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# Spectroscopic Characterization of Novel Polycyclic Aromatic Polymers

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A series of novel polyphenylenevinylene (PPV) derivative polymers were studied by absorption and photoluminescence spectroscopies. The effect of the sequential introduction of polycyclic aromatic ring substituents into the delocalized backbone was examined with relation to hypsochromatic and bathochromatic shifting. While the replacement of the phenyl units by naphthyl units results in a substantial hypsochromic shift of both the absorption and emission spectra, their subsequent substitution by anthryl units results in a bathochromic shift. The system is modeled according to, and is found to be consistent with, a previous study of donor−acceptor polyenes of varying length. The electronic structure of the backbone is found to be a balance between that of the high electron affinity polycyclic ring system and the contribution to conjugation across the linking vinyl unit. The model is adapted based on electron affinities of the constituent units, and a clear structure−property relationship for the absorption and emission properties of the system is elucidated. The Stokes shift is examined and is seen to be well-correlated with the vinyl contribution to the electron affinity total ($EA_{total}$). The trends observed in the optical properties of the polymeric system are supported by Raman spectroscopy, whereby the spectral signature of the connecting vinyl bond is seen to soften in a fashion which is correlated with the modeled electron affinity parameters.

## Introduction

Conjugated molecular and polymeric materials have attracted significant attention over the past decades due to their potential applications in a range of technological areas. Organic dyes are well established in laser applications,[1] organic molecules and polymers have long been vaunted as candidates for nonlinear optical devices,[2,3] and, in the past decade, the observation of electroluminescence and stimulated emission from polymeric thin films has rejuvenated interest in this class of materials.[4,5]

The electronic and optical properties of conjugated systems, coupled with their mechanical properties and the intrinsic ease with which they can be processed, have made them highly desirable for the lucrative electronic industry. In addition to the practical advantages, the color tunability enables structure−property relationships to be derived to aid material optimization, as well as a fundamental understanding of the underlying physical processes in these materials.

To fully utilize the advantages derived from the use of these conjugated polymers, a means for predetermining the variation of the electronic properties as the backbone structure changes is of great importance. A relationship similar to the inverse chain length dependence seen for oligomeric series would be highly advantageous in the chemical engineering of these emissive materials.[6]

To this end, this study begins with a solubilized polyphenylenevinylene (PPV), archetype of electroluminescent polymers,[1,7] and progresses through a systematic variation of the polymeric structure in an attempt to precisely elucidate structure−property relationships for the electronic properties of these systems. The PPV derivatives examined consist of a series in which the phenyl unit is systemically replaced by higher order acene units, i.e., naphthalene and anthracene; naphthyl-and anthyrl-substituted polymers have been an area of great interest in providing a means of electronic control.[8−11] This study presents an investigation where the step-by-step substitution allows analysis with essentially a single variable, increasing number of fused rings. Initially the effect of the side chains on the polymer properties is investigated, and thus the spectroscopic properties of polymers **1** and **2** are compared (Figure 1). The principle study presents an investigation into the effects of the continual progression, from polymer **2** to polymer **7**. The meta-linked poly(*m*-phenylenevinylene) (PmPV) (**6**)[12] was investigated as an indicator of the effect of disruption of the $\pi$ conjugation along the backbone. It is proposed that the variation of the band gap, extended to the Stokes shift, can be shown to have a well-defined dependence on an empirical calculated parameter based on the electron affinity of the individual moieties present in the polymer chain, thus allowing the prediction of the band gap of further substituted PPV derivatives in the series. While the variations in the optical properties are highlighted here, the sequential replacement of phenyl components by naphthyl/anthryl moieties is anticipated to significantly influence the vibrational coupling along the backbone, having a lesser influence on the electronic conjugation. This proposed reduction in vibrational coupling should limit the avenues of nonradiative decay, thus maximizing the radiative decay, i.e., fluorescence, and thus ultimately the study of the polymeric system is aimed at exploration of structure−property relationships for electron−vibrational coupling in these systems. Optical absorption and photoluminescence spectroscopies are used to elucidate the electronic behavior, and Raman spectroscopy coupled with Stokes shift is used as a probe of the vibrational coupling.

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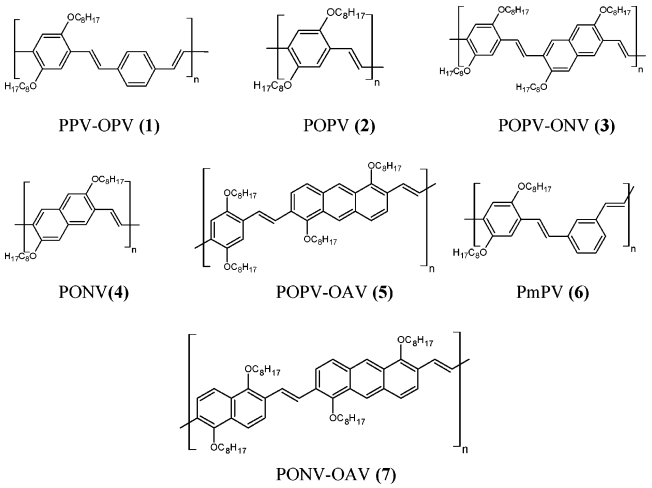


**Figure 1.** Polymer structures **1**−**7**.

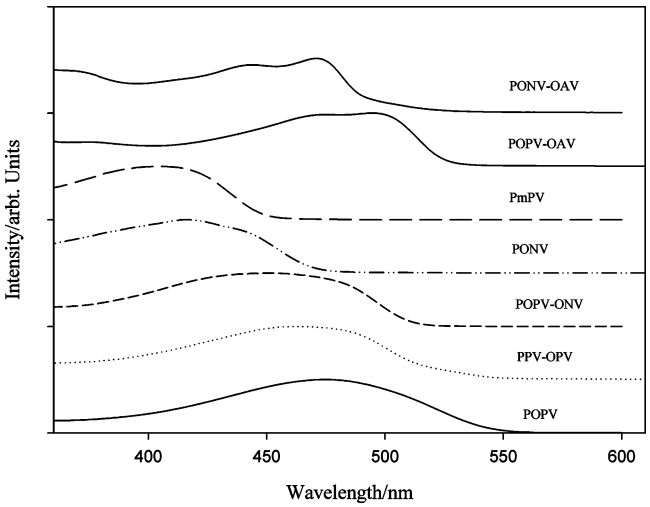


**Figure 2.** Progression of polymer absorption spectra from **1** to **7**. Spectra are offset for clarity.

## Experimental Section

The polymer systems (Figure 1) investigated were poly(*p*-phenylvinylene-*co*-2,5-bis(octyloxy)phenylvinylene), PPV-OPV (**1**), poly(*p*-2,5-bis(*n*-octyloxy)phenylvinylene), POPV (**2**), poly-(2,5-bis(*n*-octyloxy)-1,4-phenylenevinylene−1,5-bis(*n*-octyloxy)-2,6-naphthylenevinylene), POPV-ONV (**3**), poly(2,6-bis(*n*-octyloxy)-1,5-naphthylenevinylene), PONV (**4**), poly(2,5-bis(*n*-octyloxy)-1,4-phenylenevinylene-*co*-1,5-bis(*n*-octyloxy)-2,6-anthracenevinylene), POPV-OAV (**5**), poly(*m*-phenylenevinylene-*co*-2,5-bis(*n*-octyloxy)-*p*-phenylenevinylene) PmPV (**6**), and poly(2,5-bis(*n*-octyloxy)-1,5-naphthylenevinylene-*co*-1,5-bis(*n*-octyloxy)-2,6-anthracenevinylene), PONV-OAV (**7**).

Synthesis and full characterization of the novel polymers **1**−**7** have been published elsewhere.[13−15] Although all polymers are relatively short as measured by GPC, the shortest contains 10 aryl−vinyl units, and as such is sufficiently conjugated to be considered fully extended.[16] The polymers were prepared in a chloroform solution of molarity $\approx 10^{-6}$ for the absorption and luminescence spectroscopies. Concentration studies were undertaken to ensure the samples were unaffected by aggregation. Absorption spectroscopy was carried out using a Perkin-Elmer Lambda 900 UV/vis/NIR absorption spectrometer. The luminescence measurements were performed using a Perkin-Elmer LS55 luminescence spectrometer.

Raman spectroscopy was performed using an Instruments SA Labram 1B confocal Raman imaging microscope system. A helium−neon (632.8 nm/11 mW) light source was used. The light was imaged to a diffraction-limited spot via the objective of an Olympus BX40 microscope. All experiments were carried out at room temperature (300 K). For the Raman spectroscopy, the polymer solutions were examined in thin NMR tubes. A ×10 objective was used, to maximize the focal depth and so sample the bulk of the solution.

## Results and Discussion

To fully appreciate and compare the spectral changes that occur with the change in backbone structure due to either change in coupling position or addition of side chains, it is necessary to first examine the spectrum of PPV-OPV. This polymer will provide the basis for our investigation, and only slight systematic modifications will be made to this polymer to go from the well-known PPV through the novel polymers, POPV-ONV and PONV, to PONV-OAV.

The normalized absorption spectra of all the polymers can be seen in Figure 2. The principle absorption of PPV-OPV (**1**) is made up of two features at 454 and 485 nm corresponding to the phenyl ring absorption with side chain and without, respectively.[14] The structure of **1** is essentially PPV with alkoxyl side chains attached to one of the phenyl rings at the 2- and 5-positions, to aid solubility. In POPV the absorption spectrum shows a bathochromic shift with the addition of further alkoxyl side chains on the other phenyl ring (see Figure 1). The absorption peaks shift to 460 and 510 nm, respectively. This shift can be explained as being due to the steric interaction of the side chains which force the polymer to assume a more planar geometry[17] and also the electron-donating effect of the side chains. The side-chain interaction restricts torsional freedom and thus allows for an increase in the conjugation of the system leading to the aforementioned bathochromatic shift.

This slight variation of the properties due to simply doubling the side-chain number shows the ease with which the optical properties of this class of polymer can be tailored and illustrates the reason for an intensive systematic study whereby the structural variations are closely controlled.

The polymer POPV-ONV (**3**) is a variation from POPV such that alternate phenyl moieties are replaced by a naphthyl group. It should be noted, however, that all side chains were maintained in equivalent positions in the copolymer. The absorption peaks for POPV-ONV (**3**) were found to be at 460 and 480 nm. This is a significant hypsochromatic shift from POPV (**2**), which had peaks at 460 and 510 nm. This is unexpected, as it can be seen from oligomeric studies[18] that on progressing from biphenyl to naphthalene a significant bathochromatic shift is observed. The introduction of the naphthyl unit into the $\pi$-conjugated backbone appears to have the effect of partially disrupting the electronic coupling along the backbone and reducing the conjugation leading to the observed blue shift. Hypsochromatic shifts have been well documented to occur in various naphthyl-substituted polymers.[8,9,19,20] Further substitution of naphthyl units for phenyl units has the effect of a continued hypsochromatic shift leaving the absorption peaks of PONV (**4**) at 420 and 440 nm.

The absorption peaks for the first anthryl polymer, POPV-OAV (**5**), might at first be expected to follow the same trend as seen with the naphthyl-substituted polymers, i.e., a hypsochromatic shift due to the inclusion of a more conjugated subunit which leads to a disruption of the conjugated backbone. However, as can be seen in Figure 2, POPV-OAV (**5**) shows absorption features at 470 and 500 nm, longer wavelengths than those of POPV-ONV (**3**) and PONV (**4**). With the further inclusion of a naphthyl unit in PONV-OAV (**7**), prominent

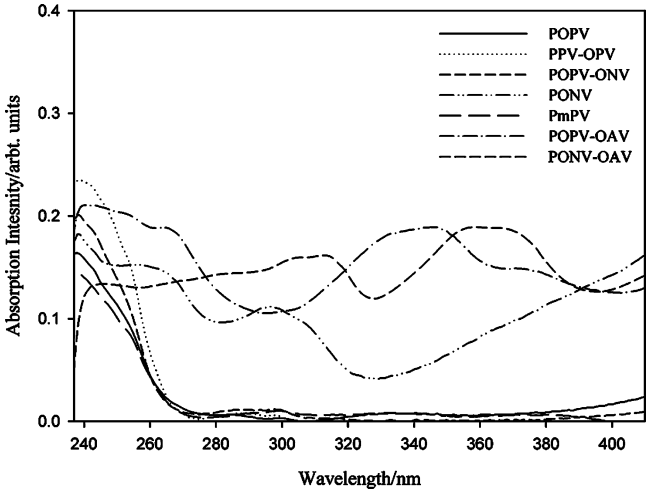


**Figure 3.** Low wavelength polymer absorption.

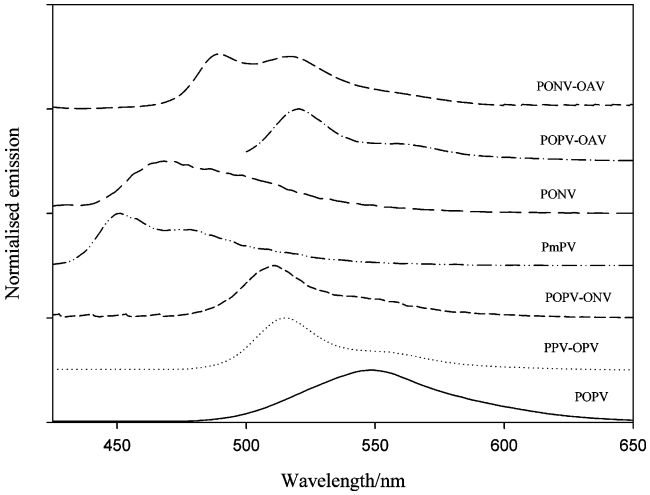


**Figure 4.** Polymer fluorescence spectra, offset for clarity.

absorption features are found at 480 and 450 nm. This is a blue shift from POPV-OAV with the inclusion of a more conjugated subsection; again this seems counterintuitive. The series from **2** to **4** (progressive inclusion of naphthyl moieties) shows a consistent blue shift, then a large red shift to **5** (first anthryl polymer), followed by a significant blue shift to **7**. It should be noted that there is no correlation between spectral shifting and polymer chain length.

The naphthyl substituent, although more conjugated than the phenyl unit, does not result in a red shift of polymer absorption, but appears to result in a reduction of polymer conjugation. The doubly substituted naphthyl polymer results in a further hypsochromic shift. The inclusion of an anthryl unit, however, results in a bathochromic shift from the doubly substituted PONV, and does appear more conjugated than the original POPV. In addition to the effect of the introduction of units of higher conjugation, there appears to be a competing effect of conjugation disruption. In order to demonstrate the effect of partial disruption of conjugation, the polymer PmPV was measured. The meta linkage means that not all the resonant structures of the backbone are conjugated, so the effect of partial disruption of conjugation is manifest.[21] Figure 2 shows the absorption spectrum of PmPV and its peak position with respect to the other polymers studied. The absorption is hypsochromically shifted to 425 nm, indicating that the disruption in the conjugation caused by the naphthyl moiety is not on the order of the disruption affected by the meta linkage. Hence the backbone remains conjugated, although the electronic coupling along the backbone is significantly hindered by the inclusion of the larger substituent moiety. As noted earlier, the anthracene-substituted polymer appears to contradict this line of thought.

In a further attempt to elucidate the degree of conjugation across the backbone, the low wavelength absorption region was examined. It should be noted that polymers that show complete conjugation show spectral features that are unique to that substance and not just an amalgamation of its component signatures. This new spectrum confirms the interaction of all parts of the polymer backbone in the conjugated system. As the electron delocalization in the polymer chain becomes less uniform, absorption features corresponding to the individual moieties comprising the polymer will become evident.

In Figure 3the lower wavelength portions of the absorption spectra of all the polymers are shown. Analysis of these will elucidate the degree of participation of the substituents, or lack of participation, in the full conjugation along the backbone. As shown earlier, the polymers comprise phenyl, naphthalene, and/or anthryl units separated by a vinyl bond. Hence if the electrons are fully delocalized across the entire polymer, fully conjugated, all components are contributing to the conjugation and there should be no appreciable absorption features relatable to isolated naphthalene or indeed anthracene prominent in the resultant spectra.

It can be clearly seen that POPV (**2**), PPV-OPV (**1**), and POPV-ONV (**3**) show negligible spectral features between 260 and 400 nm. However, PONV (**4**), POPV-OAV (**5**), and PONV-OAV (**7**) show considerably more pronounced features in this spectral window. PONV (**4**) shows absorption peaks at 270 and 300 nm which can be directly correlated with absorption features found in the naphthalene spectrum.[22] POPV-OAV (**5**) again shows strong anthracene features at 350 and 380 nm,[22] which allows one to conclude that in the latter two polymers the conjugation is being restricted to the point that the larger substituent components are acting more as single isolated moieties rather than as fully conjugated unit monomers of a polymer chain.

The fluorescence spectra for the polymers are shown in Figure 4. The intensities have been normalized and the spectra offset for visualization. In emission it can be seen that the PPV-OPV has peaks at 515 and 550 nm as compared to the double-side-chained POPV, which displays a broad peak at 545 nm. The emission shows a pattern similar to that observed in the absorption, in that the POPV peaks are bathochromatically shifted from that of the parent polymer due to the addition of the extra side chains which increase the electron-withdrawing and steric effects. It should also be noted that the emission spectrum shows much more vibrational structure due to the increased planarity of the backbone in the excited state.[23]

As in the absorption spectra, the first naphthyl substitution in POPV-ONV shifts the emission of POPV hypsochromatically. The trend is continued with the addition of a further naphthyl ring in PONV, hence giving emission peaks for POPV-ONV and PONV of 509 and 462 nm, respectively. In POPV-OAV (**5**) the emission peak is found to be at 519 nm. As is the case with the absorption, it is bathochromatically shifted from the PONV, but in this case, it is blue shifted with respect to the original POPV. The further replacement of a phenyl with a naphthyl ring gives the polymer PONV-OAV (**7**). This polymer is characterized by emission peaks at 510 and 480 nm. The highest energy peak at 510 nm is hypsochromatically shifted from that of POPV-OAV (**5**) but is highly red shifted from that of PONV (**4**).

Again, to examine the effect of a partial disruption of the conjugation, PmPV was measured. PmPV exhibits an emission

at 450 nm, which is again blue shifted from the POPV by ~100 nm. This major shift can only be attributed to the disruption in the conjugation that results from the change of the bonding position, i.e., from para to meta. The effect of partial disruption of conjugation shown by the PmPV is exhibited also by POPV-ONV and PONV, albeit to a lesser extent. It therefore can be concluded that the inclusion of the naphthyl units is prohibitive to the formation of full conjugation along the backbone. The inclusion of the anthryl units seems to incur a red shift compared to PONV and a blue shifting as compared to POPV. This seemingly anomalous behavior in the anthryl-substituted polymers suggests, however, that a more complex relationship exists.

The trends observed in both the absorption and emission spectra above do not readily correlate with variations in backbone structure as predicted simply by comparison to an oligomer study.[17] While the sequential replacement of the phenyl units by naphthyl units results in an increasing hypsochromic shift of both the absorption and emission spectra, indicating a disruption of the conjugation by the larger naphthyl units, the replacement of the naphthyl 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 of higher order acene derivatives. The introduction of the higher acene units should induce a greater torsion or bond angle across the vinylene bond. Hence one would assume that the further extension of the acene units (naphthyl to anthryl) would further disrupt the conjugation, which would result in a continued hypsochromic shift. As can be seen from POPV-ONV to POPV-OAV, there is no such blue shift.

A study by Meier et al.[24] has shown that an alternating batho-/hypsochromatic shift can be explained using a series of conjugated oligomers with terminal donor−acceptor substitution. Either a bathochromic or hypsochromic shift can be affected depending on the terminal groups. The interaction along the conjugated backbone can be separated into two distinct and at times opposing factors: that of the end groups and that of the conjugated linker. 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 $E_{DA}(n)$ of an electronic transition in such donor−$[\pi]_n$−acceptor systems of $n$ repeat $\pi$ units can be split into two parts:[19]

(1) $E_S(n)$ takes the extension of conjugation in the linking conjugated system into consideration.

(2) $\Delta E_{DA}(n)$ is a correction term for the charge-transfer effect in series with terminal donor−acceptor substitution, such that

$$E_{DA}(n) = E_S(n) - \Delta E_{DA}(n) \quad (1)$$

In the study a number of different cases were observable, depending on the relative contributions of the charge transfer compared to the increase of conjugation as the length of the conjugated linker is increased. When the contribution of the conjugated linker is on the same order as that of the end groups, a change from a hypsochromatic to bathochromatic shift is observed, or vice versa. This is similar to the case of the series POPV, POPV-ONV, and POPV-OAV, considering the $[\pi]_n$ series to be the acene unit of increasing length with symmetrically extended terminal groups T (Figure 5) which begin with a vinyl/phenyl unit. The competition between the increased conjugation of the linker unit and the electron donation to the end groups results in the reversal of hypsochromic to bathochromic shift as a function of $n$.

The series POPV-ONV, PONV, and PONV-OAV represents a similar series where the T groups begin with a vinyl−naphthyl linkage. In this case the electron-donating/-accepting contribution of the end groups is increased compared to the first series. With this case in mind it was decided to the use the equations proposed by Meier et al., for oligomers, as an approximation of the polymers synthesized. This approximation allows the model to predict the variation of the band gap of the oligomeric polymer approximations. A value of 1.0 eV was taken as the band gap of an infinitely long polyacene chain ($E_{infinity}$).[25] Using the already known values for the band gap of the nonsubstituted oligoacene series ($E_S(n)$)[18] and the polymer band gap ($E_{DA}$) values, it was possible to calculate the parameters set out in eq 1 for the series shown in Figure 5.

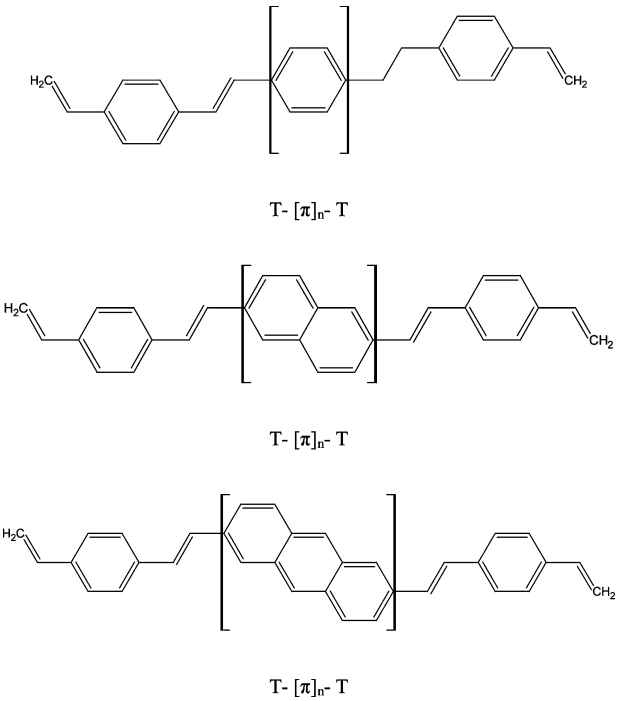


**Figure 5.** Representation of polymers **2**, **3**, and **5** as an A−$[\pi]_n$−A series with vinyl/phenyl end groups.

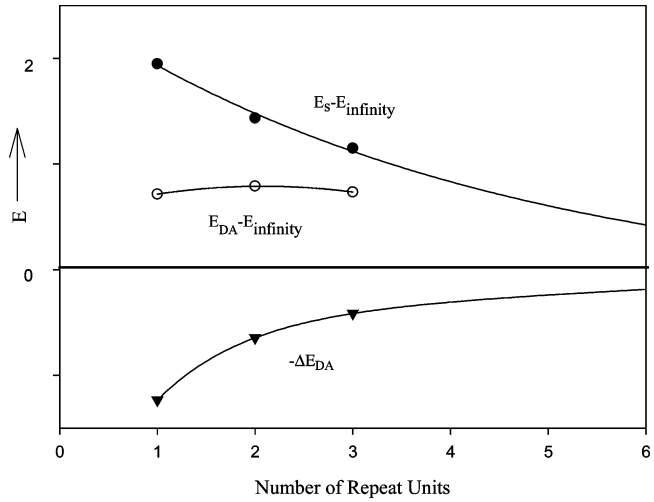


**Figure 6.** Plot of parameters outlined in eq 1 for the phenylene-terminated series.

The predicted band gaps as a function of the acene linker are shown in Figure 6 for the series POPV, POPV-ONV, and POPV-OAV. A similar behavior is observed for the sister naphthalene terminated series POPV-ONV, PONV, and PONV-OAV. The alternating batho-/hypsochromic behavior observed experimentally for the polymers can thus be predicted by an approximated oligomeric model. This behavior should be

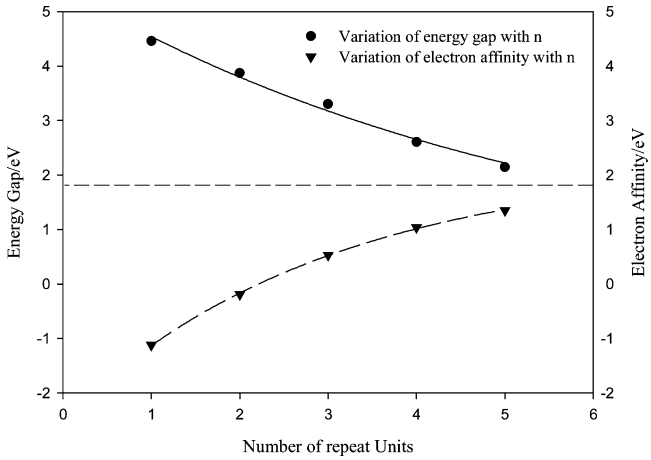


**Figure 7.** Graph of variation of band gap for the acene series and electron affinity with number of repeat units.

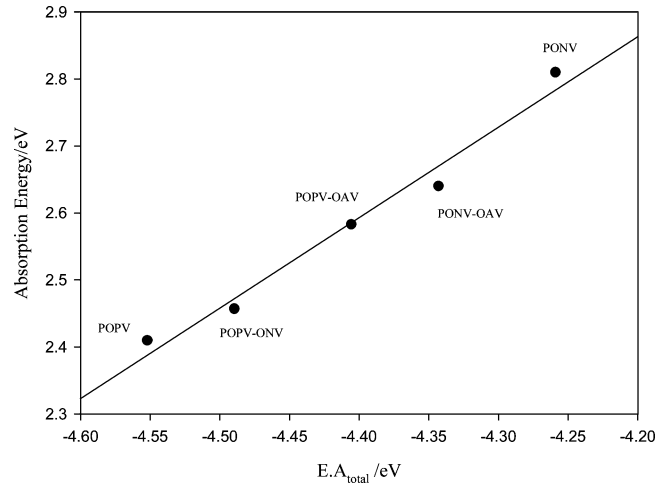


**Figure 8.** Absorption energy plotted against $EA_{total}$ for all polymers. Straight line indicates best linear fit.

extended albeit enhanced by the extension of the short chains to longer polymeric chains.

In order to extrapolate the oligomeric model to extended polymers, it is proposed that the relative contribution of a conjugated moiety can be represented by its electron affinity. Electron affinity is a measure of the capacity of an atom or molecular moiety to accept electrons and thus can be thought of as the tendency for the acene moiety to act as a donor or acceptor.

As can be seen in Figure 7, while the EA of the acene moiety increases as a function of *n*,[26] the band gap energy of the conjugated system decreases as a function of *n*,[26] where *n* is the number of repeat units. It must also be noted that the EA has a transition from a negative value to a positive value as the chain length grows from 1 to 6 repeat units. This transition from an electron donor to an electron-withdrawing species in itself shows the dramatic electronic changes that occur in the conjugated system as the chain length is increased.

The hypsochromatic shift from POPV to POPV-ONV to PONV can be explained due to the increase of electron affinity of the substituent acene unit as the number of fused rings is increased.[27] The naphthyl unit has a higher electron affinity; hence the contribution across the vinyl bond to the conjugated backbone is decreased. Thus the conjugation is effectively reduced along the whole of the chain as a result of the introduction of the more conjugated (as compared to phenyl) naphthalene units. The introduction of the anthryl unit causes a further disruption of the coupling to the terminal groups. Significantly, it is the first acene unit to have a positive EA. However, this is counteracted by the increased conjugation of the moiety itself, resulting in a bathochromic shift compared to the POPV-ONV polymer. The increased conjugation of the anthracene moiety in competition with the disruption effects is further evidenced in Figure 3 as the anthracene peaks are prominent and show their domination in the polymer spectrum. This spectral information coupled with the bathochromic shift shows that in the anthryl-substituted polymer the dominant effect is now the increased conjugation of the subunits rather than the partial disruption of the combined system. This trend is mirrored in the PONV to PONV-OAV transition.

To model the spectral changes affected by the sequential alteration of the subunits, the system can be considered in terms of the relative degree of conjugation of the polymer. The electron affinity is chosen as the parameter that can be used to represent the changes in the backbone. With reference to the Meier approach, the polymer systems studied here can alternatively be considered in terms of the electron transfer across the vinyl linkage. In this case, the conjugated linker is of constant length and the nature of the (substituent) terminal groups is varied. This allows the relative conjugation across the whole system to be gauged in terms of the electron-donating contributions of the end groups, and as such as these groups are varied, the conjugation will be increased or decreased. It must be noted that this approach does not take into account the alkoxyl side chains. Again two effects will be in competition, these being the extension of the conjugation caused by progressional inclusion of more conjugated end groups and the effect on the conjugation depending on the tendency of these groups to form a continual conjugation across the vinyl units. Hence the vinyl bond remains the constant throughout the system. Energies are expressed in terms of the electron affinities of the constituent components.

The energetics of the total system $EA_{total}$ can be separated into two distinct parts: the electron-donating/-accepting contribution of both the substituent units (i.e., phenyl, naphthyl, anthryl) to the linking vinyl bond, $EA_{vinyl}$, and the contribution of both substituent groups individually, $EA_{subst}$.

Thus

$$EA_{vinyl} = (EA_{\pi} + EA_{B}) + (EA_{\pi} + EA_{A}) \quad (2)$$

$$EA_{subst} = (EA_{B} + EA_{A})\omega \quad (3)$$

$$EA_{total} = EA_{vinyl} - EA_{subst} \quad (4)$$

$EA_{\pi}$ is the electron affinity of the linker vinyl unit, and $EA_A$ and $EA_B$ are the electron affinities of the substituent end groups. $\omega$ is a constant which compensates for the fact that the interaction of the nearest-neighbor substituent is considered rather than the interaction of the extended chain.

The dominating factor in $EA_{total}$ is $EA_{vinyl}$, which accounts for the interaction of the respective end groups with the vinylene linkage. $EA_{subst}$ takes into account the extension in the conjugation by the continual replacement of the lower order acene moieties with higher order, larger acene groups. This amalgamation of these contributions leads to an empirical electron affinity value that can accurately describe the variation in the electronic system due to the two, at times opposing, or alternatively the effect of increasing and deceasing the conjugation of the system.

As shown in Figure 8, the absorption energy plotted against $EA_{total}$ yields an approximately linear relationship. Earlier it was

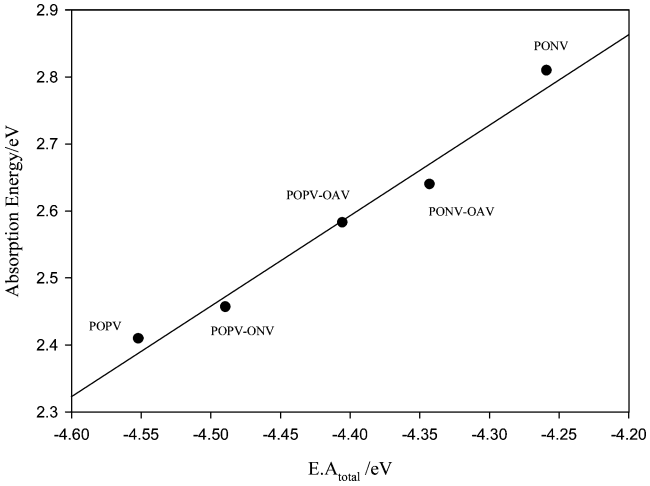


**Figure 9.** Emission energy plotted against electron affinity. Straight line indicates best linear fit.

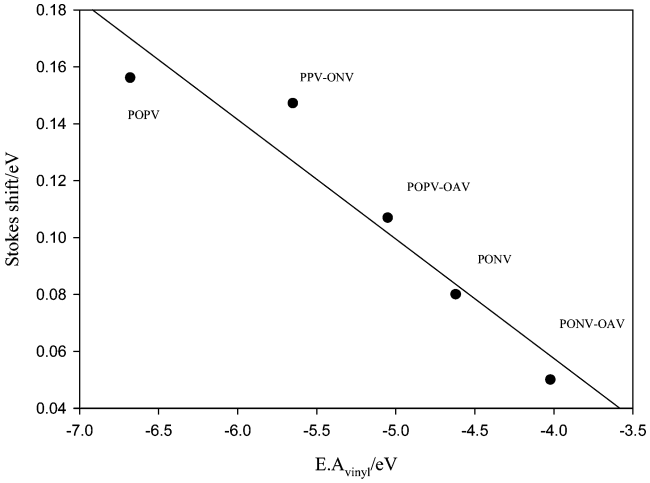


**Figure 10.** Plot of Stokes shift versus $EA_{vinyl}$.

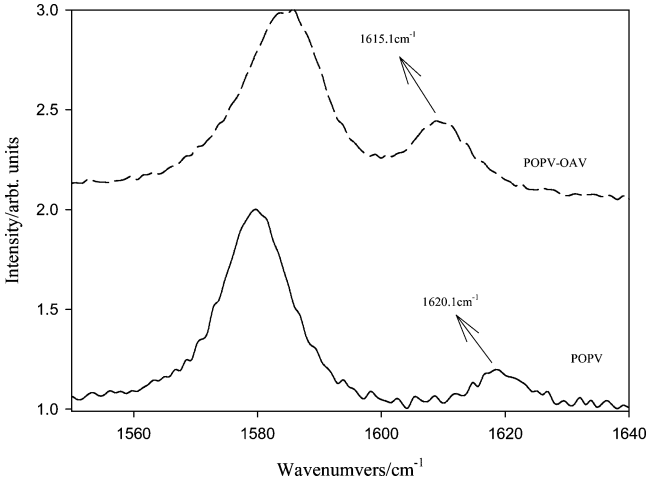


**Figure 11.** Normalized Raman spectra of the polymers.

observed that the absorption and the emission of POPV-OAV did not follow the trends that might be expected from electronic properties of the acene oligomeric series.[18] It can now be seen that the properties can be related in a predictable way to the structural variation. Using the combination of electron affinities, it is possible to get a better evaluation as to the state of the conjugated system. The inclusion of the naphthyl group as stated earlier disrupts the conjugated backbone, hence incurring a hypsochromatic shift. It was assumed this was the single and only manifestation of the substitution, but further investigation shows that along with the blue shift due to the disruption in conjugation there is also a red shift which can be attributed to the increase in conjugation by the inclusion of the more conjugated naphthalene units. However, with the naphthyl inclusion the backbone disruption is by far the greater effect and thus dominates the spectral changes. As can be seen from the values for $EA_{subst}$, an increase in this parameter represents an increasing conjugation of the substituted units. However, it must be noted that this is only an average value for the whole of the molecule. Locally specific EA values may be higher or lower, but in considering the molecular band gap of a fully conjugated molecule this is an accurate way to describe the variation in conjugation along the backbone.

Inclusion of an anthracene unit results in an increase in conjugation, which is accurately mirrored in $EA_{total}$. This increase far outweighs the further disruption in the backbone by the anthracene. The anthracene acts almost as an isolated molecule, and spectral features at 380 nm confirm this. Analysis of the structural makeup of the monomer of POPV-OAV shows that only 10 carbon atoms are present in the vinyl and phenyl units in comparison to the 14 carbons present in anthracene. With this in mind and the corresponding electron affinity of the anthryl moiety (0.530 eV), it is easy to see how the anthryl substitution does have a massive effect on the band gap of the polymer.

It should be noted that the effect of side chains on the EA of the substituents has not been included as the relative effect could not be gauged with significant accuracy to allow the differentiation between acene units with alkoxyl side chains and without, although it is known that the side chains, being electron donating in nature, have a red-shifting effect and thus reduce the EA of the units. Also, this effect would most likely have the strongest effect on the phenyl unit.

Figure 9 shows the variation of the emission energy with $EA_{total}$. It can be seen that there is also a linear correlation, as was seen with the absorption in Figure 8. Although this is not an exact calculation of the combined electron affinities of the system, it does succeed in predicting the spectral shifts affected by the substitutions, by inclusion of a two-factor equation which works as an empirical guide to the conjugation of the system.

In Figure 10, the Stokes shift for the polymers is plotted against the parameter $EA_{vinyl}$. Although an exact linear dependence is not inferred, a correlation is clearly evident. The trend is an indication that, similar to oligomeric systems,[18] a correlation can be established between the backbone structure, the electronic properties, and the vibrational structure, leading to design principles to control nonradiative decay routes.

In an effort to reinforce the empirical relationship found, using the electron affinities, Raman spectra of all the novel polymers were obtained. Figure 11 shows the normalized room-temperature Raman spectra for all the polymers. Since the electron affinity parameter contained a term that is representative of the variation of the contribution of the aryl constituent to the formation of the vinyl bond, it was decided to thoroughly examine the variation in the position of the vinyl stretch, at $\sim$1620 cm$^{-1}$ for POPV,[28,29] as a function of the backbone substituent.

As can be seen from Figure 11, as the higher conjugated acene units are inserted into the backbone of the polymer, there is a consistent softening of the vinyl stretch until in the PONV and PONV-OAV it is almost masked. The precise vinyl positions were determined by fitting the Raman spectra with Gaussian/Lorentzian functions, and they were found to be 1620.1 cm$^{-1}$

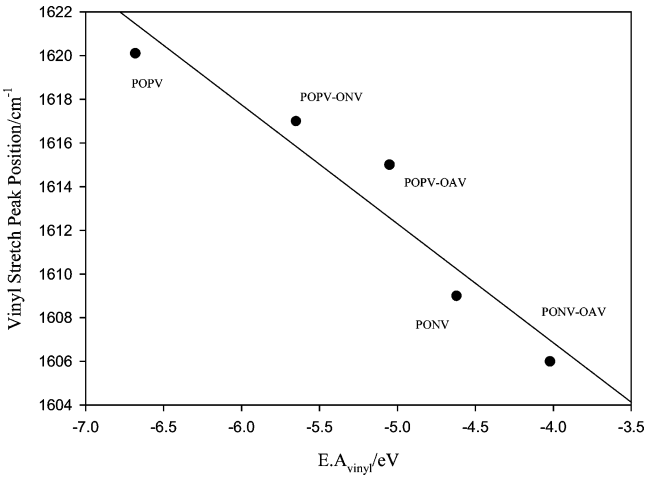


**Figure 12.** Plot of $EA_{vinyl}$ against spectral position of the vinyl stretch.

(POPV), 1616.3 cm$^{-1}$ (POPV-ONV), 1615.1 cm$^{-1}$ (POPV-OAV), 1610.3 cm$^{-1}$ (PONV), and 1607.0 cm$^{-1}$ (PONV-OAV). Thus the introduction of the high EA acene units affects an electron withdrawing from the vinyl bond, resulting in a systematic softening of the Raman mode. Figure 12 clearly shows a correlation between the vinyl vibrational frequency and the model parameter $EA_{vinyl}$.

This plot significantly shows that the parameter $EA_{vinyl}$ can indeed be used as an accurate representation of the variation of the vinyl bond as the larger, higher electron affinity units are substituted into the chain. A polymer with a chainlike structure will be limited by the weakest link, and thus the limiting of the conjugation across the vinyl bond will hinder the electron−phonon coupling being distributed across the entire polymer backbone. It is becoming apparent that there is a correlation between the electronic structure and the vibrational activity in the novel polymer systems, suggesting that the vibrational characteristics can be tailored akin to the electronic. In Figure 10 it was demonstrated that the Stokes shift, a manifestation of electron−vibrational coupling, can be correlated to the $EA_{vinyl}$ parameter. By extension, the Stokes shift is well-correlated with the vinyl bond vibrational energy and this relationship has its origin in the vibrational coupling along the polymer backbone. This ability to tailor the vibrational characteristics of the systems would potentially allow the optimization of the radiative yield through the elimination of avenues that are open for nonradiative decay.

## Conclusion

In this study empirical relationships have been found to accurately predict the band gap of a series of complex polymer systems. Linear relationships were found to be in evidence when the band gap of the polymer was plotted against the model parameter $EA_{total}$. This parameter came from an extension of the model of donor−acceptor polyenes by Meier et al. The polymers were first approximated by oligomers to show that the Meier model could explain the trends observed in the polymer series. In essence the continued substitution of the phenyl units for higher conjugated acene units results in the variation of $\Delta E_{DA}$, a charge-transfer term. The electron affinities of the constituent units are employed as a means to describe the conjugation relationship across the polymer backbone. The EA graphs resulted in a linear relationship with band gap and hence the formulation of structure−property relationships for complex polymers akin to the inverse conjugation−length relationship found in short-chain oligomers. The spectroscopic study does indicate that indeed there is a significant influence on the electronic structure of the polymers by the acene substitution. The observed correlation of the Stokes shift to the EA parameters is an indication, however, that the changes to the electronic structure as a result of the structural progression could be mirrored in the vibrational structure. Moreover, the use of Raman spectroscopy further reinforces the electron affinity approach as the softening of the vinyl bond and the electron affinity parameter accounting for the vinyl bond are seen to be well correlated.

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