volumes of 500Å and a 10000Å (top left). SEC traces of the oligomeric product and the individual fractions after preparative SEC using a column system with two columns in series with pore volumes of 100Å and a 1000Å (top right). MALDI-TOF mass spectrum of fraction 4 which is the nearly pure trimer complexed with one silver ion (bottom left). MALDI-TOF mass spectrum of fraction 1 which is a mixture of higher oligomers with the heptamer as the dominant constituent (bottom right).

From the SEC chromatogram of the low molecular weight product it was possible to discern the individual oligomers up to the pentamer and possible to obtain reasonably pure fractions of the dimer, trimer, tetramer and pentamer (figure 1, top right). It was possible to obtain MALDI-TOF data for the individual fractions when using a ratio of matrix to product of 1000:1. MALDI-OF data have also been shown in figure 1 of respectively the trimer used for carrier mobility studies (*vide supra*) and of the oligomer fraction showing a dominance of the heptamer with considerable amounts of hexamer through undecamer. The analytical data have been collected in table 1.

Photophysical measurements. The UV-vis spectra of the individual oligomers show a gradual red shift of the absorption maximum as the oligomer chain length is increased towards the value for the polymer which has a λ_{max} = 420 nm. A plot of the absorption maximum as a function of the reciprocal of the number of phenylenevinylene units is shown in figure 2. The effective conjugation length is essentially reached in the oligomer fraction (ie. with the heptamer).

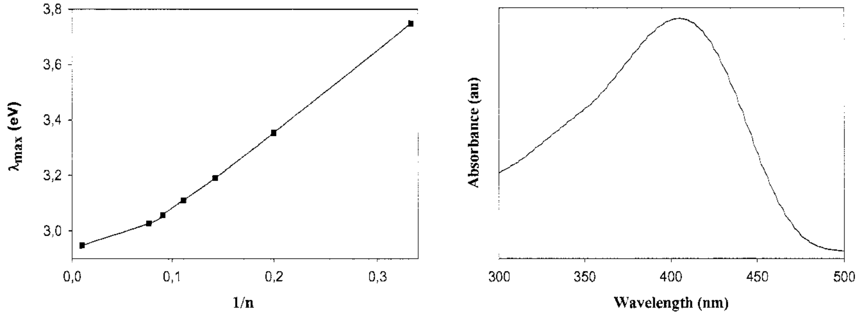


Figure 2. A plot of the reciprocal number of phenylenevinylene units. For the dimer there are three phenylenevinylene units (left). A UV-vis spectrum for fraction 2 which is mainly the pentamer (right).

The absolute position of the electronic energy levels were determined using UPS and the spectrum for **1** is shown in figure 3 along with a sketch of the electronic band structure obtained from the UPS spectrum. The values for the parameters obtained are shown in table 2 and were obtained using equations 1-5 (shown to the right of table 2).

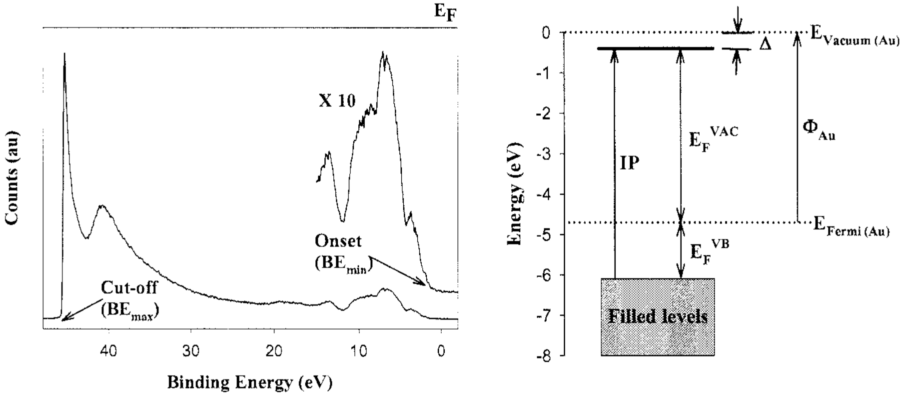


Figure 3. The UPS spectrum for a thin film of **1** on a polycrystalline gold substrate. The parameters to extract from the spectrum for the derivation of the parameters for the electronic band structure are labeled along with the position of the substrate Fermi level (left). The resulting band structure is also shown (right).

The UPS experiment involves firstly measurements on a clean substrate sample. This fixes the position of the Fermi level of the substrate and gives a value for the work function of the substrate (in this case gold) according to equation 1. The onset of photoelectrons in the case of the clean gold substrate is the zero binding energy reference level (ie. the position of the Fermi level of gold in the spectrometer). Next, a gold substrate covered with a thin polymer film is introduced and a spectrum as the one shown in figure 3 (left) is obtained. The difference between the cut-off at high binding energies (BE_{max}) and the photon energy ($h\nu$ = 50eV) now correspond to the distance from the Fermi level to the vacuum levels according to equation 2. The onset of photoelectrons towards low binding energy represents the injection barrier for holes from the gold and into the polymer material. It is the distance from the Fermi level to the upper edge of the valence band in the material and is obtained as shown in equation 3. The ionisation potential (IP) is a material constant and is obtained through equation 4. Finally the vacuum level shift (Δ) is obtained from equation 5 and represents the effect of the dipole layer formed at the interface between the polymer film and vacuum.

Table 2. Data from the photoelectron spectra for the polymer **1** on a gold substrate ($\Phi_{Au} = 4.7$ eV).

Compound	E_F^{VB}	E_F^{VAC}	BE_{max}	Δ	IP
1	1.4	4.30	-45.70	-0.40	5.70

$$\Phi_{Au} = h\nu - BE_{max} \quad (1)$$

$$E_F^{VAC} = h\nu - BE_{max} \quad (2)$$

$$E_F^{VB} = BE_{min} \quad (3)$$

$$IP = E_F^{VB} + E_F^{VAC} \quad (4)$$

$$\Delta = E_F^{VAC} - \Phi_{Au} \quad (5)$$

The general observation when introducing electron-withdrawing substituents (such a cyano or fluorine) into a conjugated polymer backbone is that the entire electronic band structure is shifted to lower energies. This is indeed observed here where the injection barrier (E_F^{VB}) is increased by ~ 0.7eV as compared to a polymer with the same structure as **1** but without the cyano group.[5d]

Carrier mobility studies. Carrier mobilities and carrier lifetimes in conjugated polymer materials are very important parameters when considering the possible performance in an application. The introduction of the cyano group to the polymer backbone was found to decrease the magnitude of the charge carrier mobility by a factor of ~ 9 when comparing to the unsubstituted polymer.[11a]

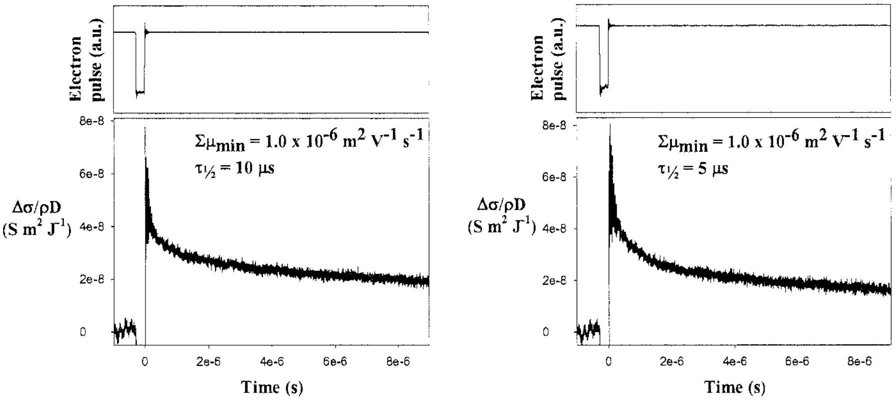


Figure 4. The conductivity transients as obtained on the polymer (left) and the trimer as obtained by preparative SEC (right). The minimum sum of carrier mobilities was obtained using a pair formation energy of 25eV.

It is interesting to note that there were negligible differences in the charge carrier mobility when comparing the polymer and the purified trimer. There were however a noticeable difference in the first half life of the charge carriers in the two samples where the half life in the polymer material was considerably longer. While there are many possible explanations for this observation it is interesting to note that the purified trimer exhibit the same carrier mobility properties as the polymer material.

Conclusions

The synthesis of a new conjugated polymer material has been presented and characterized using standard techniques. Oligomer fractions were obtained using preparative SEC. The electronic band structure and bandgap for the polymer material was determined using ultraviolet photoelectron spectroscopy and UV-vis and finally the sum of charge carrier mobilities for the polymer and a purified oligomer fraction were determined and found to be very similar in terms of magnitude but with a somewhat shorter carrier half life for the purified oligomer than for the polymer.

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