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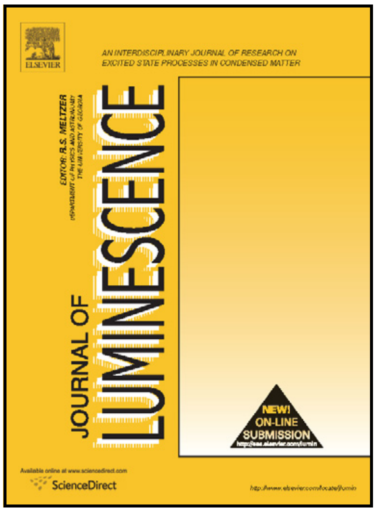

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Kinetic Studies of the Photo-Degradation of Poly Arylene Vinylenes

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Abstract

The kinetics of the degradation of a homologous series of Poly phenylene vinylenes in which the phenylene units of the PPV structure are systematically substituted by naphthyl and anthyrl units is presented. Degradation is monitored according to the decay of the long wavelength absorption maximum upon illumination with UV radiation. Compared to Toluene solution, the photo-degradation is seen to be accelerated in Chloroform solution. All decays are fitted with first order kinetics. It is found that all substitutions improve the stability of the vinylene polymers against decay. In particular the highly electro-negative naphthyl group serves to drastically increase the stability due to electron depletion across the vinyl bond. The decay rate is shown to correlate well with the variation of the electronic properties of the backbone and with the reduction of vinylene bond strength as measured using Raman spectroscopy.

Keywords: Poly Phenylene Vinylene, PPV, Poly aryl vinylenes, Vinylene Degradation.

1. Introduction

Degradation of π conjugated polymers in optical devices has been shown to be a major obstacle with regards to long-term photo-active stability [1]. Devices in operation are subject to a decrease in luminescence over time with the associated formation of dark spots. This degradation continues until the device fails [2,3]. Studies have shown that substitution with electron withdrawing or donating substituents can alter the rate of degradation of electroluminescent polymers [4,5,6]. It has been found that substitution with electron donating alkyloxy side chains increases the rate of degradation of the polymer [4], while phenyl or cyano electron withdrawing substituents lead to a decrease in the rate of degradation, particularly if the substituent is placed on the vinylene bonds [5, 6]. Trifluoromethyl substituted compounds have been shown to be particularly stable towards photo-oxidation accentuating the benefit of electron deficient vinylene linkages and pointing towards the vulnerability of this moiety to degradation [7].

Recently, the synthesis of a series of poly(aryl vinylene) derivative polymers in which aromatic units are systematically substituted with naphthyl and anthyrl units was reported [8]. The electronic properties have been shown to be systematically variable as a result of the variation of the relative contributions of each aromatic unit to the π-electron backbone conjugation and the degree of communication across the linking vinylene units [9]. Whereas the larger acene moieties add greater π-electron contributions, their electron withdrawing character reduces the communication across the vinyl bond. It was demonstrated that the systematic variation of the vibrational coupling along the backbone results in a systematic decrease in the non-radiative decay rates and thus an optimisation of the radiative yield. The systematic variation of the electron density of the vinylene bond of the polymer series by the introduction of naphthalene and anthracene moieties into the backbone [9, 10, 11] suggests that the photo-active stability can be similarly improved. This report presents a systematic study of the relative stabilities of polymers 1-6 (Figure 1).

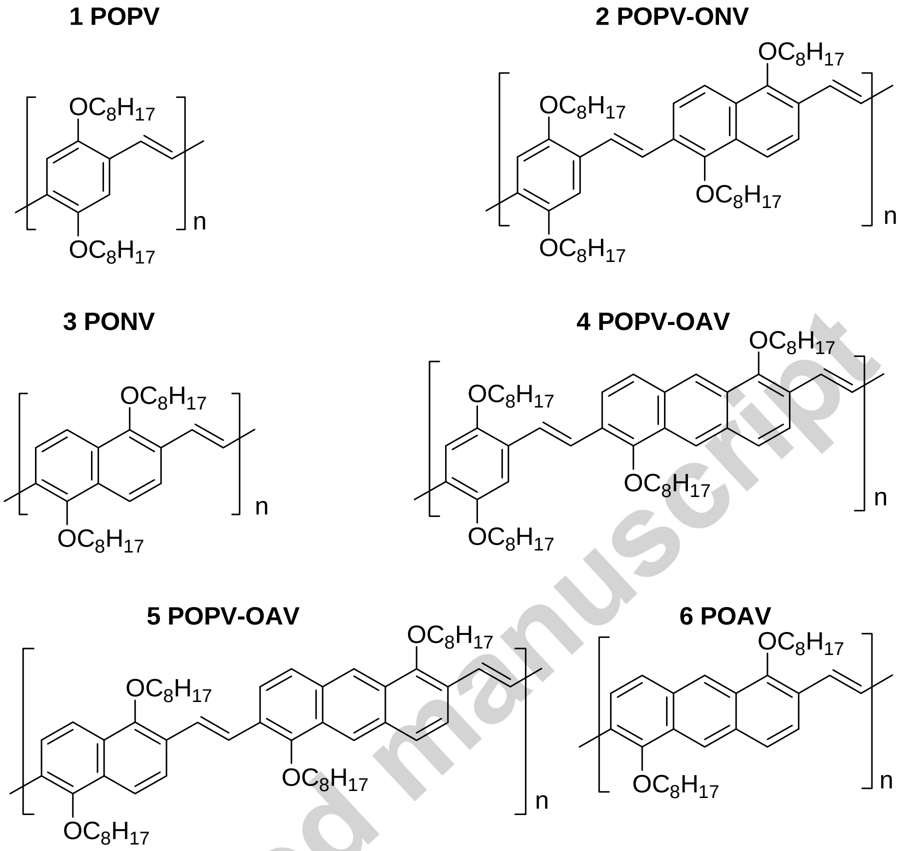

Figure 1. Polymer structures 1-6

The mechanisms and results of such degradation in conjugated polymers have been studied and presented at length in the literature [12]. In photo-oxidation studies of PPV derivatives, it was noted that the rate of decay decreased upon de-oxygenation [12] or on adding a known singlet oxygen ($^{1}\Delta_{g}$) scavenger such as diazabicyclo[2, 2, 2]octane (DABCO) [6]. Also the production of singlet oxygen was confirmed by its phosphorescence [12] and by electron spin resonance spectroscopy (ESR) spin tap experiments [4]. Other studies of the degradation process yielded spectroscopic evidence that carbonyl groups such as aldehydes were produced during the process [13, 14].

This evidence for the production of singlet oxygen by the excited polymer and its effect on the rate of reaction, together with knowledge of the chemical species produced, led to a proposed mechanism of the degradation. Upon excitation of the conjugated system, energy transfer occurs to molecular oxygen to yield singlet oxygen, whereby the excited state of the polymer is quenched. On production of singlet oxygen, a $2_\pi+2_\pi$ cycloaddition to the vinylene bond occurs, forming a dioxethane intermediate which cleaves to yield two aromatic aldehydes [12]. At the same time, a similar mechanism was proposed which involved singlet oxygen addition across the vinylene bond yielding oxygen radicals which react further with the side chains to produce aldehydes, alcohols and esters [15].

Later studies have questioned the role of singlet oxygen as the main intermediate in the photo-oxidation of luminescent polymers as the degradation rate had been shown to be unchanged by the addition of many known singlet oxygen sensitizers such as rose bengal, methylene blue and fullerenes [16]. Also the process was observed to take place on heating in an oxygen atmosphere in the absence of light [17]. 1,4-diazabicyclo[2, 2, 2]octane (DABCO) was found to quench the triplet excited state of the polymer thus limiting the formation of singlet oxygen in the previous studies [16]. It was concluded that the triplet excited state of the polymer must be responsible for the degradation when it reacts with oxygen species such as triplet molecular oxygen ($^3\Sigma_g^-$) or the superoxide radical anion (O_2^-).

Chambon *et al.* proposed that the ether groups provide the most photo-oxidisable region of the polymer and that a proton is extracted from the carbon to the oxygen by an unassigned radical, producing a macroalkyl radical which reacts with molecular oxygen to start a free radical chain reaction which breaks down the polymeric chains to produce a series of oxygen-containing functional groups [17]. The proposed mechanism succeeds in accounting for the multitude of oxygenated groups which have been identified spectroscopically [12, 17].

Many mechanisms for the photo-degradation of PPV derivatives have been proposed which account for the degradation of the polymer causing chain scission, chromophores replacement and the formation of oxygen-containing functional groups. The main consensus is that the triplet excited state of the polymer ($^{3*}PPV$) is the initiating reactive intermediate which can react through a number of pathways resulting in the degradation of the polymer and that molecular oxygen plays a pivotal role in the process.

From the summary above it can be seen that there a number of different routes by which the polymers of the series presented here may degrade, and indeed any combination of the above degradation pathways may be responsible for the observed changes in the electronic behaviour of the polymers outlined above. While the details of the mechanism of degradation are not agreed upon, there is no doubt that it is radical based.

To this end, a study of the accelerated degradation of the vinyl bond due to the presence of the Cl^- radical has been undertaken. It has been shown that the presence of Cl^- assists the UV photo-degradation of the vinyl bond and as such should allow larger variation in the degradation rates [18a, 19a]. The object of the study presented here is to explore whether the structure property relationships established for the photo-physical properties of the homologous polymer series extend to their photochemical properties and more importantly whether the tailoring of the vinyl bond strength can be employed to reduce photo-active degradation.

2. Experimental

The synthesis and characterisation of the polymers (**1-6**) has been described elsewhere [8]. 2×10^{-5} M solutions of the homo-polymers POPV (**1**), PONV (**3**) and POAV (**6**) and 1×10^{-5} M solutions of the co-polymers POPV-ONV (**2**), POPV-OAV (**4**) and PONV-OAV (**5**) were prepared in distilled chloroform. Electronic absorption spectra were obtained on a Varian Cary 50 scan single beam spectrophotometer which covered the range 190 - 800 nm with a Xenon lamp as light source. The 1 cm cuvette which was fitted with a Teflon cap was repeatedly irradiated using a using a UVP UVM-57 lamp (302 nm, 6 watt) at a distance of 20 cm for five minutes prior to subsequent spectra being obtained. The photolysis was continued until 270 minutes had elapsed or the sample had degraded to such an extent that little change in absorbance was seen on further irradiation. Two control samples were examined in toluene at the same concentrations.

Raman spectra where obtained in chloroform solution on an Instruments S.A. Labram 1B spectrometer which is a confocal Raman imaging microscope system. A Helium-Neon (632.8 nm, 11 mW) laser was used. The light is imaged to a diffraction limited spot via the objective of an Olympus BX40 microscope. Further detail on the Raman study can be found in [9].

3. Results and Discussion

The consequence of the degradation pathways outlined above can be observed in solution by observing changes in the absorption spectra upon excitation. Successive periods of photolysis of a sample have been shown to cause a decrease in absorption with a concomitant blue shift of the spectrum, resulting from macromolecular chain scission of the polymer backbone [2, 12]. As it is widely accepted that the primary degradation takes place at the vinylene bond, the concentration of the homo-polymers were doubled with respect to the co-polymers, giving a series of solutions in which the concentration of the vinylene bonds are constant. The results of successive photolysis times of 5 minutes on a sample of a POPV (**1**) solution in chloroform are shown in Figure 2.

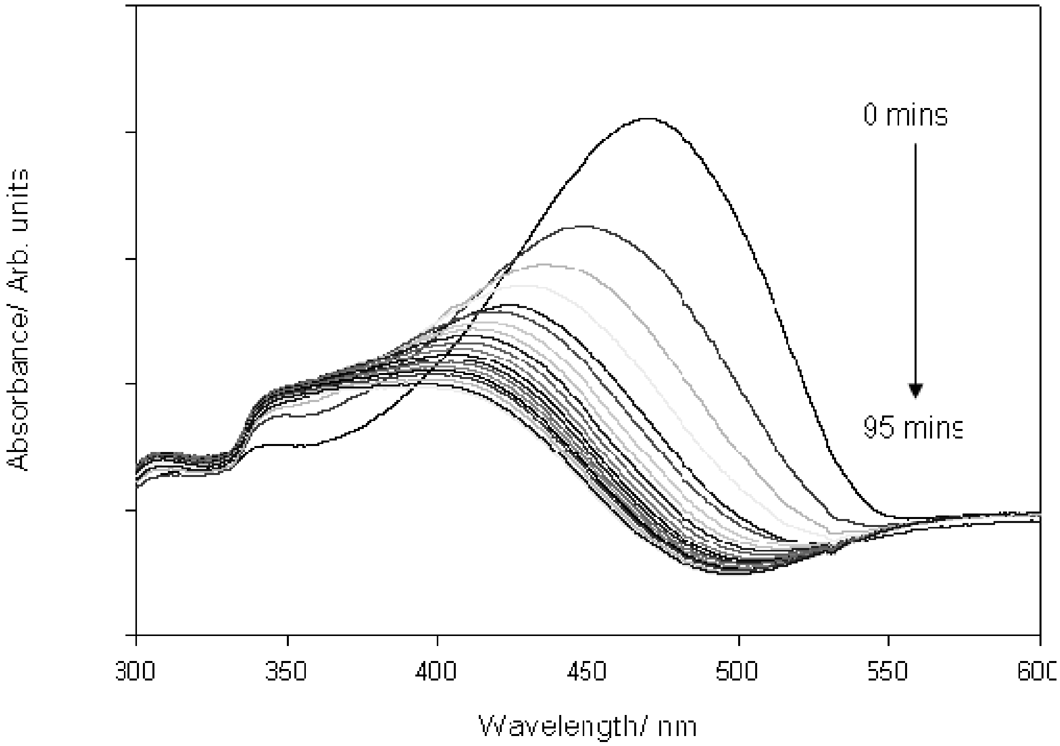

Figure 2 Degradation of POPV (**1**) in solution upon successive 5 minute irradiations.

The nature of the decay observed is consistent with results already published [2, 17]. However, in addition to the degradation of the main absorbance peak, Atreya *et al.* reported the appearance of a peak at *ca.* 284 nm in the photo-degradation of MEH-PPV which was attributed to a carbonyl product [2]. Such an increase in absorbance was not observed in this study.

The gradual decrease of the main absorption peak along with its continuous hypsochromatic shift is consistent with a degradation mechanism resulting in chain scission. The absence of an isosbestic point suggests mechanistic complexity.

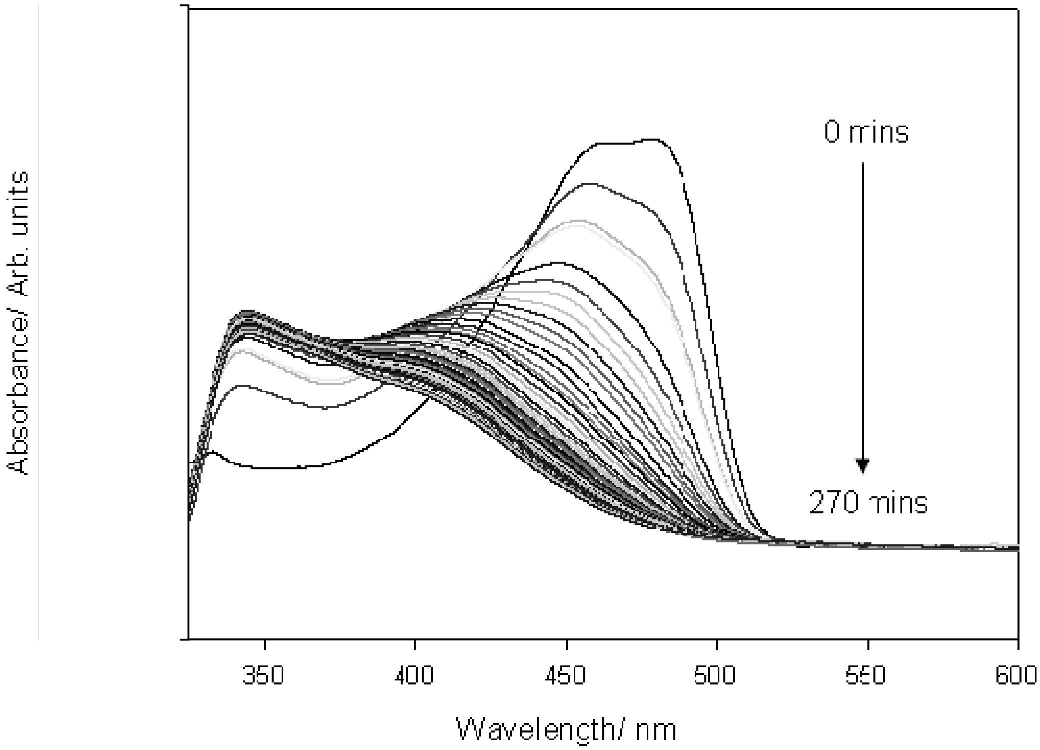

Figure 3 Degradation of POPV-ONV (**2**) upon successive 5 minute irradiations.

The photo-degradation of the co-polymer POPV-ONV (**2**) is shown in Figure 3. Again the main band is seen to decrease in intensity, while a hypsochromatic shift is also observed. There is a steady increase in absorbance of a peak at *ca.* 345 nm until a photolysis time of 100 minutes, after which the intensity is seen to decrease steadily. The sample is observed to degrade more slowly than POPV (**1**) and irradiation was continued until 270 minutes to achieve a similar degree of degradation.

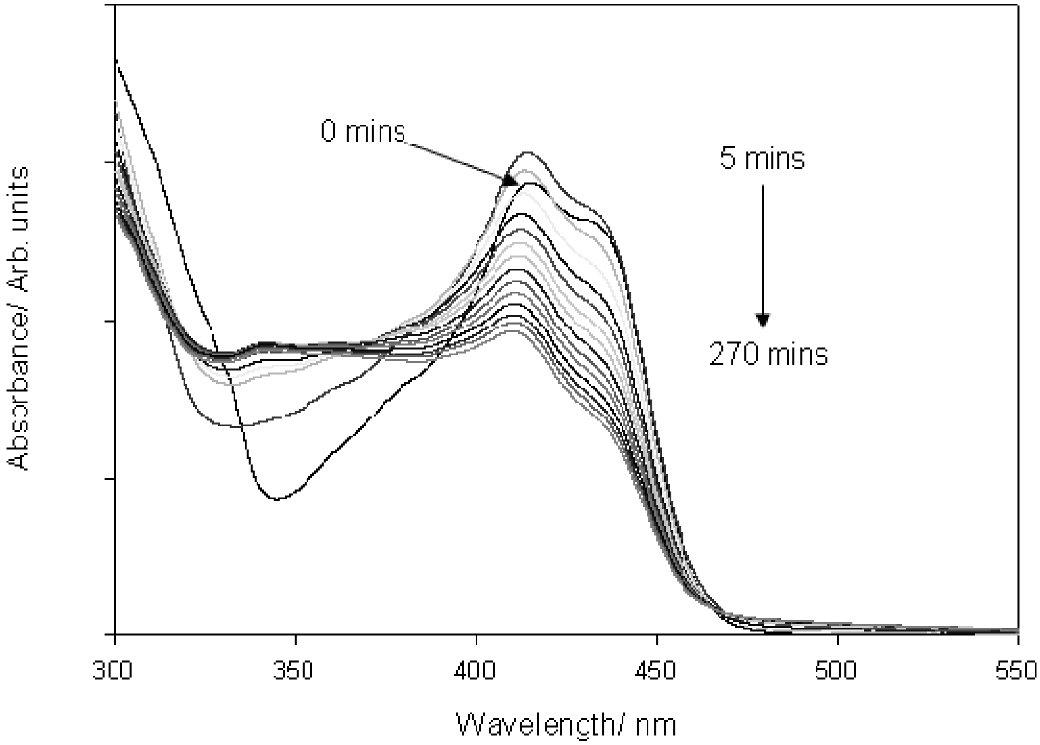

Figure 4 Degradation of PONV (**3**) upon successive 20 minute irradiations.

A sample of PONV (**3**) underwent the same photolysis and the results are shown in Figure 4. Upon excitation with UV light the absorbance of PONV (**3**) is seen to increase initially to give a new maximum which then decreases steadily in intensity upon further irradiation. A slight blue shift is seen, but this shift is much less pronounced than what has been observed for the previous polymers. The initial increase in absorbance of the main band is curious and may be due to photoisomerization of any *cis* vinylene bonds to the *trans* geometry. Katayama *et al.* reported the conversion of all-*cis* PPV to the all-*trans* isomer upon irradiation with UV light with a photolysis of 150 seconds. The *trans* isomer was seen to have a greater absorbance while its maximum was red shifted [10]. The rate of PONV **(3)** degradation was much less than that observed for the previous polymers. Very little change was observed at 5 minute irradiation intervals so every fourth scan is shown in Figure 5 (i.e. 20 minutes of photolysis between each trace).

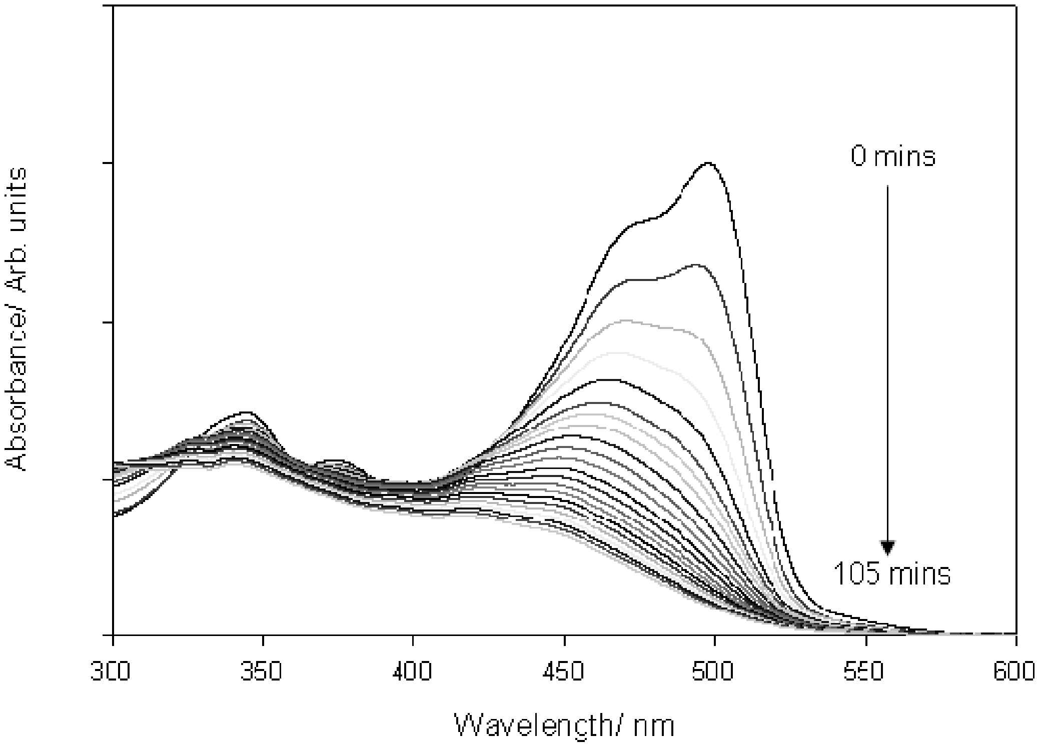

Figure 5 Degradation of POPV-OAV (**4**) upon successive 5 minute irradiations.

The photo-oxidative decay of POPV-OAV (**4**) is shown in Figure 5. The main peak of the spectrum has two distinctive vibronic bands. The longer wavelength band degrades at a much greater rate than the shoulder peak. The rate of decay of POPV-OAV **(4)** is faster than that observed for POPV-ONV (**2**) and PONV (**3**) and sufficient decay has been observed to stop the photolysis after 105 minutes of irradiation.

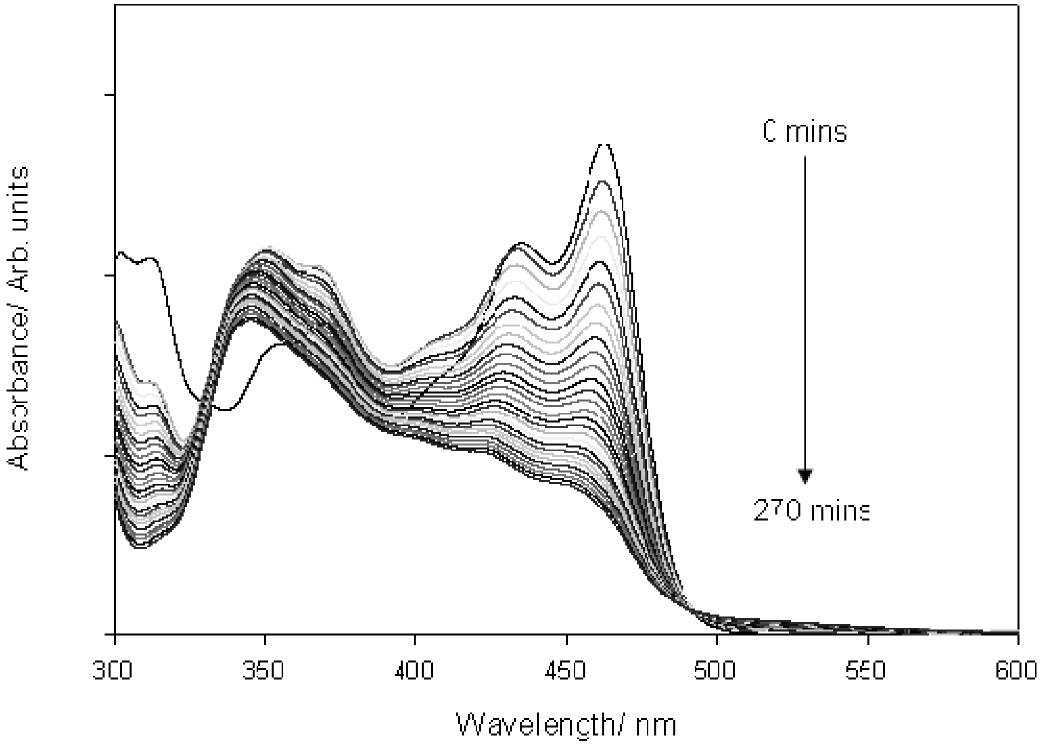

Figure 6 Degradation of PONV-OAV (**5**) in $CHCl_3$ solution upon successive 10 minute irradiations.

The photo-degradation of PONV-OAV (**5**) is shown in Figure 6. In the case of this sample, very little blue shift is observed, as the effective conjugation across the backbone is already limited so chain scission has a lesser effect. A large increase in absorption is seen at *ca.* 350nm after 20 minutes of photolysis after which this peak is seen to start to decrease slowly. A band at *ca.* 310 nm is also seen to decrease rapidly after the initial irradiation and then this band is seen to decease slowly upon further irradiation. While two main bands are also observed for this co-polymer, both rates of degradation are similar. The rate of degradation of the sample is relatively slow and every second trace is shown in the graph. Therefore 10 minutes of photolysis has elapsed between each curve.

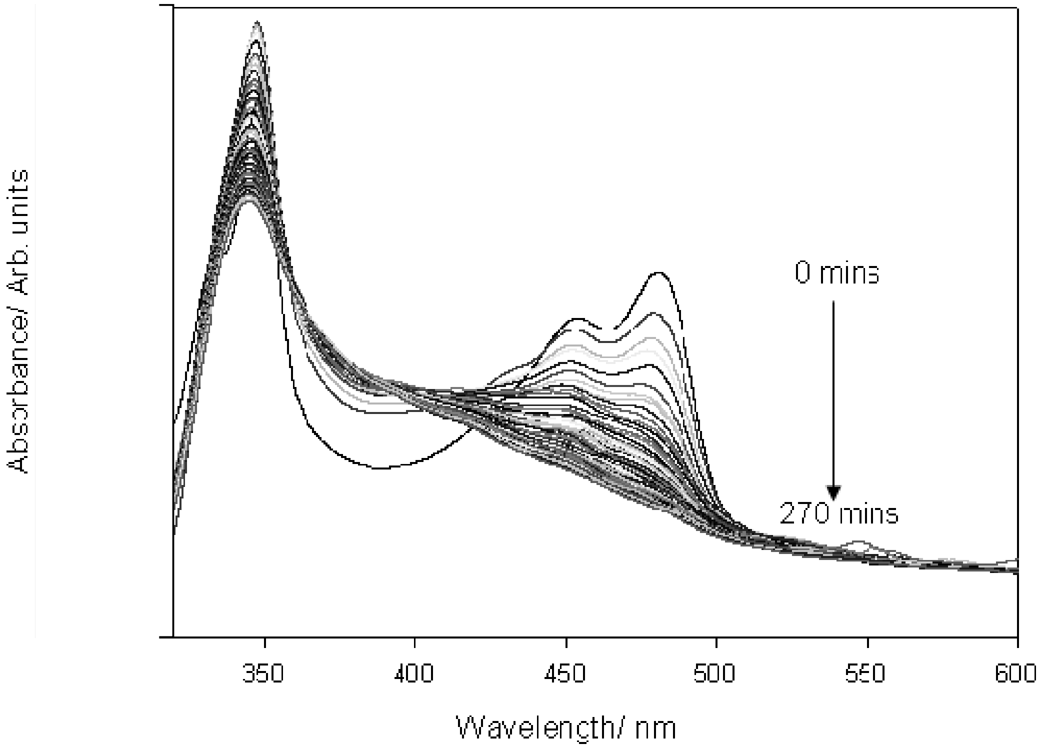

Figure 7 Degradation of POAV (**6**) upon successive 5 minute irradiations.

The photo-degradation profile of POAV (**6**) is shown in Figure 7. The main band at 480 nm is seen to decrease in intensity with a slight blue shift, while the second large peak at 350 nm increases significantly after the first 5 minutes of irradiation, after which it slowly decreases. The rate of degradation is intermediate in the series, and after 270 minutes of photolysis, the initial peak is nearly fully degraded with a broad band evolving at *ca.* 450nm. This indicates extensive chain scission leading to a large variance in molecular weight distribution.

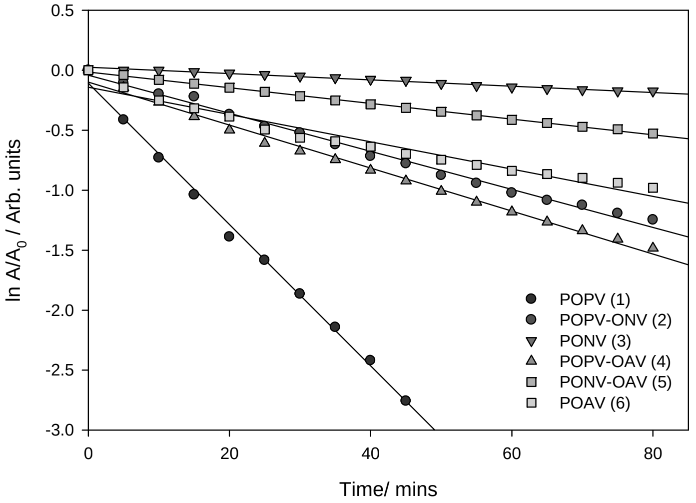

Figure 8 First order plot of ln A/A$_0$ against time for the polymer series

In order to determine the reaction order the integrated rate law was used and the first order plots of ln A/A$_0$ against time for the different polymers are shown in Figure 8. For all samples, the fixed wavelength of the initial longest wavelength absorption maximum was chosen to monitor the degradation rate. The degradation profiles for most of the polymers show good correlation to first order kinetics. However, due to the number of overlapping bands and the different competing degradation mechanisms, some of the degradation reactions may be more complex, including, for example, two simultaneous first order reactions. The slopes of the linear fits yield first order rate constants which are presented along with relative rate constants and half-lives in Table 1.

From the kinetic data, it can be seen that POPV (**1**) has by far the greatest rate of degradation while PONV (**3**) has the greatest resistance to photo-degradation. The last homo polymer, POAV (**6**), has a rate of degradation which is intermediate. It is noteworthy that the co-polymers have rates of degradation which are in between their homo-polymers counterparts.

From the relative rates, it can be seen that by introducing anthracene or naphthalene moieties into the polymer backbone, the rate of decay is reduced to approximately a quarter of its initial (POPV) value. On replacing all the phenylene rings with anthrylene rings, the rate is reduced to one fifth, while replacement with naphthylene rings reduces the rate twenty five times.

Table 1 Summary of kinetic data, (T) indicates toluene, all others in chloroform.

Polymer	Rate / min^{-1}	Relative rate / min^{-1}	Half-life / min
POPV (1)	0.059	1	11.8
POPV-ONV (2)	0.016	0.27	43.6
PONV (3)	0.003	0.05	266.6
POPV-OAV (4)	0.018	0.31	38.7
PONV-OAV (5)	0.007	0.11	106.6
POAV (6)	0.011	0.19	60.8
POPV-ONV(T)	0.0011	N/A	N/A
POPV-OAV(T)	0.0013	N/A	N/A

The degradation of the vinylene bond is primarily caused by the UV stimulated dissociation of $CHCL_3$ into Cl radials. These subsequently attack the highly susceptible vinyl regions as proposed by Bronze-Uhle *et al.* [18,19].

The proposed reaction mechanism is further reinforced when comparing the degradation rates between differing solvents. In figure 9, the degradation rates of the POPV-ONV and POPV-OAV polymers in both chloroform and toluene are plotted. It is clearly evident that degradation is greatly accelerated in the presence of chloroform. It is noted that the there is a 93% increase in the degradation rate when in the presence of Cl radials. The increase in the degradation rates as a result of the systematic structural variation of the backbone is approx the same, see table , Therefore, the degradation rates calculated in chloroform are seen to be indicative of the photo-oxidative rate in toluene and hence the trends established in terms of structural variations remain valid. The mechanism of attack on the vinyl bond is irrespective as the results show the inclusion of highly electro-negative naphthyl group serves to drastically increase the stability due to electron depletion across the vinyl bond.

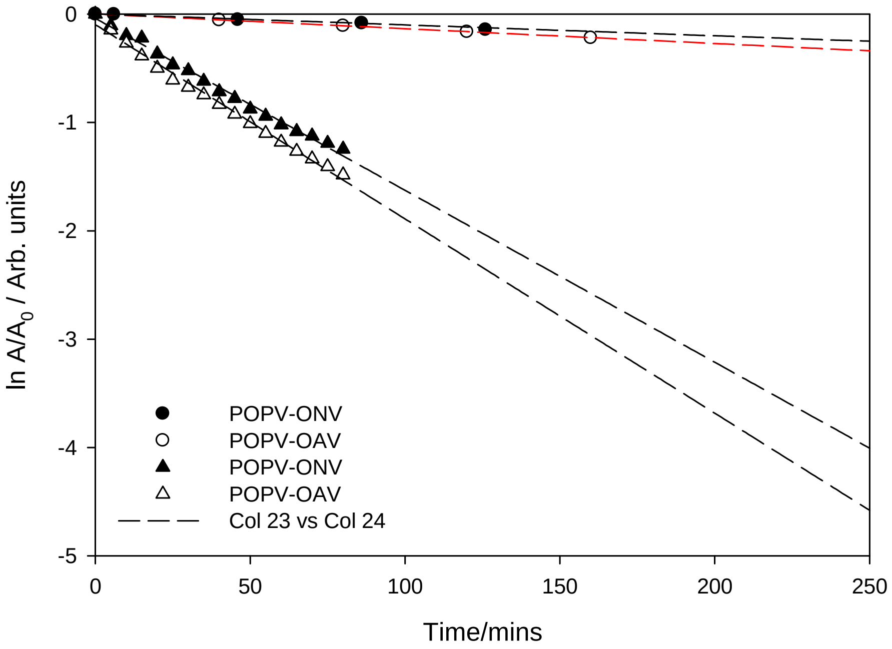

Figure 9 First order plot of ln A/A_0 against time for the polymer series, Triangle and circle represent chloroform and toluene solutions respectively

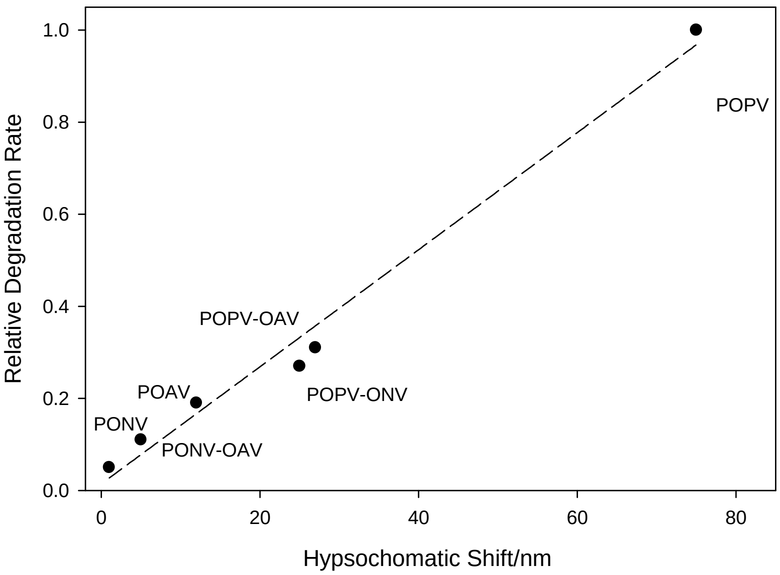

Figure 10 A plot of the absorption degradation rate versus the hypsochromatic shift for each polymer.

To further illustrate the varying degrees of photodegradation in the polymer series, the relative degradation rate as a function of the hypsochromic shift of the absorption maximum is plotted in Figure 10. For each polymer, the hypsochromatic shift was calculated as the shift in wavelength of the 0-0 absorption peak after 60 minutes. The hypsochromic shift of the longest wavelength absorption band is indicative of the degree of chain scission [20]. As is apparent from Figures 3-7, the extent of blue shift of the absorption is systematically reduced with increasing order of the anthrylene substituent. This reduction is shown graphically in Figure 11, wherein a linear dependence of hypsochromic shift on degradation rate is evident, indicated by the dashed line. PONV is close to the extrapolation of no chain scission, consistent with the maximum depletion of electron density, reducing the susceptibility of the vinylene bond to attack.

These results show that the introduction of higher order anthrylene units into the polymer backbone renders the compounds more resistant to photo-oxidation. In previous studies, introduction of electron withdrawing substituents onto the vinylene bond has been shown to decrease their rate of oxidation [5, 6, 7]. Thus, it is implicit that the vinylene units adjacent to anthrylene units are deficient in π electrons, rendering them more stable to attack.

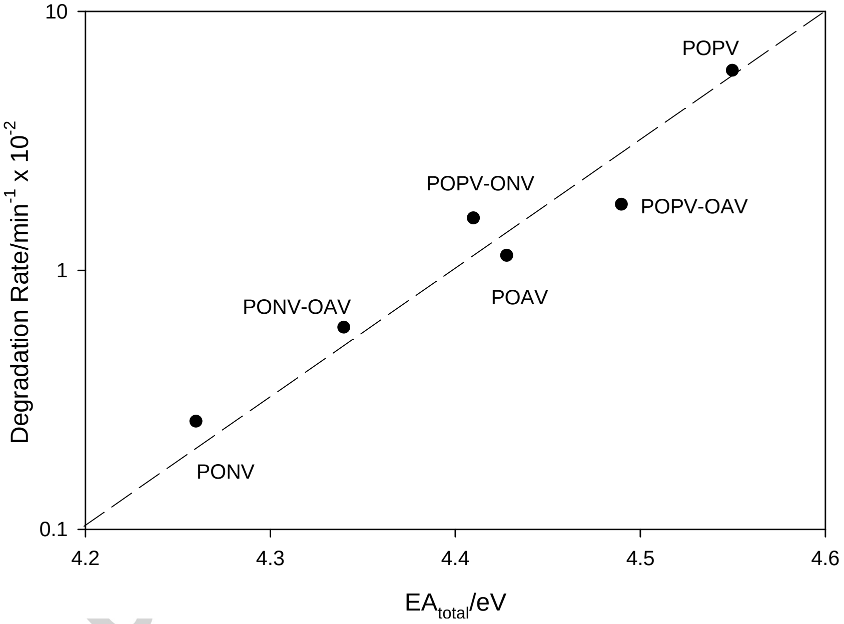

Figure 11 A plot of the total electron affinity (EA$_{total}$) versus the relative rate of degradation for each polymer

In previous analyses, it has also been shown that the electronic properties of the homologous series are determined by the combined effects of the increased electron density of the arylene units and the reduced electronic conjugation across the vinylene bond and that an empirical parameter derived from the sum of the electron affinities of the constituent units, EA$_{total}$, can be used to represent the effective conjugation of the systems [9]. Figure 11 is a plot of the variation of the polymer degradation rate against

EA_{total} for the polymer series. As can be seen, the rate of degradation as a function of variation of the electron affinity across the backbone can be well fitted by a single exponential. This indicates that the systematic structural dependence of the rate of degradation can be accounted for by the combined effects of the reduction in electron density across the vinylene bond and the increasing electron density of the arylene units.

To explore the specific dependence of the degradation rate on the vinylene bond strength, Raman spectroscopy was used to measure the reduction in the vinylene bond strength in the pristine polymers. For a simple harmonic oscillator model of a diatomic molecule, the frequency ν, of vibration is related, by Equation 1, to the square root of the bond strength k, divided by the reduced mass μ of the two atoms (m_1 and m_2), and thus the parameter $\nu^2\mu$ provides a measurable estimate for the bond strength.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \textbf{Equation 1}$$

For the polymer series, the reduced mass is taken to be that of the combined (monomeric) end groups, including one of the carbons of the vinyl bond and the solubilising alkyl sidegroups. The electron withdrawing substituents on the vinylene bond primarily reduce its π character and therefore the bond strength.

The Raman active vinylene C=C stretch between 1640 and 1610 cm^{-1} was identified for each of the polymers [21, 22]. As the band of interest is close to the aromatic C=C stretch for some of the polymers, the band position was determined by fitting Gaussian/ Lorentzian functions [9]. If the photo-oxidative degradation rate, as predicted, is dependent on the strength of the vinyl bond, then the rate should vary systematically across the homologous series. A plot of the relative rate of degradation for each polymer against the square of the fitted frequency of this vinylene band from the Raman spectrum of the polymer, multiplied by the respective reduced mass (μ) for each polymer, is shown in Figure 12.

Notably, the relationship between reaction rate and bond strength, as estimated using Raman spectroscopy is relatively flat, except for the case of POPV (**1**). The experimental data relating the degradation rate K to the bond strength can be fitted by an exponential function of the form of Equation 2, where A is a pre-exponential factor and B is an activation constant for the reaction, which is linearly dependent on the bond strength.

K = A* exp [-B] **Equation 2**

In terms of the vinyl bond strength and π-electron character, therefore, it appears that the susceptibility to photo-oxidative attack is initially substantially reduced by the mono substitution of naphthyl groups into the backbone, and little further reduction is affected by further substitution, although the vinyl bond frequency continues to soften.

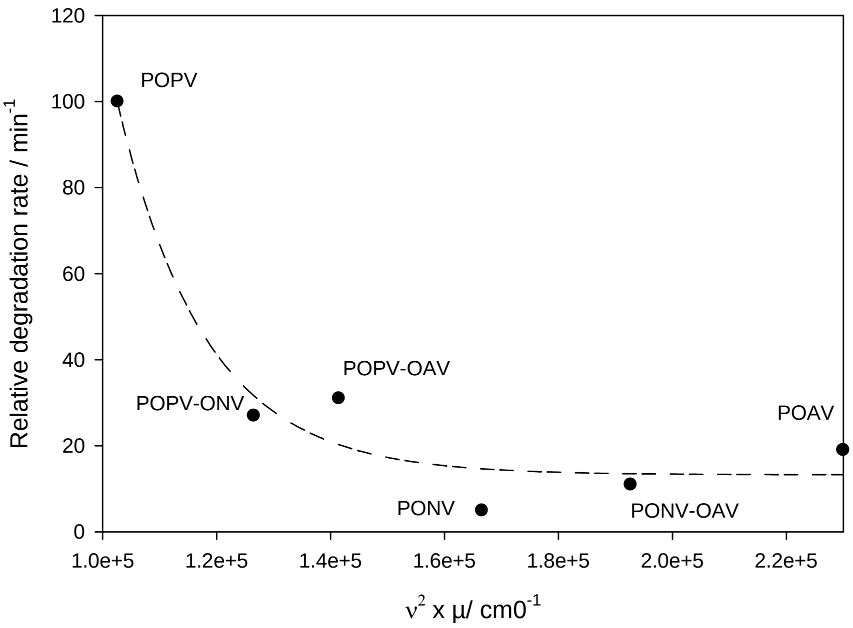

Figure 12 A plot of the Raman vinylene band frequency versus the relative rate of degradation for each polymer

Conclusions

It has been demonstrated that, similar to their photophysical properties, the photochemical properties of the homologous series of poly arylene vinylene polymers can be understood and therefore potentially controlled through systematic structural modification. The results are consistent with degradation across the vinylene bond, which becomes electron deficient upon substitution with the higher order arylene units. The almost complete stabilisation of the polymers to highly efficient Cl radical attack at an apparent threshold π-electron density may lend further insight into the mechanisms of degradation.

Although the studies presented here are made in solution rather than in the solid state, in which the materials may most likely find applications, it may be projected that the structural trends may be extrapolated from solution to the solid state. Since degradation of organic LEDs is a major restriction to their economic success, the synthetic design principles applied here may lead to devices having greater life spans than those produced using many of the PPV derivatives in common use today.

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- Novel polymer degradation investigating
- Systematic changing of polymer back-bone served to extend stability
- Raman spectroscopy shows vinyl bond weakening correlated with extended stability
- Degradation rate not solely dependant on electron changes on vinyl bond