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Systematic Study of the Effects of Naphthalene and Anthracene Substitution on the Properties of PPV Derivative Conjugated Systems

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ABSTRACT: The systematic synthesis of poly(phenylvinylene) (PPV) derivatives by the Wittig−Horner reaction is reported. The phenyl units of the PPV structure are methodically substituted by naphthyl and anthryl units to form a homologous series of structures. The 2,6-attachment of the vinylene linkage on the anthryl ring provides novel structures that have not been reported before due to their synthetic inaccessibility. The introduction of naphthyl units results in a hypsochromatic shift in the absorption and emission spectra, while the introduction of anthryl units leads to a bathochromic shift relative to the naphthylene structures. The observed structural variation of the spectroscopic properties is explained in terms of a combination of the increased conjugation of the substituent acene units and the decreased electronic contribution across the vinyl linkage.

Introduction

Since the discovery that poly(phenylvinylene) (PPV) exhibited a strong electroluminescence, there have been many studies involving structural variation of the PPV polymer backbone. Despite this, there is still a great need for new materials, with improved properties, in order for this technology to fulfill its commercial potential. In many studies structural variation has improved properties, in order for this technology to fulfill its commercial potential. Therefore, this was the route chosen to synthesize structures 1−5 (Figure 1). An octyloxy-substituted PPV derivative (1) was first synthesized to allow for direct comparison of properties with later structures. The introduction of naphthyl units begins first by replacing alternate substituted phenyl units with substituted naphthyl units to give structure (2), and finally all phenyl units were replaced to produce a fully conjugated naphthalene structure (3). In the same manner as for the naphthalene structures, anthryl units are introduced into the polymer backbone first with alternating phenyl units (4) and then with alternating naphthyl units (5).

Results and Discussion

Our synthetic strategy for polymerization via the Wittig−Horner route involved synthesizing the appropriate polymeric system from the required dialdehyde and diphenosphonate ester. The synthesis of the phenyl intermediates is shown in Scheme 1. 1,4-Di-n-octyloxybenzene (6) was synthesized in 74% yield from commercially available p-hydroquinone using the method of Johnstone and Rose. All spectra and the melting point were as reported. The bromomethylation of 6 using a method similar to that reported carried out in acid-washed glassware using paraformaldehyde and KBr in acetic acid produced di-n-octyloxy-1,4-bis(bromomethyl)benzene (7) in 73% yield. The Arbusov reaction yielded 2,5-di-n-octyloxy-1,4-xylene−diethylphosphonate ester (8) in a 71% yield. The dialdehyde was produced from 6 by lithiation of the appropriate ortho positions with a n-butyl lithium−tetramethylethylenediamine (TMEDA) complex in diethyl ether followed by formylation with DMF. Any monoaldehyde side product which formed was removed by column chromatography, and the purity of 9 was confirmed by NMR spectroscopic analysis.

The synthesis route to the corresponding naphthalene dialdehyde and diphenosphonate ester is shown in Scheme 2. Again, the commercially available diol was employed as the starting material which was substituted with alkyloxy groups to produce...
1,5-bis(n-octyloxy)naphthalene (10) using potassium carbonate as a base in MEK and giving 10 in 85% yield. In the case of the naphthalene derivatives bromomethylation of the alkyloxy derivative was not successful, and the bromomethylated product was therefore produced via the aldehyde. For lithiation of 10 hexane was employed as the solvent as it proved more efficient at solubilizing the monolithiated intermediate which precipitates from solution. Formylation again with DMF afforded 11 in 24% yield. Reduction of 11 using stoichiometric equivalents of sodium borohydride produced 12, which was brominated with phosphorus tribromide to produce the desired 1,5-bis(n-octyloxy)-2,6-dibromomethylnaphthalene (13). In the Arbuzov reaction no excess of triethylphosphite was used, and 1,5-bis(n-octyloxy)-2,6-dimethylnaphthalene—bis(ethylphosphonate ester) (14) was produced in 93% yield without purification as the product was unstable.

To produce the anthracene derivatives, anthracene-1,5-diol was not a suitable starting material as it is very sensitive to oxidation. Anthraquinone-1,5-diol was chosen instead. The synthetic route employed is shown in Scheme 3. For the addition of the octyloxy side chains the same method as that used for the naphthalene products was employed, but in this case DMF was found to be a better solvent, producing 1,5-bis(octyloxy)-anthraquinone (15) in 42% yield. The reduction of the anthraquinone to 1,5-bis(octyloxy)anthracene (16) was attempted using various methods,28,29 but the reduction by sodium borohydride proved to be the most effective.27 It was found that addition of 5% water to the solvent system helped to drive the reaction to completion, giving improved yields of 64.5%. Lithiation and formylation of the 2,6-positions was carried out as before, but in the case of the anthracene substrate the conditions were changed from a 24 h reflux to a 96 h room temperature stir for the lithiation step. The resultant 1,5-bis(n-octyloxy)-2,6-anthracenedialdehyde (17) was produced in 39% yield.

The polymerization route employed is shown in Scheme 4. Studies have shown that the Wittig–Horner reaction carried out at 80 °C employing DMF as the solvent produced the longest chain polymers in the highest yields.20 Therefore, these conditions were used to produce materials 1–5.

The properties of each polymer are listed in Table 1. Number-average molecular weight values were calculated by both NMR end-group analysis and gel permeation chromatography using polystyrene standards. This study revealed that both methods gave comparable results for all the polymers except PONV, for which a much higher molecular weight was obtained from NMR.
analysis. In all other cases GPC gave a slightly higher result. It is noted that while the same synthetic methods were employed, the copolymeric structures tended to have higher molecular weights. The solubilities of the copolymers are also less, and interestingly PONV (3) is more soluble than POPV (1), while POPV−OAV (4) is less soluble than PONV−OAV (5). POPV−OAV (5) is the least soluble polymer in the series, to the extent that a suitable quality 13C NMR spectrum could not be obtained even with extended accumulations. The molecular weights of these materials are too low to produce high quality thin films which is important for device manufacture. However, oligomeric studies of a range of ð-conjugated systems have shown that the electronic properties asymptotically approach the infinite chain limit with an inverse conjugation limit dependence.30−34 In addition to electron−electron and electron−vibration coupling, excitations can be confined by backbone torsion and other morphological effects, limiting the effective conjugation length. As a result, studies have found that the electronic properties of extended polymers mirror their oligomeric counterparts with ð repeating monomer units.35 With regard to PPV type polymers, it has been shown that, in terms of electronic properties, changes caused by increasing the conjugated length saturate at ca. 5−7 repeating units.36,37 To allow for direct comparison between the polymers within this series, this converts to 15−20 conjugated bonds along the polymer backbone. The shortest oligomer POPV (1) has 15 conjugated bonds along its shortest length. Therefore, the chain lengths synthesized here are sufficient to represent extended ð-systems for this study aimed at the elucidation of the effects of structural variation on the electronic properties of the systems. Thus, while it is recognized that these systems are not truly polymeric, the phrase polymer rather oligomer is used throughout this paper.

The optical properties of the polymers are also shown in Table 1, and the absorption and emission spectra are shown in Figure 2. In both cases the maxima have been normalized to 1. Polymer POPV (1) was synthesized to allow for direct comparison of the optical properties of the later polymers in the series. It can be seen that replacement of phenyl units of the polymer backbone with naphthalene (2) results in a hypsochromatic shift in the spectra. This trend is continued in the all naphthyl polymer PONV (3). This was at first unexpected as we are introducing a more conjugated unit into the polymer backbone, and yet a blue shift characteristic of a decrease in the conjugation is observed. It can be seen that the introduction of the heavier electrophilic naphthyl units disrupts and hinders the formation of the conjugation along the backbone and as such increases the band gap and thus the absorption energy. Contrary to what has been observed above, the introduction of the anthryl units into the backbone in the structure POPV−OAV (4) results in a bathochromic shift relative to its naphthalene counterpart POPV−ONV (2). The effective conjugation is now seen to increase with the introduction of the antrhyl units. Finally, we observe that with the polymer PONV−OAV (5) the spectra are hypsochromatically shifted relative to 4 yet red-shifted relative to 2.

From the absorption wavelengths given in Table 1 we observe that the band gap increases as we add naphthalene units into

<table>
<thead>
<tr>
<th>polymer</th>
<th>λmax(abs), nm</th>
<th>λmax(em), nm</th>
<th>Stokes shift, eV</th>
<th>Mn(NMR), g/mol</th>
<th>Mw(GPC), g/mol</th>
<th>Mn(GPC), g/mol</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>POPV (1)</td>
<td>510</td>
<td>545</td>
<td>0.38</td>
<td>1745</td>
<td>1850</td>
<td>2530</td>
<td>1.37</td>
</tr>
<tr>
<td>POPV−ONV (2)</td>
<td>480</td>
<td>510</td>
<td>0.31</td>
<td>6774</td>
<td>7020</td>
<td>17150</td>
<td>2.44</td>
</tr>
<tr>
<td>POPV (3)</td>
<td>440</td>
<td>460</td>
<td>0.30</td>
<td>4237</td>
<td>7040</td>
<td>13840</td>
<td>1.97</td>
</tr>
<tr>
<td>POPV−OAV (4)</td>
<td>500</td>
<td>520</td>
<td>0.09</td>
<td>6628</td>
<td>3285</td>
<td>3310</td>
<td>1.61</td>
</tr>
<tr>
<td>PONV−OAV (5)</td>
<td>470</td>
<td>489</td>
<td>0.10</td>
<td>3285</td>
<td>3310</td>
<td>5330</td>
<td>1.61</td>
</tr>
</tbody>
</table>

The Stokes shift is the difference in energy between the λmax absorbance and λmax emission. Mn is the number-average molecular weight as determined by NMR end-group analysis and GPC. Mw is the weight-average molecular weight. Mw/Mn was calculated from GPC data.
the backbone while the Stokes shift decreases from 0.38 to 0.30 eV. For the polymers containing anthryl units, the band gap is seen to decrease while the Stokes shift also decreases greatly to 0.09 eV.

As we have shown, sequential replacement of the phenyl units by naphthyl units results in an increasing hypsochromatic shift of both the absorption and emission spectra, indicating a disruption of the conjugation by the larger naphthyl units. The replacement of the naphthyl units by anthryl in the POPV-OAV polymer reverses this trend. This behavior cannot be fully explained by steric interactions or bond torsions introduced by the substitution with bulkier aromatic units. This should induce a greater torsion or bond angle across the vinylene bond, and hence one would assume further disrupt the conjugation which would result in a hypsochromatic shift. As can be seen on going from POPV–ONV to POPV–OAV, there is no such blue shift. In order to understand this behavior, both the electronic contribution of the acene unit across the vinyl bond and the contribution of the acene unit itself to the electronic conjugation must be considered.

A study by Meier using a series of conjugated oligomers with terminal donor–acceptor substitution has shown that in these systems either a bathochromic or a hypsochromatic shift can be affected, depending on the terminal groups. The systems were modeled to predict the spectral shifts affected by various donor and acceptor groups on the oligomers. It was found that the energy \( E_{\text{DA}}(n) \) of an electronic transition in such donor–acceptor systems of \( n \) repeating \( \pi \) units can be split into two distinct and at times opposing factors: an increase in conjugation caused by the extension of the \( \pi \) systems and the electron donating/accepting contribution of the terminal groups to the linking \( \pi \) system. In the study a number of different cases were observed, depending on the relative contributions of the charge transfer compared to the increase of conjugation as the length of the conjugated linker was increased.

When the contribution of the conjugated linker is of the same order as that of the end groups, the effect of the different end groups can cause either a bathochromic or a hypsochromatic shift. This is similar to that observed for the \( \text{T} - [\pi]_n \text{-T} \) series POPV (1), POPV–ONV (2), and POPV–OAV (4) in which we approximate the interactions to a single acene unit of increasing length (i.e., phenyl, naphthyl, anthryl) to be the \( [\pi]_n \) with constant terminating group \( \text{T} \) on either side, being in the case of this series a vinylene phenyl group. The competition between the increased conjugation of the linker unit and the electron donation to the end groups results in the reversal of hypsochromatic to bathochromatic shift as a function of \( n \). Within our structures another similar series of POPV–ONV (2), PONV (3), PONV–OAV (5) occurs; in this case the \( \text{T} \) groups begin with a vinylene naphthyl linkage, and the electron donating/accepting contribution of the end groups is increased compared to the first series. We can model these series in a similar manner to Meier taking \( E_{\text{DA}}(n) \), the band gap of an infinitely long polyacene chain, as 1.3 eV.39

As can be clearly seen in Figure 3, \( E_{\text{DA}} - E_{\text{infty}} \) reaches a maximum as the acene unit goes from phenyl to naphthalene, and with further addition of fused rings the band gap begins to reduce again. The behavior of alternating bathochromatic/hypsochromatic behavior observed experimentally for the polymers can thus be observed in the approximated oligomeric model. This behavior should be enhanced by the extension of the short chains to longer polymeric chains. Meier’s model then does provide information on the variation on the polymers synthesized, albeit when considered as short chain molecules.

Interestingly, in the oligomer studies published by Meier, it was noted that in the case where the oligomer showed an initial increase in absorption energy reaching a peak value a subsequent decrease was never observed experimentally. All previously studied systems reached a minimum energy which increased again to a higher energy. This work therefore extends the study of Meier.

It can be seen that the properties can be related in a predictable way to the structural variation. The inclusion of the naphthyl group as stated earlier disrupts the conjugated backbone, hence causing a hypsochromatic shift. Opposing this, inclusion of naphthalene into the polymer backbone would cause a red shift due to the increase in conjugation by the inclusion of the more conjugated units. However, with the naphthyl inclusion the backbone disruption is by far the greater effect and thus dominates the spectral changes. Inclusion of an anthryl unit results in an increase in conjugation. This increase far outweighs further disruption in the backbone by the anthryl unit. Thus, it is the substituent tendency to aid delocalization of electrons across the vinylene linkage and therefore along the polymer chain as well as the effective increase in conjugation of the higher order acene units that must be considered. With this in mind it is easy to see how anthryl substitution does have a very different effect on the band gap of the polymer when compared to naphthyl substitution.

Because of our synthetic strategy, the inclusion of side chains on every aromatic unit should minimize any inconsistencies in the model. A further discussion of the adapted model and its observed trend is outside the scope of this paper and can be found elsewhere.40

Conclusion

A series of novel polymers containing naphthalene and anthracene groups were synthesised by the Wittig–Horner polymerization. Their absorbance and emission spectra show a hypsochromatic shift due to the introduction of naphthyl units and a bathochromic shift due to the introduction of anthryl units. The systematic changes made to each structure allows us to derive a relationship between order of the acene substituents and the properties of the polymers. The merits of the production of the systematically varied, homologous series can be seen through the ability to elucidate and understand the origin of the structure–property relationships.

Experimental Section

Characterization Techniques. NMR spectra were recorded in deuterated chloroform with tetramethylsilane (TMS) as an internal
reference. Spectra of intermediate samples were obtained on a Varian Gemini 200 instrument with an Oxford 200 superconducting magnet. The system operates at 200 MHz for ^1H and 50 MHz for ^13C spectra. Spectra of the polymerization starting materials and polymer samples were obtained on a Bruker Avance 400. The system operates at 400 MHz for ^1H and 100 MHz for ^13C spectra.

FTIR spectra were recorded at room temperature using a Perkin-Elmer Spectrum GX FTIR spectrometer. This is a single-beam, Michelson interferometer based, Fourier transform infrared spectrometer. It has a dual level optical module that is sealed and desiccated. The system is configured with a mid-infrared single source. MIR and FIR beam splitters and a DTGS detector allow the system to operate in transmission or reflectance modes.

Spectra were obtained of solid samples as KBr disks, except where otherwise stated. The spectra were measured over a range of 4000 – 370 cm^-1 with a resolution of 4 cm^-1, an interval of 1 cm^-1 and an accumulation of 64.

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cm³) was added slowly with vigorous stirring. The resulting two-phase system was stirred for an additional 30 min. The organic layer was separated, washed with 0.5 mol dm⁻³ HCl (150 cm³), saturated NaHCO₃ solution (150 cm³), and brine (150 cm³), and then dried over MgSO₄. The solution was concentrated under reduced pressure to give a brown solid. The crude product was purified by column chromatography (silica gel, DCM:hexane 1:4) and left to crystallize as a pale yellow solid (3.24 g, 24.1%); melting range: 116 °C.

1H NMR (CDCl₃, ppm): 7.78 (d, 2H), 7.65 (t, 2H), 7.59 (t, 2H), 4.07 (t, 4H), 1.84 (qui, 4H), 1.46 (qui, 4H), 1.21 (m, 16H), 0.80 (t, 6H). 13C NMR (CDCl₃, ppm): 152.85, 129.26, 126.61, 118.43, 113.96, 75.41, 60.64, 31.81, 30.38, 29.24, 26.22, 26.06, 22.63, 14.09. FTIR (KBr pellet, cm⁻¹): 2929 (br), 2932 (s), 2852 (s), 1723 (m), 1679 (vs), 1401 (m), 1378 (m), 1350 (m), 1228(s), 809 (m), 696 (vs), 606 (s), 531 (s), 392 (m), 307 (w), 2923 (w), 2917 (w), 2852 (s), 1727 (s), 1679 (s), 1401 (s), 1378 (s), 1349 (s), 1323 (m) 1049 (m), 1004 (s), 815 (s) 719 (m).

Synthesis of 1,5-Bis(n-octyloxy)-2,6-dibromomethylphthalene (12). A solution of 1,5-bis(n-octyloxy)-2,6-naphthalenedialdehyde (3.00 g, 7.4 mmol) was dissolved in absolute ethanol (60 cm³) and THF (9 cm³). Tribromide (0.6 cm³, 6.31 mmol) was added within 5 min, giving a white precipitate. The reaction mixture was allowed to warm to room temperature, stirred for 20 h, and then concentrated under reduced pressure. The residue was taken up in dichloromethane (150 cm³) and 3 mol dm⁻³ HCl (150 cm³) with vigorous stirring. The organic layer was separated, and the aqueous layer was washed twice with saturated NaHCO₃ solution (150 cm³), and brine (150 cm³), and then dried over MgSO₄. The solution was then concentrated by rotary evaporation, and recrystallized from methanol to give yellow crystals (9.56 g, 78.0%); melting range: 65-67 °C.

1H NMR (CDCl₃, ppm): 7.65 (d, 2H), 7.40 (d, 2H), 4.76 (t, 2H), 4.01 (t, 4H), 2.45 (d, 4H), 1.82 (qui, 4H), 1.46 (qui, 4H), 1.23 (m, 16H), 0.82 (t, 6H). 13C NMR (CDCl₃, ppm): 152.85, 129.26, 126.61, 118.43, 113.96, 75.41, 60.64, 31.81, 30.38, 29.24, 26.22, 26.06, 22.63, 14.09. FTIR (KBr pellet, cm⁻¹): 2929 (br), 2932 (s), 2852 (s), 1727 (s), 1679 (s), 1401 (s), 1378 (s), 1349 (s), 1323 (m) 1049 (m), 1004 (s), 815 (s) 719 (m).

Synthesis of 1,5-Bis(n-octyloxy)-2,6-dibromomethylphthalene (13). A solution of 1,5-bis(n-octyloxy)-2,6-naphthalenedialdehyde (2.00 g, 4.8 mmol) was dissolved in THF (40 cm³). Pyridine (0.18 mmol) was added, and the reaction mixture was cooled to 0 °C. Phosphorus tribromide (0.6 cm³, 6.31 mmol) was added within 5 min, giving a white precipitate. The reaction mixture was allowed to warm to room temperature, stirred for 20 h, and then concentrated under reduced pressure. The residue was taken up in toluene (65 cm³) and water (100 cm³). The organic layer was separated, and the aqueous layer was extracted twice with toluene (20 cm³). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure to give a brown solid (2.36 g, 78.0%); melting range: 65-67 °C.

1H NMR (CDCl₃, ppm): 7.65 (d, 2H), 7.40 (d, 2H), 4.76 (t, 2H), 4.01 (t, 4H), 2.45 (d, 4H), 1.82 (qui, 4H), 1.46 (qui, 4H), 1.23 (m, 16H), 0.82 (t, 6H). 13C NMR (CDCl₃, ppm): 152.85, 129.26, 126.61, 118.43, 113.96, 75.41, 60.64, 31.81, 30.38, 29.24, 26.22, 26.06, 22.63, 14.09. FTIR (KBr pellet, cm⁻¹): 2929 (br), 2932 (s), 2852 (s), 1727 (s), 1679 (s), 1401 (s), 1378 (s), 1349 (s), 1323 (m) 1049 (m), 1004 (s), 815 (s) 719 (m).
Poly(2,6-bis(n-octyloxy)-1,5-naphthalenevinylene), PONV (3). Yield: 0.087 g (44.4%) of a yellow powder. 1 H NMR (CDCl₃, ppm): 7.83, 7.35, 6.83, 4.12 1.93, 1.53, 1.32, 0.91. 13 C NMR (CDCl₃, ppm): 154.7, 126.8, 125.1, 114.0, 105.2, 68.2, 31.9, 29.4, 29.35, 29.3, 26.3, 22.7, 14.2. FTIR (KBr pellet, cm⁻¹): 2962 (s), 2923 (vs), 2853 (s), 1685 (m), 1611 (w), 1466 (w), 1407 (w), 1343 (w), 1262 (vs), 1097 (vs), 1029 (vs), 802 (s), 702 (w), 7.64, 7.25, 4.15, 2.43, 1.86. 1.63 1.33, 0.90. 13 C NMR (CDCl₃, ppm): 152.6, 151.2, 132.7, 127.6, 125.6, 124.9, 123.8, 123.4, 123.1, 121.3, 110.3, 69.6, 31.9, 29.4, 29.3, 26.5, 25.6, 22.7, 14.1. FTIR (KBr pellet, cm⁻¹): 2925 (vs), 2854 (s), 1682 (w), 1616 (w), 1468 7.76, 4.00, 1.98, 1.51 1.33, 0.90.

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Supporting Information Available: Proton NMR’s of polymerization starting materials and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

Effect of Structure on PPV Derivative Properties 7901

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