

SPECTROSCOPIC INVESTIGATION OF POLYVINYL CHLORIDE
PHOTODEGRADATION IN BLENDS WITH BASIC TRAPS

A THESIS

SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
AND THE INSTITUTE OF ENGINEERING AND SCIENCES
OF BILKENT UNIVERSITY

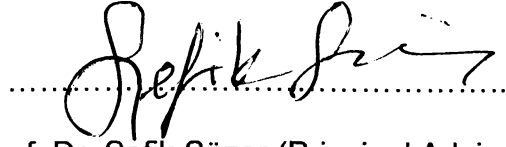
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER IN SCIENCE

By

ÖZGÜR BİRER

December 1999

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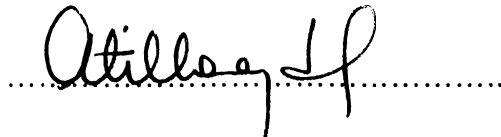
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ABSTRACT

SPECTROSCOPIC INVESTIGATION OF POLYVINYL CHLORIDE PHOTODEGRADATION IN BLENDS WITH BASIC TRAPS

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Supervisor: Prof. Dr. Şefik Süzer

December 1999

Polyvinyl chloride degrades via loss of HCl when it is exposed to heat, energetic particles or photons. The mechanism is known as the zip mechanism and results in conjugated segments, polyenes. Degradation also leads to loss of mechanical properties of PVC. However, from another point of view, PVC is a Bronsted acid source, with controllable emission. Furthermore, the polyenes are small segments of polyacetylene, which itself is a very interesting one-dimensional system. Understanding the building blocks clearly helps to envisage larger systems.

This study has two main goals. The first goal is benefiting from the radiation induced *in-situ* created HCl by incorporating basic traps into the polymer matrix and inducing optical or electrical conductivity changes. The second goal is to tune the wavelength of photodegradation by introducing sensitizers into the polymer matrix to affect the chain length of the polyenes.

For the first part of the study, pH indicators, and basic forms of conducting polymers were blended with PVC and the films were irradiated with UV radiation. Optical changes were monitored with UV-Vis-NIR Spectroscopy. Similar to several other dyes tried, Bromocresol Green, and Methyl Violet changed their optical properties when they were exposed to UV radiation in the PVC matrix. However, Methyl Violet, being resistant to UV radiation, proved to be a suitable component for possible dosimetric and lithographic applications.

Basic forms of polyaniline and poly-2-chloro aniline were blended with PVC, and upon irradiation of the blend, they were converted to conducting salt forms as a result of doping with *in-situ* created HCl. The structural changes were monitored with UV-Vis-NIR spectrophotometry as well as FTIR spectroscopy. PVC/2-Cl PANI blends gave better results compared to PVC/PANI blends.

For the second part of the study, hydroquinone, anthraquinone, and anthracene were introduced into the PVC matrix. The samples were irradiated with monochromatic UV radiation at the absorption maxima of these sensitizers. It was established that the nature of polyene formation is dependent on the wavelength of irradiation as well as the amount of energy transferred to the PVC chains.

Keywords: Polyvinyl chloride, polyene, polyaniline, poly-2-chloro-aniline, photodegradation, lithography, UV-Vis-NIR spectroscopy

ÖZET

BAZIK TUZAKLI KARIŞIMLAR İÇİNDE POLİVİNİL KLORÜRÜN FOTO BOZUNMASININ SPEKTROSKOPİK İNCELENMESİ

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Poli vinil klorür, ısıya, yüksek enerjili parçacıklara veya fotonlara maruz kaldığında HCl salarak bozunur. "Zip" olarak da bilinen bu mekanizma sonucunda, polien adı verilen konjüğe parçalar oluşur ve bozunma PVC nin mekanik özelliklerini yitirmesine neden olur. Ancak, bir başka açıdan, PVC salınımı kontrol edilebilen bir Bronsted asiti kaynağıdır. Polienler ise çok ilginç tek boyutlu bir sistem olan poliasetilenin yapı taşlarıdır. Küçük yapı taşlarının oluşum mekanizmasının anlaşılması daha büyük sistemlere ışık tutabilir.

Bu çalışmanın iki temel amacı vardır. Birincisi, polimer matrisi içerisine uygun bazik tuzaklar yerleştirerek, ışınlanma sonucu oluşan HCl den yararlanmak ve karışımların optik veya elektriksel iletkenlik özelliklerini

değiřtirmektedir. İkincisi ise foto bozunmanın gerekleřtiđi ışık dalga boyunu deđiřtirerek oluřan polienlerin zincir uzunluklarını etkilemektedir.

alıřmanın birinci blmnde, PVC nin asit-baz belirteleri ve iletken polimerlerin bazik formları ile karıřımları hazırlanmıř, UV kaynakları ile ışınlanmış ve optik deđiřiklikler mortesi ve grnr blge spektroskopisi ile incelenmiřtir. İncelenen diđer boyalar gibi, Bromkresol Yeřili ve Metil Violet katıldıkları PVC matrisinde ışınlanınca bazı optik zelliklerini kaybetmektedirler. Metil Violet ise ışınlanmaya karřı direncini kanıtlayarak, olası dozimetri ve litografi uygulamaları iin uygun bir aday olarak tespit edilmiřtir.

Polianilin ve poli-2-kloro anilinin bazik formları PVC ile karıřtırılmıř ve ışınlanma sonucu yerinde oluřan HCl tarafından iletken tuz formuna evrilmiřlerdir. Yapısal deđiřiklikler mortesi-grnr-yakın kırmızı tesi spektroskopisi ve FT kızıl tesi spektroskopisi ile takip edilmiřtir. PVC/2-Cl PANI karıřımları, PVC/PANI karıřımlarına kıyasla daha iyi neticeler vermiřtir.

alıřmanın ikinci kısmında, hidrokinon, antrakınon ve antrasen PVC matrisine karıřtırılmıřtır. rnekler, bu duyarlařtırıcıların sođurduđu dalga boylarında tek renkli mor tesi ışıkla ışınlanarak polien oluřumunun, dalga boyuna olduđu kadar, PVC zincirlerine aktarılabilen enerji miktarına da bađlı olduđu tespit edilmiřtir.

Anahtar Kelimeler: PVC, polien, polianilin, poli-2-kloro-anilin, foto-bozunma, litografi, Mor ötesi – Görünür - Yakın kızılötesi Spektroskopisi

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1. INTRODUCTION

1.1. Polyvinyl chloride

Polyvinyl chloride is one of the world's most used plastics. It has been used for production of water pipes, wall and floor covers, window and doorframes, food packaging, blood transfusion sets and many more. The reasons of its wide spread use are its resistance against corrosion, fire retardant and insulating properties. It has been reported that PVC production reached 6.60 million tons in US in 1998 [1], 5.60 million tons in Western Europe in 1997 [2], and 224,650 tons in Japan in 1997 [3]. European Council of Vinyl Manufacturers announced the European uses for PVC by market share as shown in Figure 1 [4].

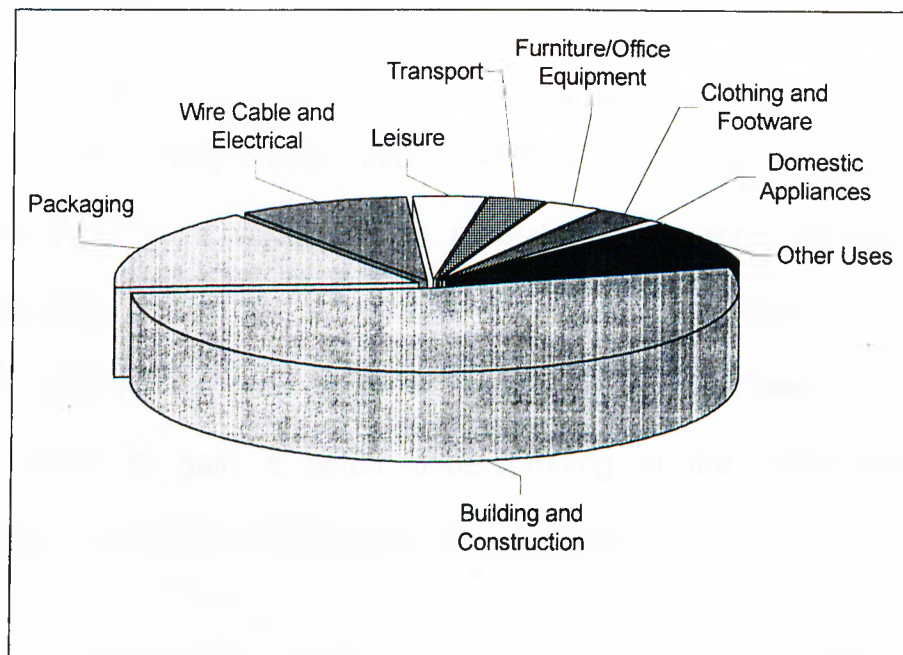
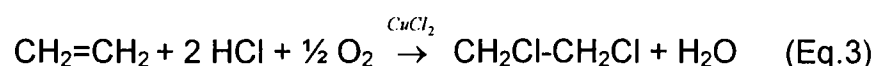
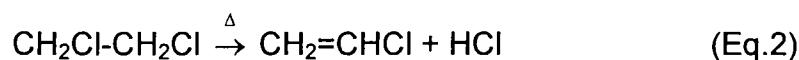
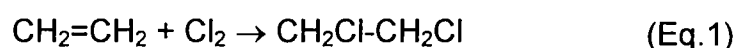


Figure 1. The European use of PVC by market share

Vinyl chloride monomer ($\text{CH}_2=\text{CHCl}$) was first produced by Regnault in France in 1835 and its polymerisation was achieved for the first time in 1872 by Baumann who exposed the monomers to sunlight in a sealed tube. The first PVC production plants were constructed in the USA in the early 1930's.

In modern industry, vinyl chloride monomer is produced by reacting ethene with chlorine (Eq.1), and decomposing the produced 1,2 dichloroethane at high temperature (Eq.2). The evolved HCl is further reacted with ethene in the presence of oxygen and copper chloride catalyst to yield 1,2 dichloroethane (Eq.3), which is fed into the pyrolysis reaction (Eq.2) [5]. Polyvinyl chloride, $\{-(\text{CH}_2-\text{CHCl})_n-\}$, is obtained by radical polymerisation of the monomer.



PVC is a very cheap material and has many applications. Outdoor PVC products have various kinds of stabilisers in their formulations to increase their service life. However, pure PVC has a rather low stability against heat and energetic photons. For this reason extensive research has been carried to gain a better understanding of the mechanism(s) of degradation, mainly for the purpose of preventing it.

1.2. Decomposition of PVC

PVC degradation has been studied by means of thermal decomposition, photo and particle beam decomposition, and chemical decomposition [6-34].

When PVC decomposes, HCl is eliminated from the chain, and conjugated double bonds, polyenes, $\{-(CH=CH)_n-\}$, form in the polymer chain. Ionic, radical and molecular elimination mechanisms together with autocatalytic effect of HCl have been proposed to explain the phenomena but none of them could bring a complete explanation of the observed facts. As the number of double bonds exceed 6, the polyenes start to absorb light in the blue region of the visible spectrum and the material appears yellow. The Yellowness index, established by the American Society for Testing and Materials, has been used to gauge the extent of decomposition [6-8].

1.2.1. Thermal Decomposition

In the thermal decomposition studies, it has been shown that impurities such as solvent and initiator residue [9], plasticisers [10], structural irregularities such as carbon-carbon double bonds and carbonyl bonds [11], reduce the stability of PVC and initiate the dehydrochlorination reaction. Conjugated unsaturation ranging from short polyenes ($n=2-4$) up to long polyenes ($n=15$) as a result of thermal decomposition was detected by UV-Vis absorption spectroscopy [12] and FTIR spectroscopy [13]. Side reactions,

like photooxidation as detected by FTIR Spectroscopy [13], and cyclisation as detected by Mass Spectroscopy [14] accompany polyene formation during thermal degradation.

As a result of these studies, several stabiliser compounds such as barium, calcium, lead, cadmium, zinc stearates, dibutyltin distearate, dibutyltin maleate, and dioctyltin di(octylthioglycolate) [11,12,14,15] were proposed to inhibit or retard dehydrochlorination of PVC.

1.2.2. *Photo-Decomposition*

Photo-decomposition of PVC has been widely studied in the spectral range from long wavelength UV radiation up to gamma radiation. In the studies where solar radiation was simulated with several different Xe sources, exposure duration exceeding 1000 hours was necessary to create polyenes with a wide range of n number in the polymer [16-19]. The maximum rate of dehydrochlorination was reported to occur at 370 nm [19]. Formation of the carbonyl moiety (1720 cm^{-1}), the hydroxide moiety (3200 cm^{-1}), and the C-H moiety (1400 cm^{-1}) as a result of weathering were reported [18]. Photostabilisers such as dibutyltin bis(octylmaleate), dibutyltin bis(octylthioglycolate), and dibutyltin bis(2-ethylhexylthioglycolate) [16], benzylidene malonate [17], and rutile [19] were proposed.

Studies on the effects of more energetic UV radiation required employment of low, medium and high pressure Hg sources. These sources

emit mainly at 254 nm, and a broad emission tail grows as the pressure increases from low to high. PVC samples irradiated with medium to high pressure mercury lamps degrade rather quickly, and considerable changes in the UV-Vis spectra of the PVC samples occur in 1-3 hours. Surface oxidation, photo-bleaching and deconjugation of the polyenic sequences were reported in the presence of oxygen for irradiated samples [20,21]. Effect of tacticity on degradation was investigated as well [22]. Low pressure Hg lamps require more exposure, on the order of several hours, to create polyenes in PVC. In these studies, low concentration of longer polyenes compared to shorter ones, were reported [23]. Several oxidation products were detected and assigned by deconvolution of the carbonyl region in FTIR spectroscopy, and the quantum yield for n=3 polyene was calculated as 1.6×10^{-4} [24]. Although pure PVC is transparent in visible and UV region down to 200 nm, light absorbing impurities such as solvent residues, carbonyl bonds, and internal double bonds are considered to be the initiation centres in photo-dehydrochlorination of PVC [20-23].

Gamma ray irradiation creates polyenes in PVC in just minutes, and ESR spectra of gamma irradiated PVC samples indicate the presence of the polyenyl radical, an unpaired electron associated with a long sequence of conjugation, with a symmetric singlet signal with no apparent fine structure [25]. Effect of gamma ray irradiation on crosslinking and physical properties of the polymer with and without stabilisers were studied extensively [26-28].

Particle induced effects on PVC were studied by means of beta [29], proton [30], and neutron [31] irradiation, but these studies attracted less interest.

1.2.3. Chemical Decomposition

It is also possible to employ chemical means for dehydrochlorination of PVC. Use of strong bases such as potassium tertio-butylate [32] and 1,8-diazabicyclo[5,4,0]undec-7-ene [33], and phase transfer catalysts such as poly (ethylene glycol)s [34], in solution, led to polyacetylene like material by almost complete dehydrochlorination.

1.2.4. Theoretical Calculations and Modelling

Quantum chemical calculations on PVC and model compounds such as various chloroalkanes and chloroalkenes and mathematical modelling were carried out for obtaining a better understanding of elimination mechanisms by comparing activation enthalpies as well as kinetic data. In these studies, activation, termination of the elimination and effect of HCl on the kinetics of degradation, were discussed in the context of molecular, ionic and radical mechanisms with defect free polymers [35-43].

According to these studies, in the initial stages of thermal degradation, at low temperatures and in inert atmosphere, HCl is eliminated from a monomeric unit by a 1,2 elimination. The transition state has four centers and

it requires a synperiplanar conformation and extensive polarisation of the C-Cl bond [35]. In the presence of HCl, 1,2 elimination through a six-centre transition state is possible with lower activation energy and lower activation entropy [35,36] as shown in Figure 2. In the presence of a double bond elimination of HCl is much faster due to the allylic activation of α -chlorine. Allylic activation arises, due to increase in total energy as a result of chlorine and double bond repulsion, and stabilisation of the transition state as a result of π -electron conjugation between transition state and carbon carbon double bond [37]. Activation exists for β -chloro allylic fragments as well [38].

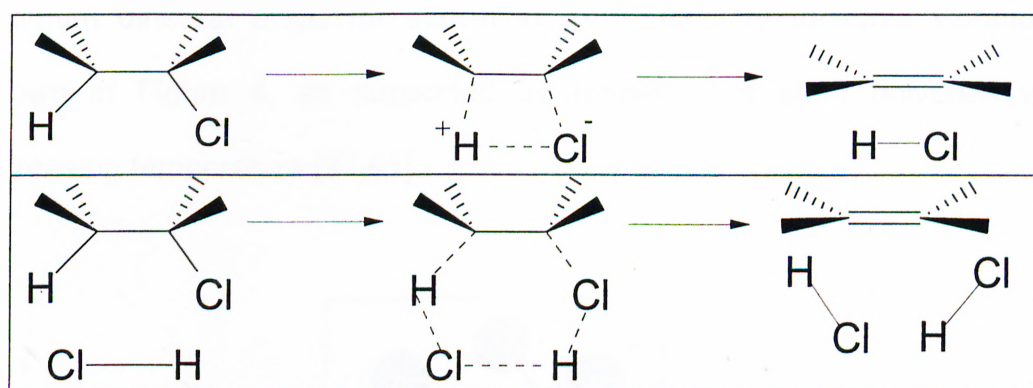


Figure 2. HCl elimination from PVC in the absence and presence of HCl

The polyene growth proceeds by 1,4 elimination of HCl through a six centre transition state and 1,3 rearrangement of hydrogen atoms catalysed by HCl, as presented in Figure 3. The reaction stops when a trans double bond is formed and there is no HCl to catalyse trans-cis isomerisation. The autocatalytic effect of HCl on PVC degradation is linked to the interaction of HCl with the double bonds. The π -complex formed accelerates the reaction and increases number of conjugation [39].

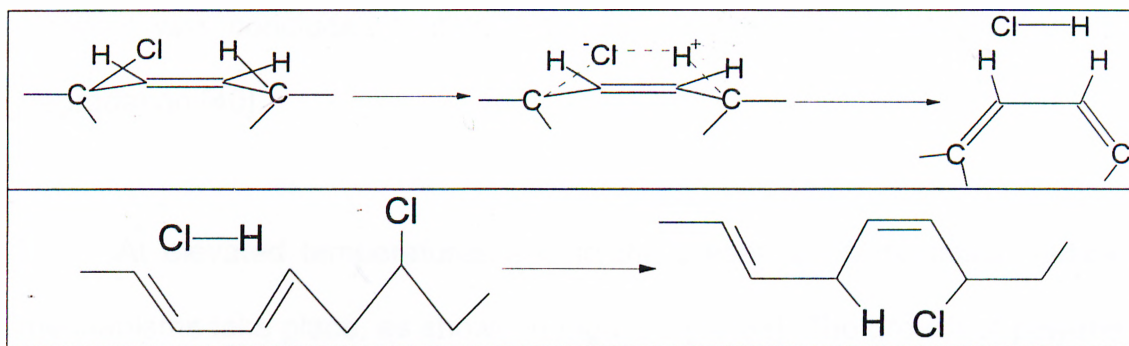


Figure 3. 1,4 elimination of HCl and 1,3 rearrangement of hydrogen atoms

The activation energy of decomposition of PVC remains almost constant as the polyene chain grows and number of conjugated double bonds increases. One of the proposed termination reasons is the loss of optimum dihedral angle for activation as a result of torsional vibrations, shown in Figure 4, as supported by formation of short polyenes with increasing temperature [37,41].

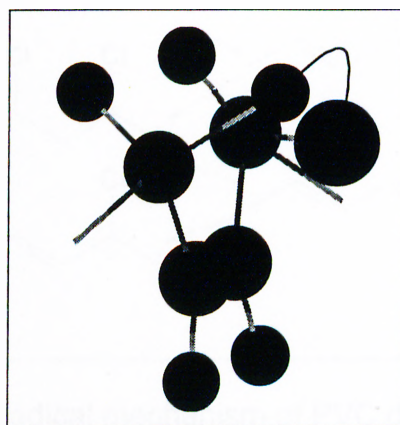


Figure 4. The optimum dihedral angle for HCl elimination

The effect of tacticity of polymer on degradation is still uncertain. In early experimental studies, isotactic [22], and syndiotactic [37] sequences were reported to yield longer polyenes. However, in a recent theoretical

paper it was concluded that tacticity has no significant effect on thermal degradation [40].

At elevated temperatures and in the presence of impurities, radical mechanisms take place, as shown in Figure 5 [35,38]. The growth of polyene sequence, in this case, is one directional and in the direction of allylic chlorine since dissociation energy of the C-Cl bond is about 90 kJ/mol less than that of the C-H bond. The radical mechanism plays a significant role in photo-degradation as well.

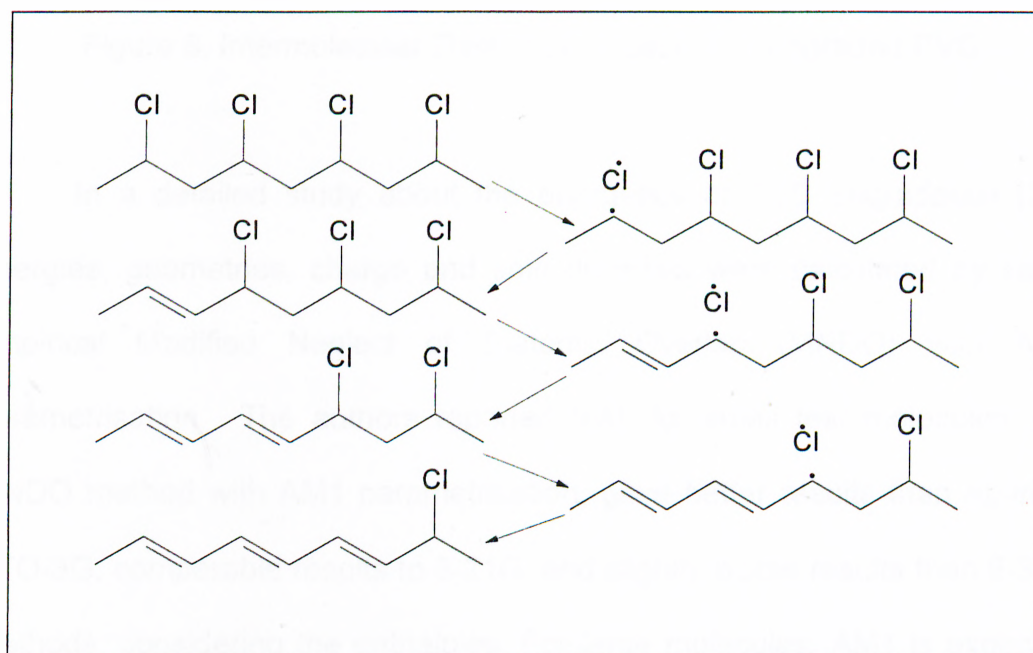


Figure 5. Radical mechanism of PVC degradation

Recently, the energies for S_0-S_1 and S_0-T_1 electronic transitions and of energy barriers for rotation about double bonds in polyenes and polyenyl carbocations have been calculated and reactivity of polyenes was discussed [36]. It has been reported that polyenes having more than 8 conjugated

double bonds are highly reactive at 180-200 °C and that Friedel-Crafts alkylations, inter and intramolecular Diels-Alder cyclisations occur as shown in Figure 6 [35,36].

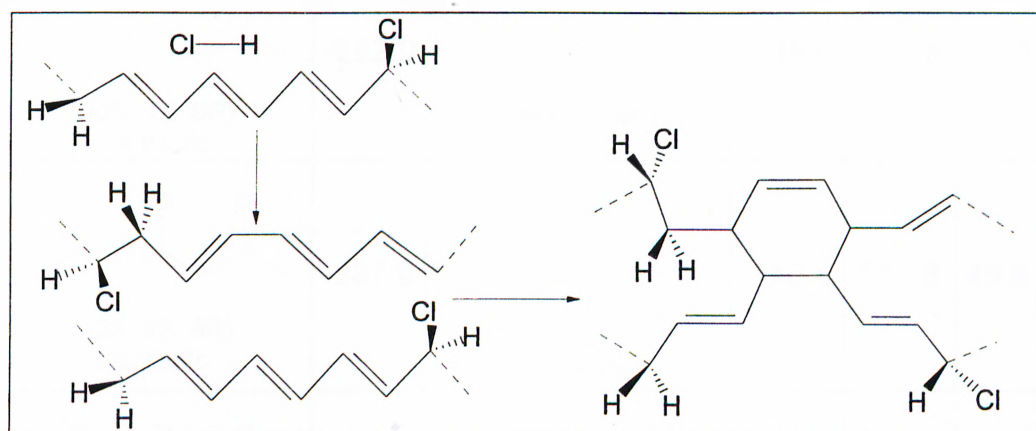
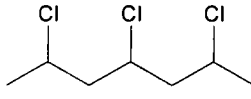
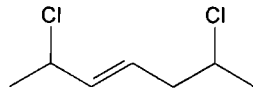
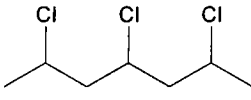
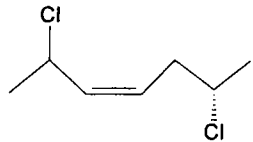
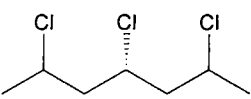
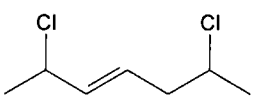
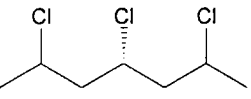
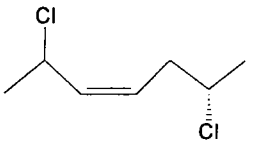
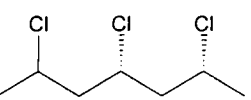
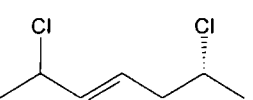
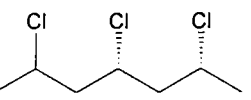
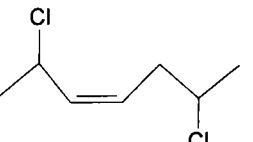


Figure 6. Intermolecular Diels-Alder Reaction in degraded PVC

In a detailed study about the energetics of PVC degradation [35], energies, geometries, charge and spin densities were calculated by semi-empirical Modified Neglect of Diatomic Overlap (MNDO) with AM1 parametrisation. The authors reported that, for small test molecules, the MNDO method with AM1 parametrisation, gave better results than ab-initio STO-3G, comparable results to 3-21G, and slightly worse results than 6-31G methods, considering the enthalpies. For large molecules, AM1 is expected to perform even better, due to built-in corrections for electron correlation.

Activation enthalpies calculated for dehydrochlorination of 2,4,6-trichloroheptane stereoisomers are given in Table 1. The overall enthalpy of dehydrochlorination reaction is about 40-44 kJ/mol, while the activation enthalpy is about 225 kJ/mol.

Table 1. Activation enthalpies dehydrochlorination of 2,4,6-trichloroheptane stereoisomers [35].

Reactant		Product		Reaction	
Configuration	ΔH_f^a	Configuration	ΔH_f	ΔH_r^z	ΔH_r^b
 (2S, 4S, 6R) isotactic	-282.0	 <i>trans</i> (2S,6R)	-149.0	223.8	40.6
 (2S, 4S, 6R) isotactic	-287.9	 <i>cis</i> (2S,6R)	-146.4	231.8	49.0
 (2S, 4R, 6R) syndiotactic	-286.6	 <i>trans</i> (2S,6R)	-149.0	220.1	45.2
 (2S, 4R, 6R) syndiotactic	-282.0	 <i>cis</i> (2S,6R)	-146.4	225.1	43.1
 (2S, 6S) atactic	-279.5	 <i>trans</i> (2S,6S)	-148.5	219.2	38.5
 (2S, 6S) atactic	-273.2	 <i>cis</i> (2S,6S)	-145.2	228.0	35.6

^a Calculated formation enthalpy for the conformer that generates the product

^b Difference between the reagent and the product including HCl ($\Delta H_f = -92.5$ kJ/mol)
Enthalpy values are in kJ/mol

1.2.5. Prevention of Degradation

Several stabilisers have been proposed to prevent the degradation. These stabilisers added into the polymer, for thermal or photo-stabilisation purposes must meet some basic requirements [44]. These requirements can be summarised as;

- a. Absorption and neutralisation of HCl evolved,
- b. Displacement of active, labile substituent groups, such as the chlorine atom attached to a tertiary carbon, or an allylic chlorine,
- c. Neutralisation or inactivation or stabiliser degradation products,
- d. Ability to disrupt progression of chain reactions,
- e. Neutralisation or inactivation of resin impurities, contaminants, catalyst residues, end groups etc.,
- f. Provision of a shield, protective screen for UV radiation.

The most effective stabilisers are those which function by actively attacking weakly held labile chlorine atoms on PVC and replacing these with other groups of inherently greater stability. Heavy metal carboxylates and mercaptides, such as soaps of cadmium and zinc, and the dialkyl tin carboxylates and mercaptides stabilise PVC by exchanging their ligands with the labile chlorines on PVC. However, the effectiveness of these displacements is limited. Since carboxylates and mercaptides also react with HCl, they are consumed over time. Furthermore, the formed heavy metal chlorides are Lewis acids, which catalyse degradation reactions. Thus, co-stabilisers are required to remove heavy metal chlorides from the system. The widely used chlorine acceptors are the alkaline earth metal carboxylates, such as barium laurate, $(-\text{C}_{10}\text{H}_{19}\text{O}_2)_2$, soap. In the presence of the

co-stabiliser, the stabiliser is regenerated by transfer of ligands from the co-stabiliser to the stabiliser, and alkaline earth metal chlorides form. Heat stabilisers and co-stabilisers are generally used in mixtures of 1:2 or 2:1 ratio.

On the other hand, UV radiation screens, being transparent in the visible region of the spectrum, should be able to absorb UV radiation and dissipate the energy harmlessly. The photo-stabilisers, which are widely used in suntan lotions as well, are the 2-hydroxybenzophenones, the 2-(2'-hydroxyphenyl)benzotriazoles, the salicylate esters, the aryl-substituted acrylates, and the p-aminobenzoates.

1.2.6. Utilisation of Degradation

The simplest conducting polymer, polyacetylene, is composed of alternating single and double bonds, and it is a model for infinite one-dimensional system [45]. It is actually composed of very long polyene chains of different lengths. Exploring how the small building blocks behave under certain stimuli may offer a better understanding on how the real system works. For this reason, studying polyenes is important to have a better understanding of non-linear optical and electrical properties of polyacetylene. Several theoretical studies combined with experimental work have been carried out to explore the electronic structure of polyenes with different lengths [46-49]. Since one of the easiest methods for obtaining polyenes is the dehydrochlorination of PVC, the current study can be summarised as;

i) Benefiting from photo-dehydrochlorination of PVC by capturing the released HCl by basic molecular and/or polymeric traps, which change their optical and/or electrical properties upon capture,

ii) Investigation of polyene formation in photo-dehydrochlorination of PVC using different wavelengths of UV light and wavelength tuning agents as sensitizers.

1.3. Conducting Polymers

Conducting polymers, with conductivities ranging from that of pure silicon to that of copper, have delocalised π -electrons along the conjugated polymer backbone. Due to the overlap of π orbitals of one monomeric unit with that of its neighbours, valence and conduction bands form. These extended orbitals give rise to high electron mobilities along the polymer chain. In the undoped state, these polymers are wide-band-gap semiconductors and are mainly insulating. However, when charge transfer agents (dopants) are added to the polymer, they can oxidise or reduce the polymer, dramatically changing the geometry and electronic structure. The partially oxidised polymer backbones with associated counterions are electron deficient or have excess of electrons on the chain producing defect states in the gap and possibly a metallic like partially filled band and a high conductivity [50].

Polyaniline is usually synthesised by oxidative polymerisation of aniline with ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, in acidic medium [51].

Polyaniline is composed of reduced and oxidised repeat units as shown in Figure 7. The relative amounts of oxidised and reduced units determine the intrinsic oxidation state of the polymer. The oxidised and reduced units can be monitored by FTIR spectroscopy with the N=Q=N stretching peak around 1600 cm^{-1} and N-B-N stretching peak around 1500 cm^{-1} , where Q and B designate the quinoid and benzoid forms, respectively [52].

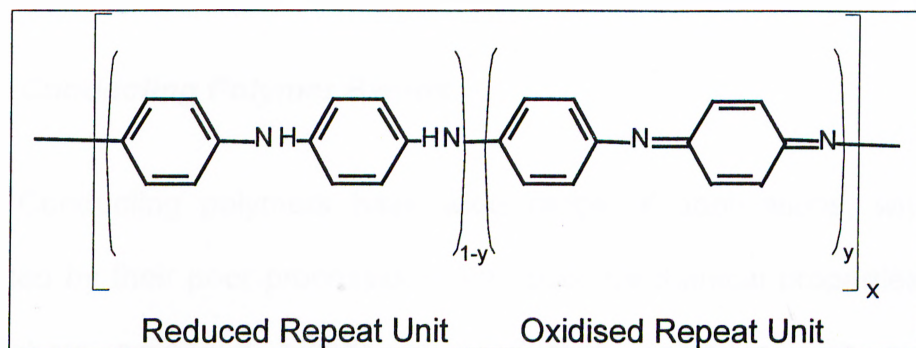


Figure 7. The general form of polyaniline

The metallic form of polyaniline, known as the emeraldine salt, can be obtained by either oxidation of neutral leucoemeraldine ($y=0$), or by protonation of the emeraldine base ($y=0.5$). In the latter case, there is no change in total number of π electrons, the metallic state results from the internal redox reaction, proton induced spin unpairing as pictured in Figure 8 [50,53].

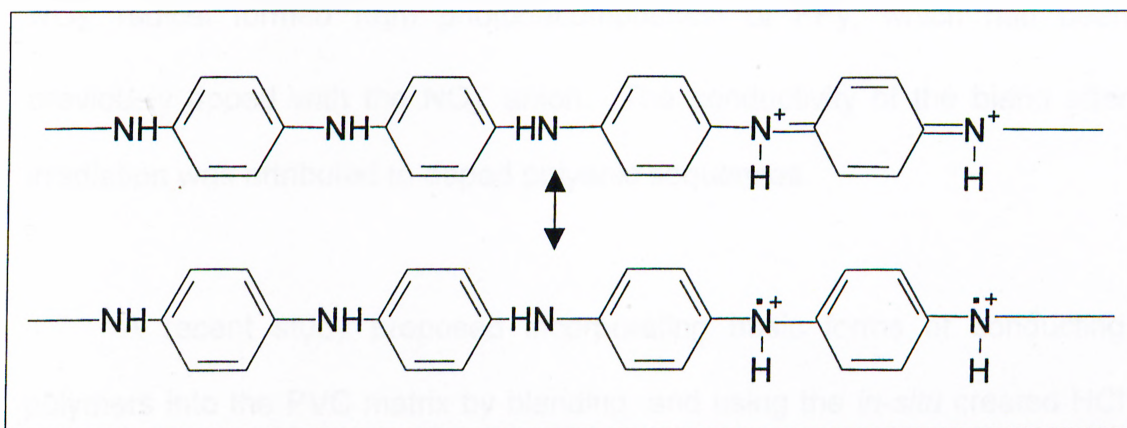


Figure 8. Internal redox reaction of Emeraldine Salt

The conducting form of polyaniline, has a broad polaron band starting from approximately 800 nm and extending to NIR region [54]. 2-Cl PANI can be thought of modified PANI and it has oxidised and reduced units as well. The spectroscopic comparison of PANI and 2-Cl PANI will be discussed in the later chapters.

1.4. Conducting Polymer Blends

Conducting polymers have wide range of applications, which are restricted by their poor processibility and poor mechanical properties. Many researchers proposed blends of conducting polymers with insulating polymers to improve their mechanical properties. Some of these studies included polyvinyl chloride and polyaniline/polypyrrole blends [55-61].

Preparation and characterisation of electrically conductive PVC by dehydrochlorination from PVC/PPy composite film was also reported [62]. In this paper, authors without much of supporting data, claimed that the UV radiation photodegraded PVC and the formed polyenes were doped by the NO_2^\cdot radical formed from photodecomposition of PPy, which had been previously doped with the NO_3^- anion. The conductivity of the blend after irradiation was attributed to doped polyenic sequences.

A recent study proposed incorporating basic forms of conducting polymers into the PVC matrix by blending, and using the *in-situ* created HCl during photodegradation of PVC as dopant to convert the nonconducting

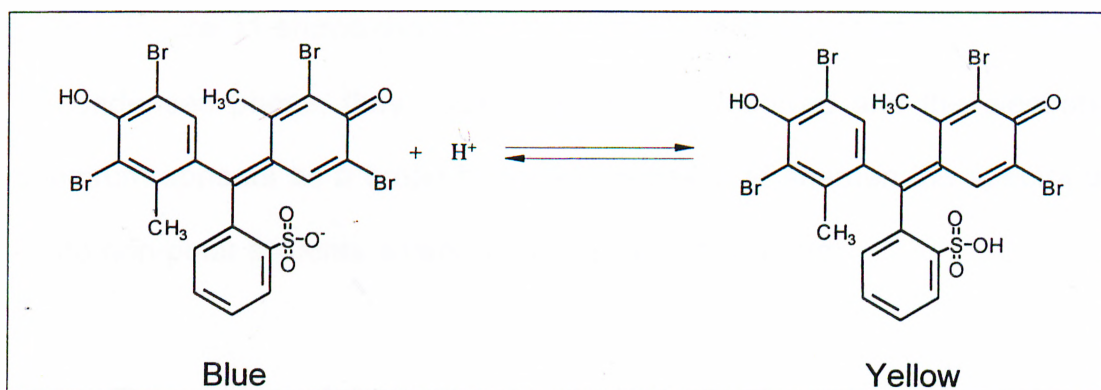


Figure 10. Structure of base and acid forms of Bromocresol green

1.6. *Electronic Spectroscopy*

Electronic Spectroscopy deals with transitions of electrons from a low energy orbital to a high energy orbital, or rearrangements of electrons within a set of degenerate orbitals so that the overall energy is increased. Since the energy required for such processes are on the order of several electron volts, the portion of the electromagnetic spectrum of interest lies in the visible (800-400 nm), ultraviolet (400-200 nm), and vacuum ultraviolet (200-10 nm) regions.

Molecular orbitals can be approximated as linear combinations of atomic orbitals, and each molecular orbital forms a basis for an irreducible representation of the point group of the molecule.

Since electronic energy levels also contain vibrational energy levels, the electronic transition from the ground electronic state to excited electronic state can be associated with a vibrational transition. These vibronic transitions, still being one-photon processes, can be resolved in the gas

phase. Figure 11 shows the gas phase vibronic transitions of CO. However, in condensed phase, they usually can not be resolved and the electronic spectrum appears as a broad band. It is possible to sharpen the spectra by using non-polar solvents and/or reducing the temperature.

The relative “allowedness” of electronic transitions depends on selection rules, which arise from quantum mechanical considerations such as antisymmetrisation of the total wavefunction, transition moment integral, and the Franck-Condon principle [66-68]. The relative “allowedness” directly reflects on the extinction coefficient, ϵ , which is an intrinsic property of molecules. For spin forbidden transitions, ϵ lies in the range of 10^{-5} - $10^0 \text{ M}^{-1} \text{ cm}^{-1}$.

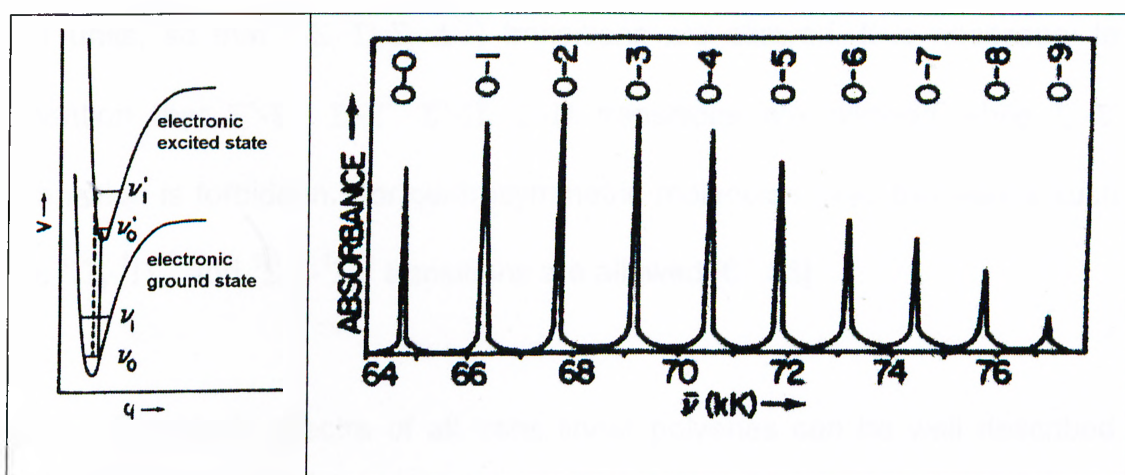


Figure 11. The electronic transition with 0-0 vibrational (solid line), and 0-1 vibrational (dashed line) transition, ($1 \text{ kK} = 1000 \text{ cm}^{-1}$) [66]

For spin allowed, but orbitally forbidden transitions, the range for ϵ is 10^0 - $10^3 \text{ M}^{-1} \text{ cm}^{-1}$. For both spin and orbitally allowed transitions, ϵ reaches the range of 10^3 - $10^5 \text{ M}^{-1} \text{ cm}^{-1}$. Since the geometries of a molecule in its electronic ground state and its electronic excited state are not necessarily the

same, the 0-0 transition is not necessarily the most intense transition. The Franck-Condon Factor, which is actually the overlap integral of vibrational wavefunctions of ground and excited electronic states, determines the intensities of vibronic transitions within the above given limits [66].

The selection rules can be summarised as follows;

The Spin Selection Rule: A transition is spin allowed if and only if the multiplicities of the two states are identical. This follows from the orthogonality of spin wavefunctions. Spin selection is the strictest selection rule [67,68].

The Orbital Selection Rule: An electronic transition is orbitally allowed if and only if the triple direct product $\Gamma(\psi'_e) \times \Gamma(\mu_e) \times \Gamma(\psi_e)$ contains the totally symmetric irreducible representation of the point group of the molecule. A simpler expression is that orbital angular momentum should change by 0 or ± 1 units, so that $\Sigma-\Sigma$, $\Pi-\Sigma$, $\Delta-\Pi$ transitions are allowed. It is necessary to mention that $\Sigma^+-\Sigma^+$, $\Sigma^--\Sigma^-$, $\Sigma^+-\Pi$, $\Sigma^--\Pi$ transitions are allowed while $\Sigma^+-\Sigma^-$ transition is forbidden. For centrosymmetric molecules $g \leftrightarrow u$ transitions such as ${}^1\Pi_g-{}^1\Pi_u$, and ${}^1\Sigma_u^+-{}^1\Sigma_g^+$ transitions are allowed [67,68].

Electronic spectra of all trans linear polyenes can be well described within the Born-Oppenheimer approximation, where the total wavefunction is factorised into nuclear, electronic, and vibrational parts. The discussion can be reduced to many electron states built from Π orbitals only. Considering the linear combinations of 2p atomic orbitals per one sp^2 hybridised carbon atom, and even number of electrons, the final states will have either A_g or B_u symmetry of the C_{2h} point group. The ground state of a linear polyene is 1^1A_g

with lowest energy molecular orbitals doubly occupied. The next excited state, 2^1A_g is a correlated state, which is a combination of doubly excited A_g2 (promotion of two electrons from HOMO to LUMO), and A_g3 (promotion of one electron from HOMO to LUMO+1 or from HOMO-1 to LUMO), as shown in Figure 12. The first transition is dipole forbidden. The second excited state, $1B_u$, is generated by excitation of one electron from HOMO to LUMO without change of spin and is the first allowed transition in the electronic spectrum of linear polyenes.

Figure 13 shows the optical spectra of diphenylhexatriene in the gas phase. The smooth curve from 3200 to 3600 Å is the absorption of vapor at 90 °C. The highly structured spectrum is the fluorescence excitation spectrum for diphenylhexatriene vapor seeded into supersonic He expansion. The first transition is the allowed $1^1B_u \leftarrow 1^1A_g$ transition (3200-3450 Å), and the second one is the forbidden $2^1A_g \leftarrow 1^1A_g$ transition (3450-3500 Å) [69].

As the number of conjugated double bonds in linear polyenes increases, the number of peaks in electronic spectra increases and shifts to longer wavelength. Table 2 lists the allowed electronic transitions of some polyenes, in n-pentane, together with the vibrational transitions and relative extinction coefficients in parenthesis [70].

As seen in Table 2, peaks of different polyenic sequences overlap with each other. Therefore, the electronic spectrum of dehydrochlorinated PVC is the superposition of peaks contributing for each polyenic sequence present, weighted by its concentration, as presented in Figure 14.

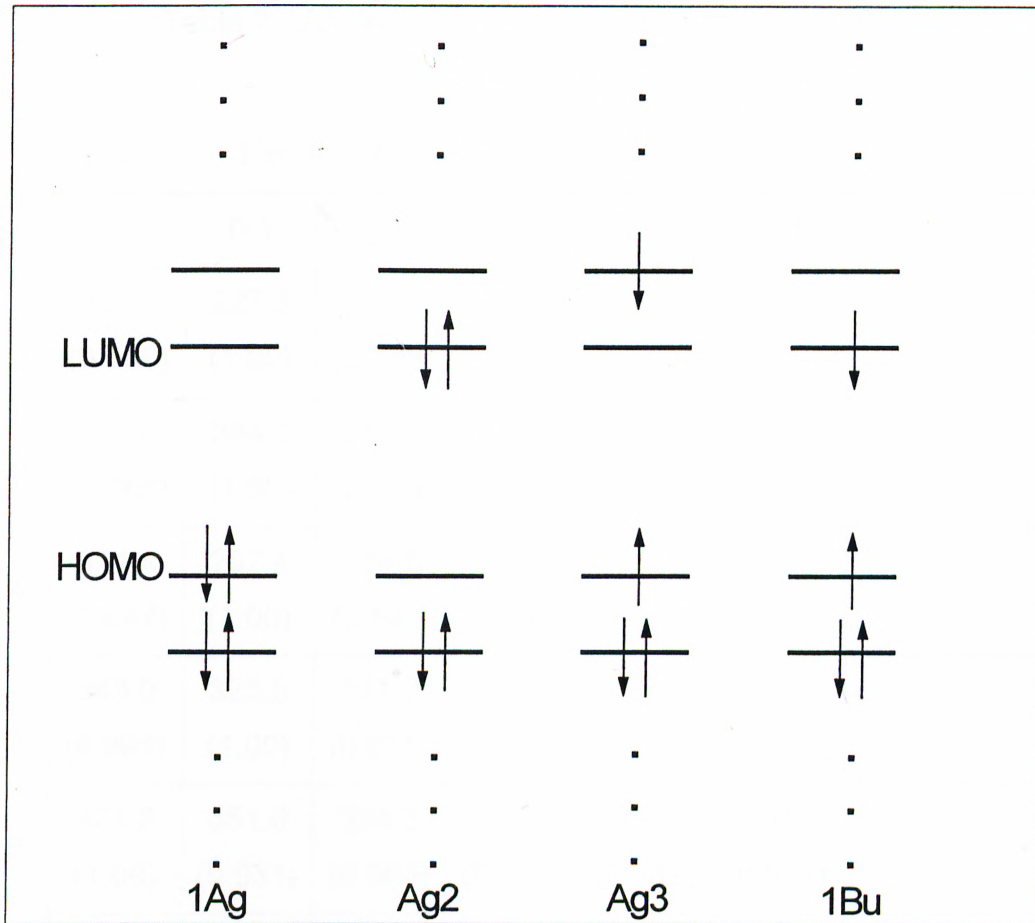


Figure 12. Ground and excited state configurations of linear polyenes

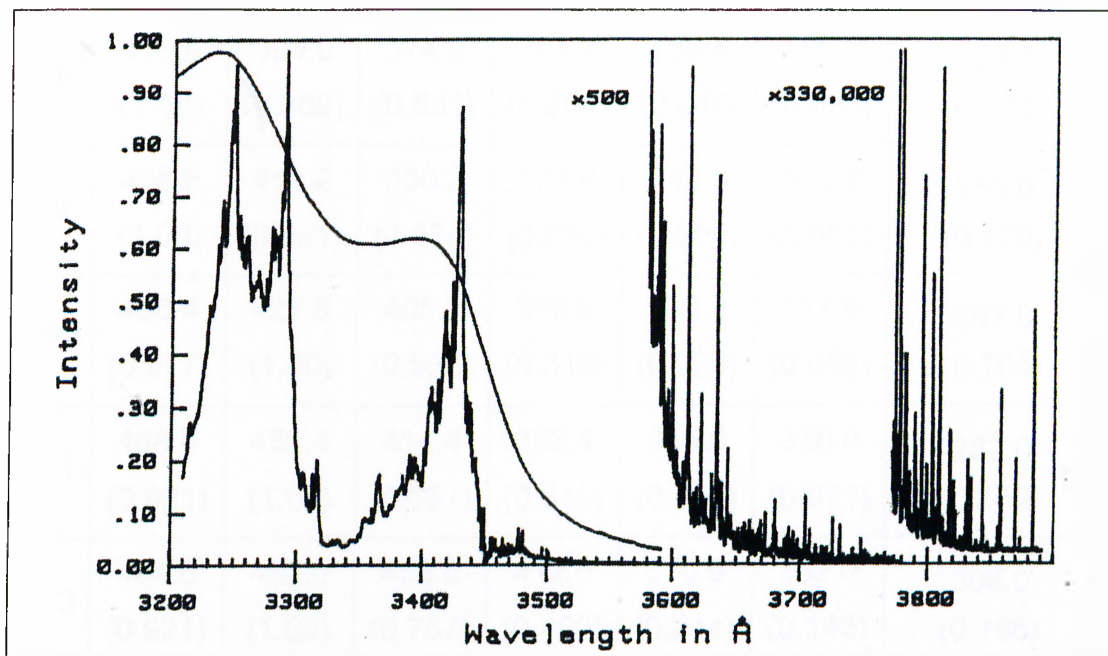


Figure 13. Electronic spectra of diphenylhexatriene vapor showing the first and second transitions.

Table 2. UV-Vis data of polyenes in n-pentane [70].

n	$1^1B_u \leftarrow 1^1A_g$				$3^1B_u \leftarrow 1^1A_g$		$2^1B_u \leftarrow 1^1A_g$
	0-0	0-1	0-2	0-3	0-0	0-1	0-0
2	237.2 (0.688)	227.8 (1.00)	219.8 (0.948)				
3	275.6 (0.766)	264.8 (1.00)	255.6 (0.779)				
4	311.4 (0.897)	297.4 (1.00)	284.8 (0.683)	274.6 (0.369)			
5	343.0 (0.991)	325.8 (1.00)	311.0 (0.615)	279.8 (0.294)	237.8 (0.062)		
6	371.2 (1.00)	351.0 (0.931)	334.2 (0.558)	319.0 (0.258)	258.2 (0.037)	250.0 (0.032)	
7	396.2 (1.00)	373.6 (0.906)	355.6 (0.520)	338.0 (0.239)	277.6 (0.035)	267.8 (0.026)	
8	418.8 (1.00)	394.0 (0.869)	374.0 (0.531)	354.2 (0.254)	296.4 (0.046)	285.6 (0.033)	239.0 (0.123)
9	438.8 (1.00)	411.2 (0.921)	390.2 (0.574)	371.8 (0.290)	313.6 (0.080)	301.8 (0.059)	253.0 (0.179)
10	456.4 (0.977)	427.8 (1.00)	405.2 (0.638)	382.6 (0.310)	330.8 (0.099)	317.6 (0.056)	267.8 (0.165)
11	468.8 (0.921)	439.4 (1.00)	414.4 (0.657)	393.4 (0.340)	346.0 (0.106)	330.0 (0.071)	282.0 (0.159)
13	494.0 (0.921)	462.0 (1.00)	438.0 (0.757)	412.0 (0.450)	370.0 (0.214)	352.0 (0.143)	306.0 (0.186)

Numbers are in nanometers and relative extinction coefficients are in parenthesis.

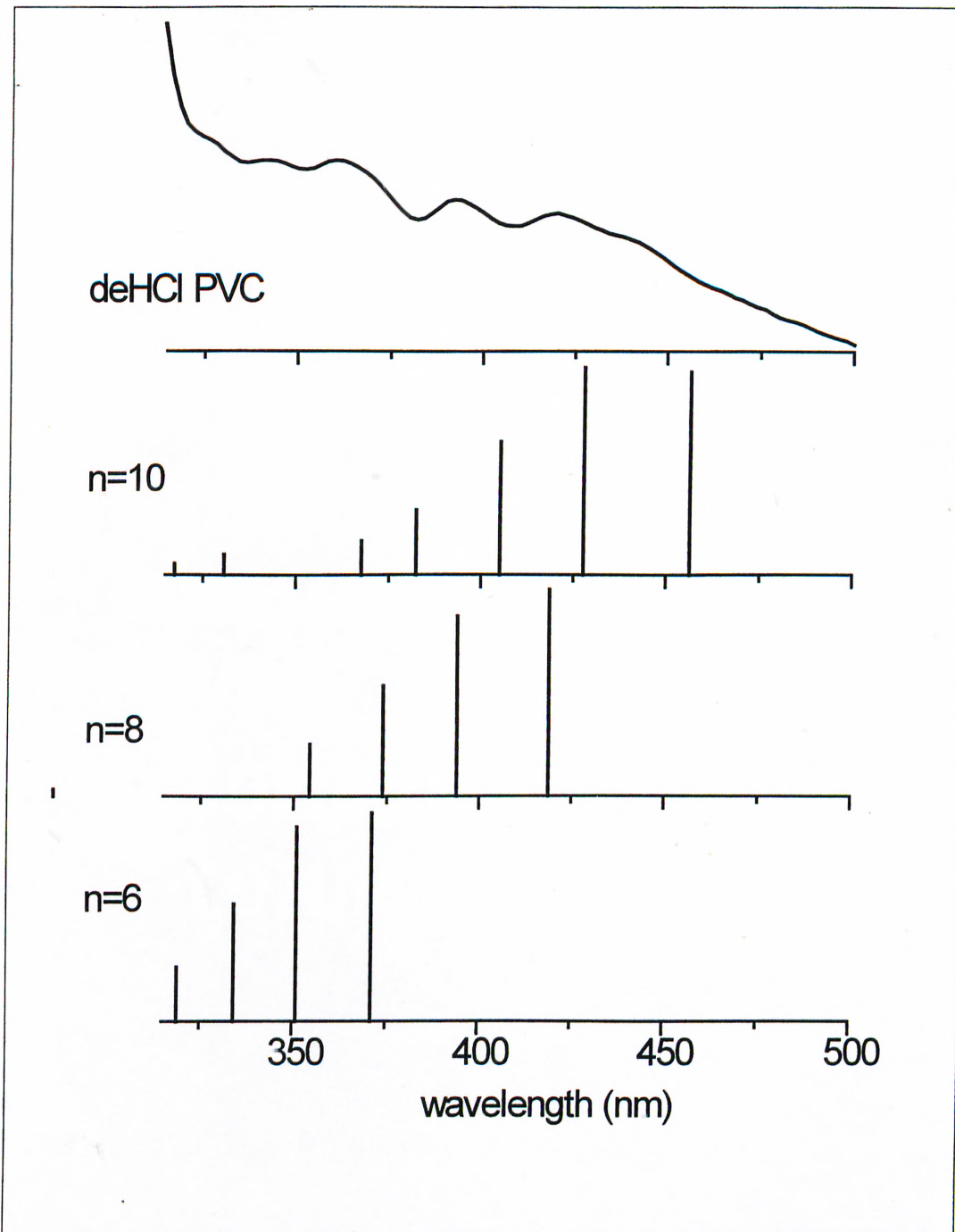


Figure 14. UV-Vis Spectrum of degraded PVC with polyene peak positions

1.7. Infrared Spectroscopy

A chemical bond between two atoms can be modelled as a harmonic oscillator, a spring with two masses on each end. The restoring force is written as, $F = -kq$, where k is the force constant, and q is the displacement from equilibrium position ($r-r_e$). The potential energy, the coordinate derivative of force, can be written as $V = \frac{1}{2}kq^2$. Quantum

mechanically, the molecule can have only discrete energy levels in the harmonic oscillator potential well, and this is expressed as

$$E_\nu = \left(\nu + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} = \left(\nu + \frac{1}{2}\right) \hbar\omega, \text{ where } \omega = \frac{1}{2} \sqrt{\frac{k}{\mu}}, \text{ } k \text{ is the oscillator}$$

strength and μ is the reduced mass ($\mu = \left(\frac{m_1 + m_2}{m_1 m_2}\right)^{-1}$). The values of ν can

only be positive integers, and when $\nu=0$, the zero point energy of the

molecule is equal to $E_0 = \frac{1}{2} \hbar\omega$. It is clear that ΔE can only be integer

multiples of $\hbar\omega$. In reality, the potential is not a perfect harmonic oscillator

potential, but it has the form, $V = D_e \left(1 - e^{-\beta q}\right)^2$, which is called the Morse

potential as shown in Figure 15. D_e is the depth of the potential well, and β

is a measure of the curvature at the bottom of the well.

Using this potential, vibrational energy levels are calculated as

$$E_\nu = \omega_e \left(\nu + \frac{1}{2}\right) - \omega_e x_e \left(\nu + \frac{1}{2}\right)^2, \text{ where } \omega_e \text{ is the oscillator strength, and } \omega_e x_e$$

is a small anharmonic correction [66]. The oscillator strengths fall in the

region of 10^2 - 10^3 cm^{-1} , and infrared region (4000-200 cm^{-1}) of electromagnetic spectrum has the right amount of energy to raise the energy level of a bond. The frequencies of respective bonds in a molecule are affected by the molecular environment, so they cover a range of frequencies instead of a single frequency. Figure 16 shows the stretching and bending vibration ranges of organic molecules [71]. For an IR absorption to take place, the electronic charge distribution within the molecule must change during vibration.

With the introduction of Fast Fourier Transform technique and interferometry based instruments, FTIR spectroscopy provides quick and reliable information about the chemical structure of a molecule. Chemical changes such as bond breaking, or bond formation, during a process can easily be monitored with FTIR spectroscopy.

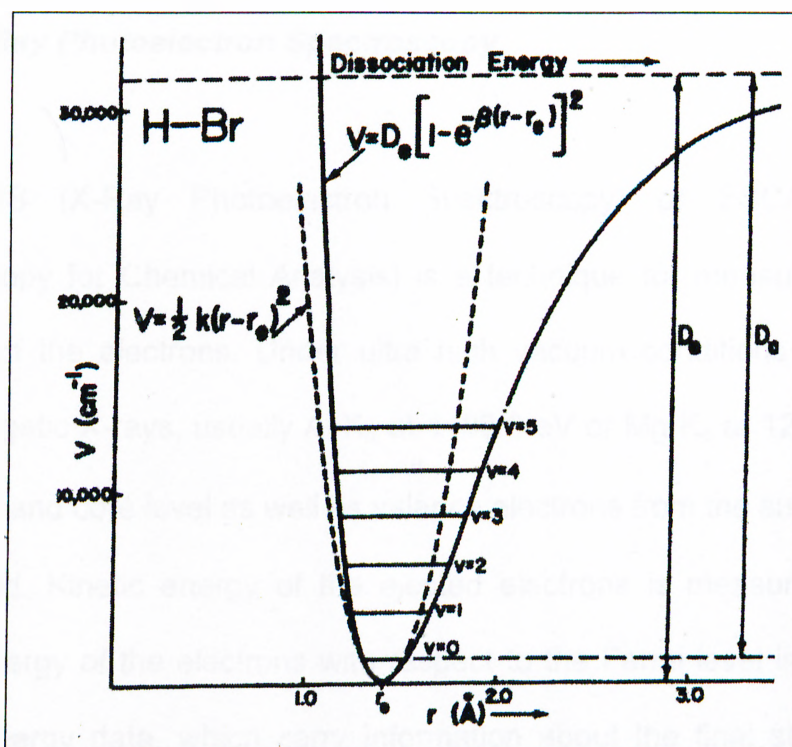


Figure 15. Comparison of harmonic potential and Morse potential for HBr molecule

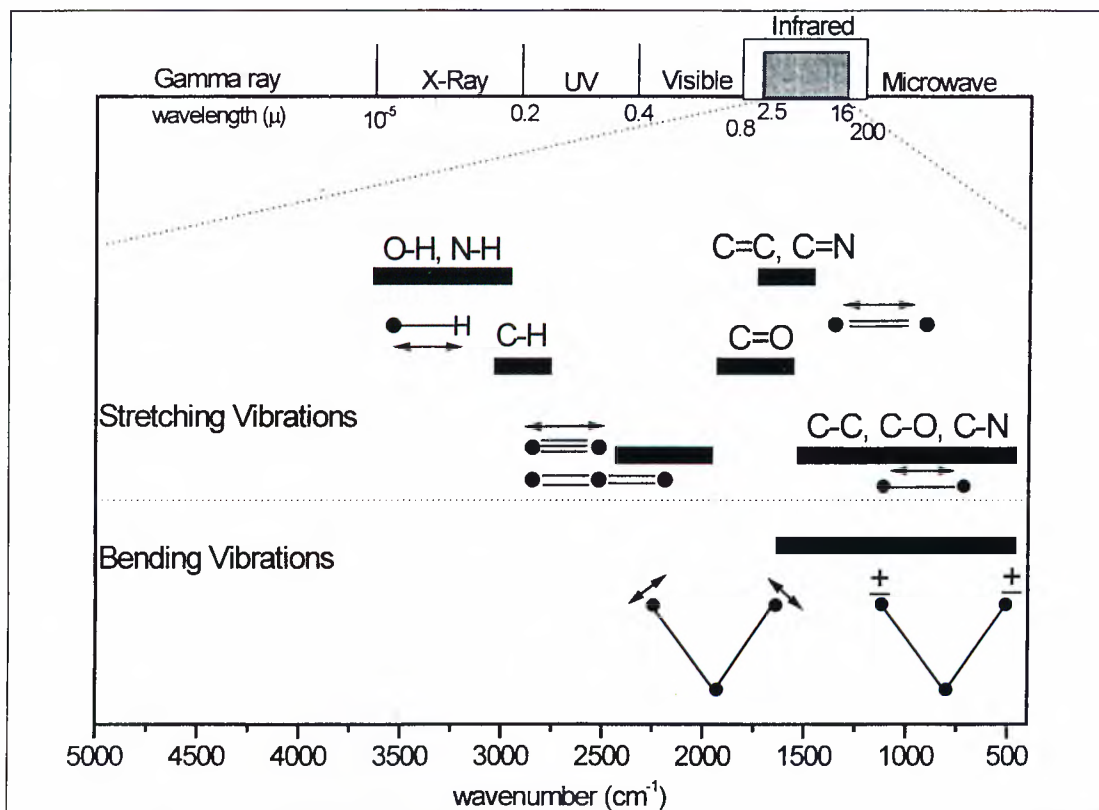


Figure 16. Vibrational infrared frequencies of organic molecules

1.8. X-Ray Photoelectron Spectroscopy

XPS (X-Ray Photoelectron Spectroscopy) or ESCA (Electron Spectroscopy for Chemical Analysis) is a technique for measuring binding energies of the electrons. Under ultra high vacuum conditions (10^{-9} Torr), monoenergetic X-rays, usually Al K_{α} at 1486.6 eV or Mg K_{α} at 1253.6 eV, hit the target, and core level as well as valence electrons from the surface atoms are ejected. Kinetic energy of the ejected electrons is measured and the binding energy of the electrons with respect to the Fermi level is computed. Binding energy data, which carry information about the final states of the atoms, are used for identifying the elements in the sample. Depending on the

chemical environment and the oxidation state, small shifts in binding energy, on the order of few eV, are observed for elements. These shifts, known as the chemical shifts, help to distinguish between different forms of the same element. XPS data can be quantified when line intensities are corrected for photo-ionisation cross sections of the elements [72].

2. EXPERIMENTAL

2.1. Sample Preparation

Polyvinyl chloride was purchased from Aldrich and was used without further treatment. The FTIR spectrum of PVC as a KBr pellet is given in Figure 17. The spectrum indicates the absence of any significant impurity and UV absorbing chromophore groups such as carbonyls. The assignment of the bands is given in Table 3 [13]. XPS spectrum of PVC powder, indicating the presence of O, C, and Cl in the structure is shown in Figure 18. Source of oxygen is mainly the adsorbed water [73].

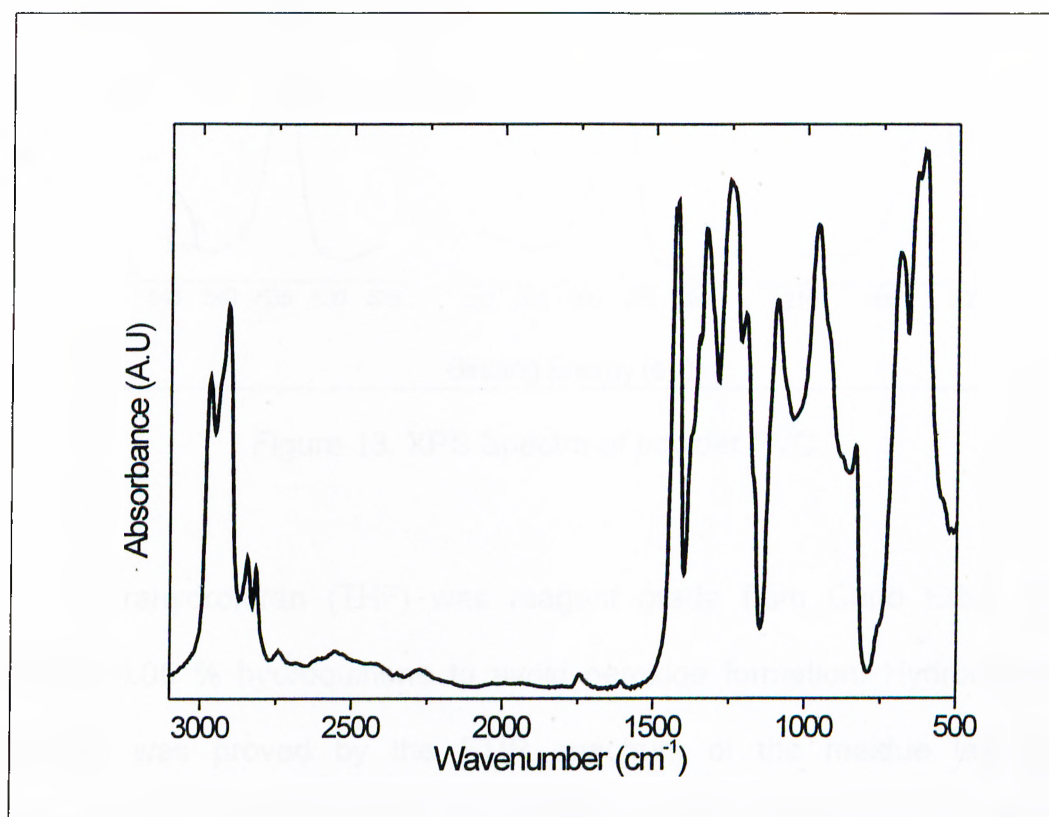


Figure 17. The FTIR spectra of PVC powder

Table 3. FTIR Band Assignments of PVC [13]

Band Position (cm ⁻¹)	Assignment
2970	C-H Stretch of CHCl
2912	C-H Stretch of CH ₂
1900	C=C=C-H
1718	C=O (photooxidation)
1595	Conjugated Double Bonds
1435	CH ₂ Deformation
1331	C-H Deformation of H-CCl
1099	C-C Stretch
966	CH ₂ Rocking
600-700	C-Cl Stretch

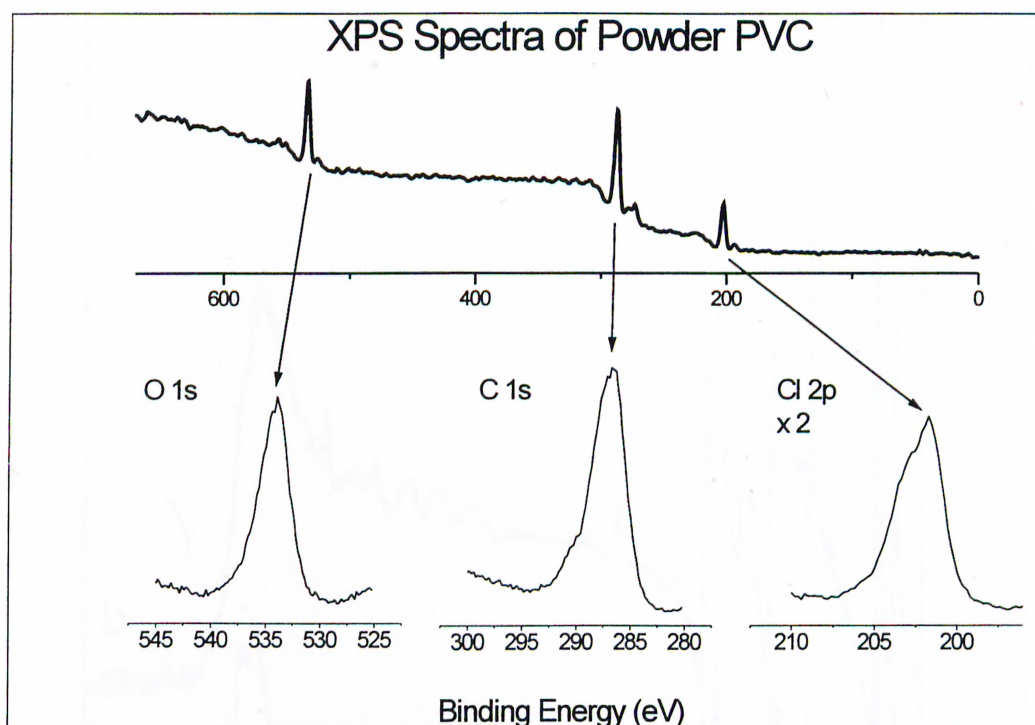


Figure 18. XPS Spectra of powder PVC

Tetrahydrofuran (THF) was reagent grade from Carlo Erba. THF contains 0.05 % hydroquinone to avoid peroxide formation. Hydroquinone presence was proved by the FTIR spectrum of the residue left after continuous evaporation of THF on a NaCl disk. The FTIR spectrum of the

residue and the reference spectrum of hydroquinone are given in Figure 19. The most intense peak of THF at 1070 cm^{-1} , and the most intense peak of hydroquinone at 1240 cm^{-1} are used to monitor these species in polymer blends. Hydroquinone in THF was removed by distillation over KOH prior to use. The UV spectra of THF, before and after distillation, are given in Figure 20. The characteristic peaks of hydroquinone disappear after distillation.

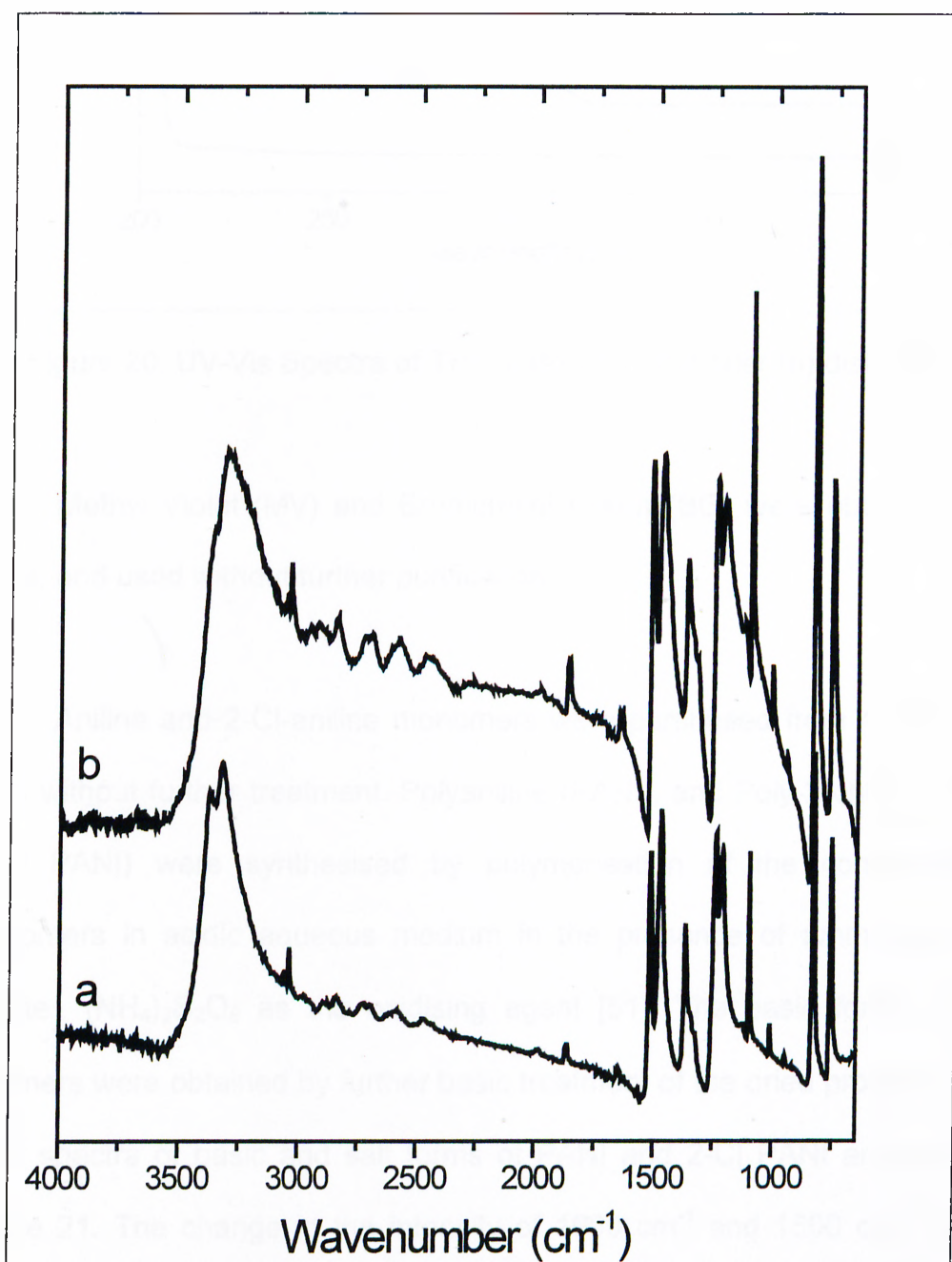


Figure 19. FTIR Spectra of hydroquinone (a), and THF residue (b)

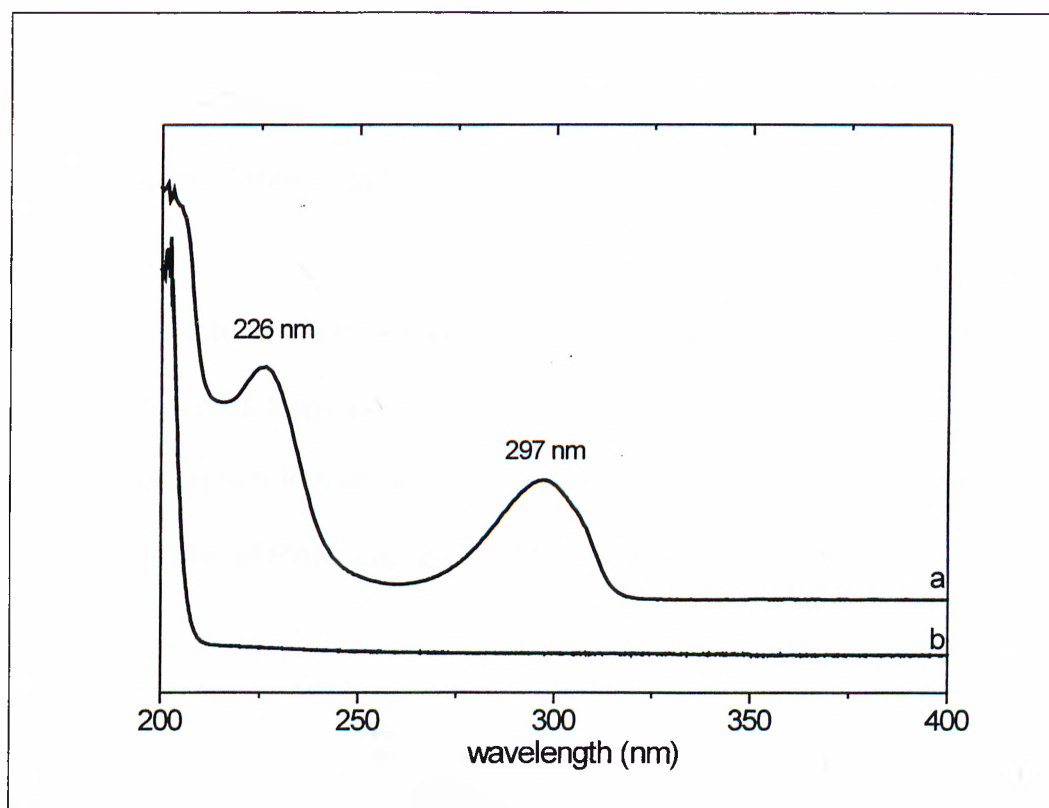


Figure 20. UV-Vis Spectra of THF, before (a) and after (b) distillation

Methyl Violet (MV) and Bromcresol Green (BG) were obtained from Fluka, and used without further purification.

Aniline and 2-Cl-aniline monomers were purchased from Aldrich and used without further treatment. Polyaniline (PANI), and Poly-2-chloro aniline (2-Cl PANI) were synthesised by polymerisation of the corresponding monomers in acidic aqueous medium in the presence of ammonium per sulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidising agent [51]. The basic forms of the polymers were obtained by further basic treatment of the dried products. The FTIR spectra of basic and salt forms of PANI and 2-Cl PANI are given in Figure 21. The change in the intensity of 1600 cm^{-1} and 1500 cm^{-1} peaks indicate the protonation of the imine nitrogens [52], conversion to amine

nitrogens by the internal redox reaction [50,53], transforming the insulating base form to the conducting salt form. Detailed assignment of the IR bands of PANI is given in Table 4 [52].

The structural change can be monitored by UV-Vis-NIR spectroscopy. The salt form has a large polaron band [54], whereas the base form does not have any absorption in that region. The UV-Vis-NIR spectra of insulating and conducting forms of PANI and 2-Cl PANI are given in Figure 22.

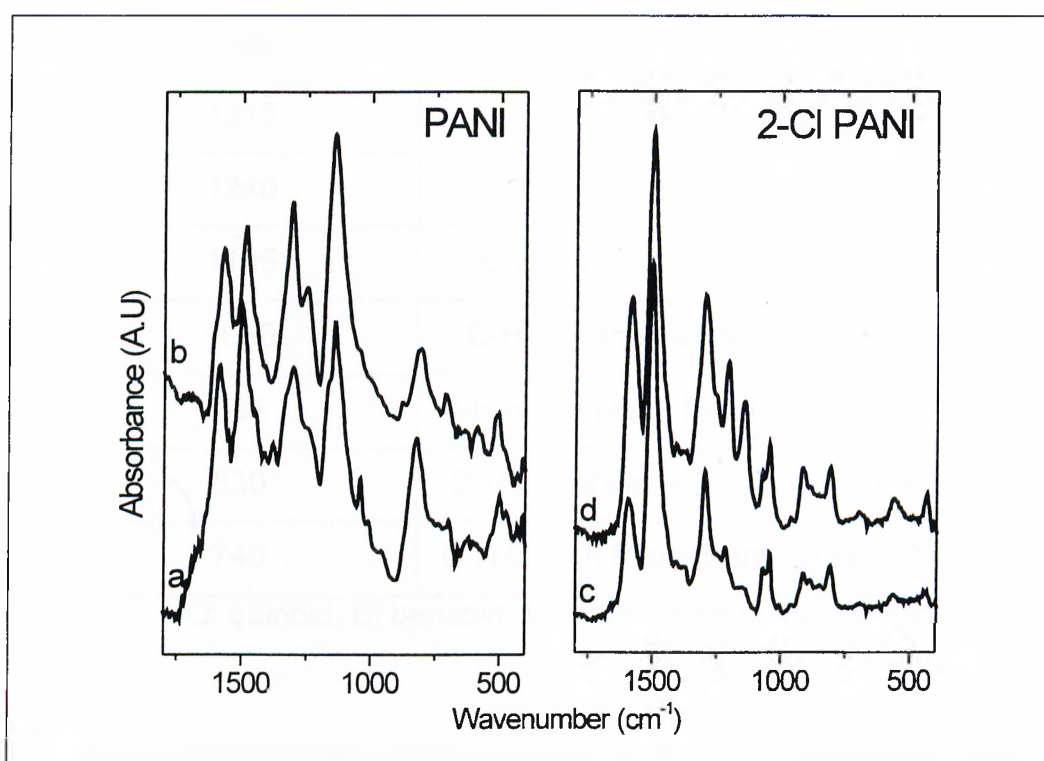


Figure 21. FTIR Spectra of PANI base (a), PANI salt (b), 2-Cl PANI base (c), and 2-Cl PANI salt (d)

Table 4. Assignment of IR bands of PANI [52]

Band Position (cm ⁻¹)	Assignment
3460	NH ₂ Asymmetric Stretch
3380	NH ₂ Symmetric Stretch, NH Str.
3310	H-Bonded NH Stretch
3170	=N-H Stretch
1587	Stretch Of N=Q=N
1510	Stretch Of N-B-N
1450	Stretch Of Benzene Ring
1380	C-N Stretch in QB _t Q
1315	C-N Stretch in QB _c Q, QBB
1240	C-N Stretch in BBB
1105	C-H in plane Bending on 1,4-Ring
1060	C-H in plane Bending on 1,2,4-Ring
895	C-H out of plane Bending on 1,2,4-Ring
830	C-H out of plane Bending on 1,4-Ring
740	C-H Out Of Plane Bending on 1,2-Ring

Q: quinoid, B: benzoid, B_t: *trans*-benzoid, B_c: *cis*-benzoid

Hydroquinone (HQ), anthraquinone (AQ), and anthracene (AC) were from Merck and used without further purification.

PVC, binary systems of PVC/MV, PVC/BG, PVC/HQ, PVC/AQ, PVC/AC, PVC/PANI, PVC/2-Cl PANI and tertiary systems of PVC/HQ/MV, PVC/AQ/MV, PVC/AC/MV were prepared by dissolving the components in distilled THF with 1 hour ultrasonic bath. Ratio for binary systems of

PVC/MV, PVC/BG, PVC/HQ, PVC/AQ, and PVC/AC was 10:1 w/w, and ratio for binary systems of PVC/PANI, and PVC/2-Cl PANI was 1:1 w/w. The ratio for tertiary systems of PVC/HQ/MV, PVC/AQ/MV, and PVC/AC/MV was 10:1:1 w/w. The solutions were cast onto quartz windows for UV-Vis-NIR spectroscopic investigations and onto KBr windows for FTIR studies. The solvent was evaporated, at room temperature, under saturated THF atmosphere for slow and uniform film formation. The average thicknesses of the films were of the order of several micrometers. Solvent residue detected by the IR peak at 1070 cm^{-1} , was removed by pre-heating the films with IR lamp for 15 minutes. The temperature under IR lamp was measured as $70\text{ }^{\circ}\text{C}$.

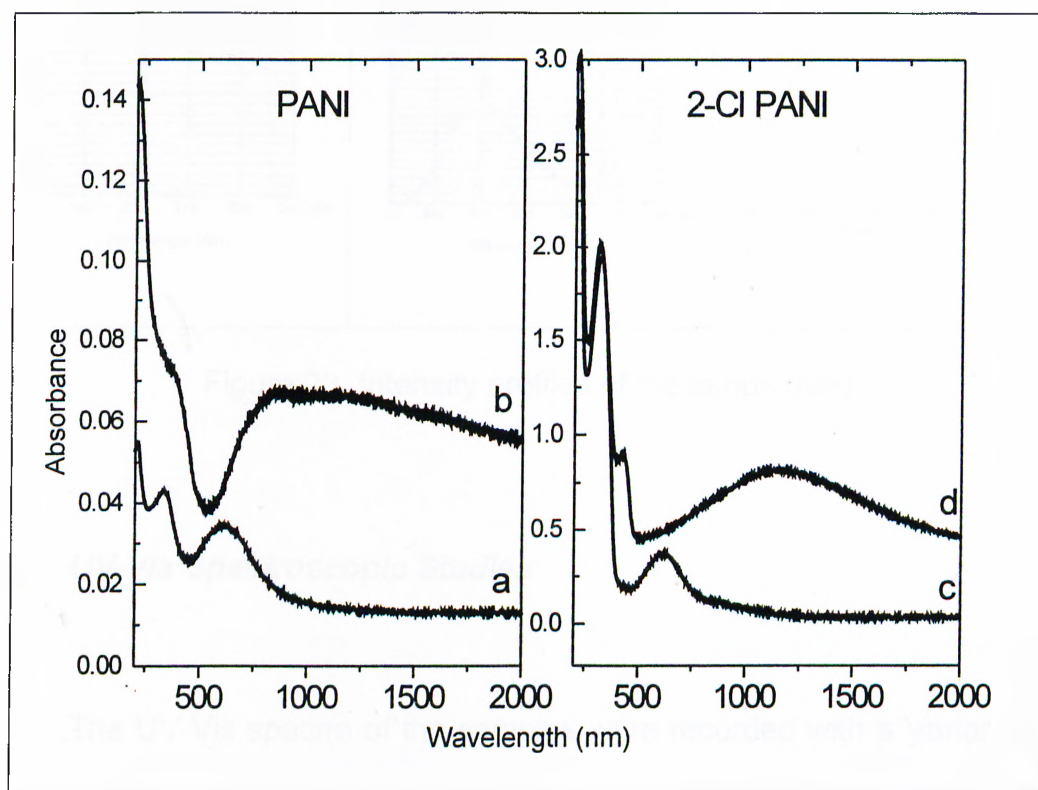


Figure 22. UV-Vis-NIR Spectra of PANI base (a), PANI salt (b), 2-Cl PANI base (c), and 2-Cl PANI salt (d)

2.2. Irradiation Studies

Irradiation studies were carried out with a low-pressure mercury lamp (7 mW/cm^2) emitting a single line at 254 nm, a low-pressure fluorescent filter coated lamp (8 mW/cm^2), which emits mostly at 312 nm, and with a 75 W Xe source equipped with a monochromator. The intensity profiles of the lamps are given in Figure 23.

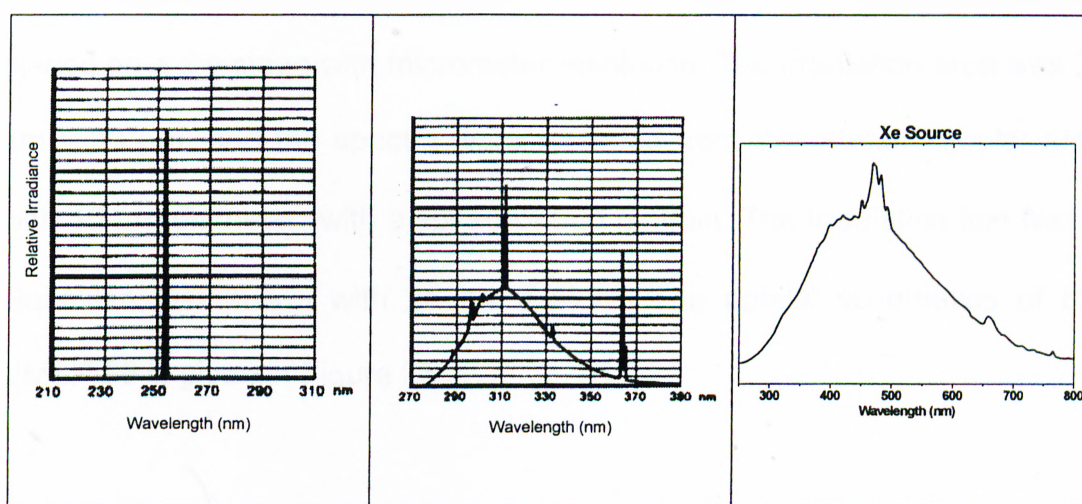


Figure 23. Intensity profiles of the lamps used

2.3. UV-Vis Spectroscopic Studies

The UV-Vis spectra of the samples were recorded with a Varian Cary 5 spectrophotometer, and a Zeiss UMSP 80 microscope spectrometer.

Cary 5 is a double beam spectrophotometer with deuterium / tungsten source, 1200 lines/mm diffraction grating and photomultiplier tube for detection. The samples irradiated with 254 nm and 312 nm lamps were put in the spectrometer following the irradiation and their spectra were recorded with 300 nm/min speed and 2 nm spectral band width, through an aperture with 5.0 mm diameter. The optical schematics of Varian Cary 5E is given in Figure 24.

The UMSP 80, is a microscope spectrometer with a 75-Watt Xe source, two monochromators and a photomultiplier tube. The samples were placed on a x-y stage with micrometer resolution. The irradiation area was 30 μm x 30 μm , and the spectra were recorded from the interior circular area with 10 μm diameter with a speed of 600 nm/min. The irradiation line was a Gaussian distribution with 25 nm FWHM. The optical schematics of the UMSP 80 is given in Figure 25.

In the spectrometers, the detector response is converted to intensity ratio of the transmitted light through the sample and the reference for every wavelength. The ratio, known as the transmittance, can be converted to percent transmittance by normalisation with respect to reference. The more informative quantity, the absorbance, is the logarithm of reciprocal transmittance. The absorbance is related to concentration by the famous Beer-Lambert Law, ($A=\epsilon bc$), where ϵ is the molar extinction coefficient, b is the sample path length, and c is the concentration [74].

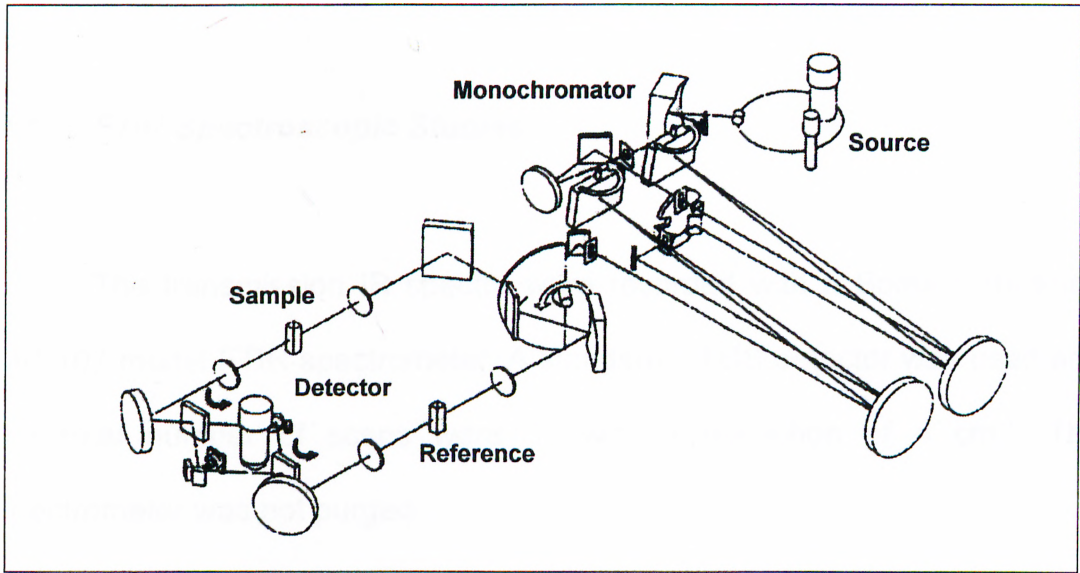


Figure 24. Optical schematics of Varian Cary 5E spectrophotometer

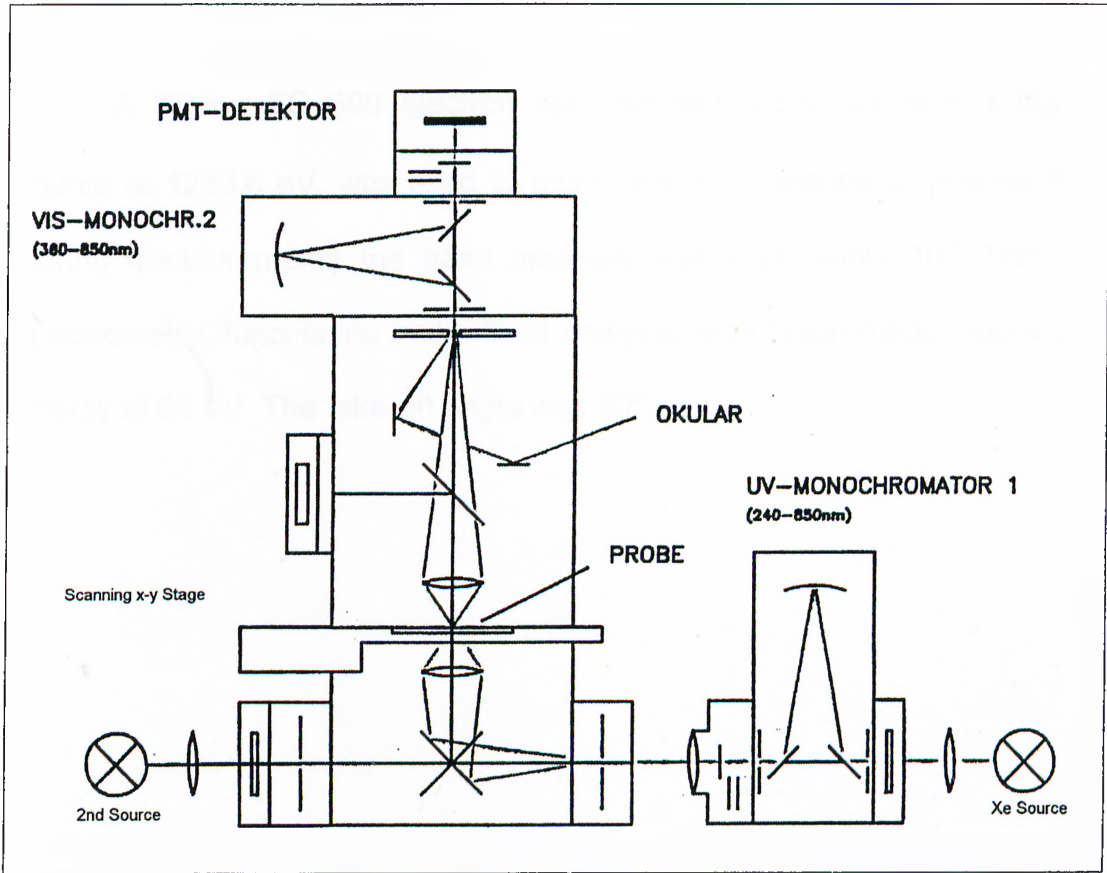


Figure 25. Optical schematics of the UMSP 80

2.4. FTIR Spectroscopic Studies

The transmission IR spectra were recorded with a Bomem Hartman MB-102 model FTIR spectrometer. A standard DTGS detector was used and the total number of scans were 32 with a resolution of 4 cm^{-1} . The spectrometer was not purged.

2.5. XPS Study

A Kratos ES 300 electron spectrometer, equipped with a Mg $K\alpha$ source at 1253.6 eV, was used to record the XPS spectra of powder PVC. During measurements the base pressure was kept below 10^{-8} Torr. The spectrometer, functioning in the fixed analyser retardation mode, had a pass energy of 65 eV. The take-off angle was 90° .

3. RESULTS AND DISCUSSIONS

3.1. Photo-degradation of PVC

When solvent cast films of PVC are irradiated at 254 nm and 312 nm, photo-degradation takes place and HCl is evolved. The degradation can be monitored with the addition of an acid-base indicator, for instance Methyl Violet, into the polymer matrix. Figure 26 shows the UV-visible spectrum of the irradiated PVC/MV blend. The gradual decrease in intensity of the Methyl Violet peak, around 550 nm indicates photo-degradation.

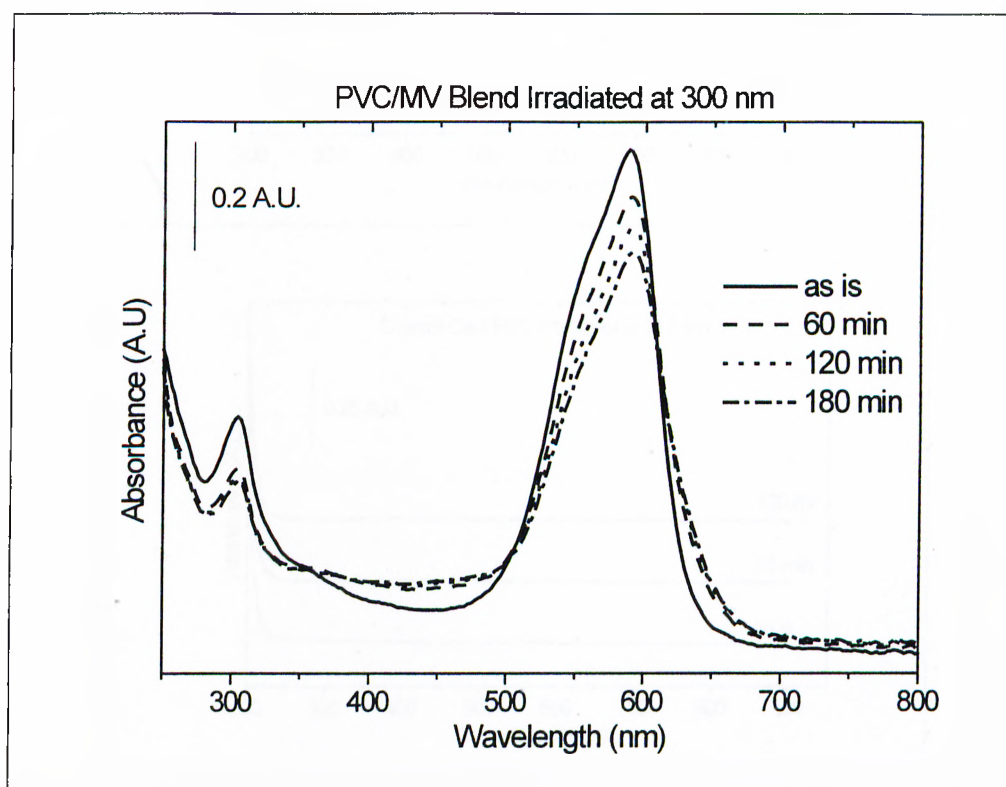


Figure 26. Visible spectrum of irradiated PVC/MV blend

However, the absence of any change in the spectral window of 300-500 nm, shows that although some dehydrochlorination takes place, it is not sufficient to lead to polyene formation during irradiation at 254 nm and 312 nm within a few hours. Figure 27 shows the UV-Vis spectra of solvent cast PVC samples exposed to 254 nm and 312 nm irradiation for two hours. This conclusion is supported with FTIR spectra of the same samples (Figure 28), that shows no significant change in the intensities of the C-Cl and the C-C stretching, and the C-H bending vibrations.

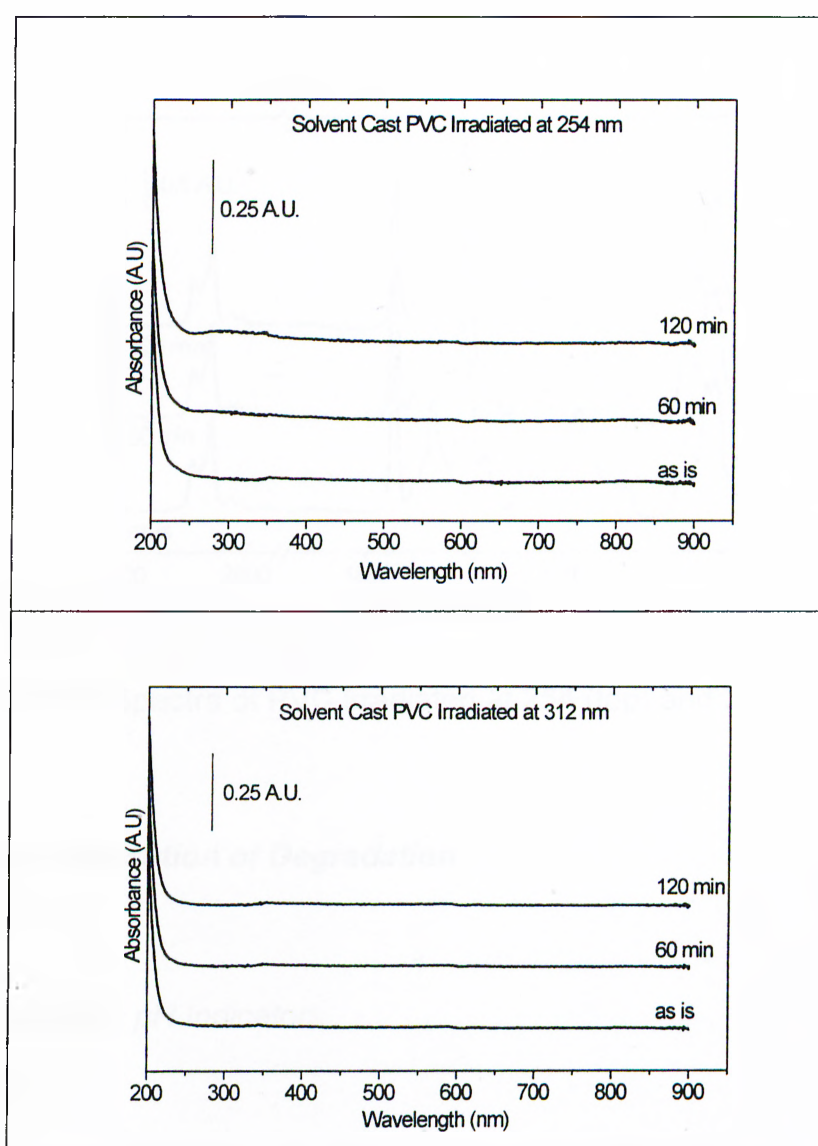


Figure 27. UV-Vis Spectra of PVC irradiated at 254 (top) and 312 (bottom) nm

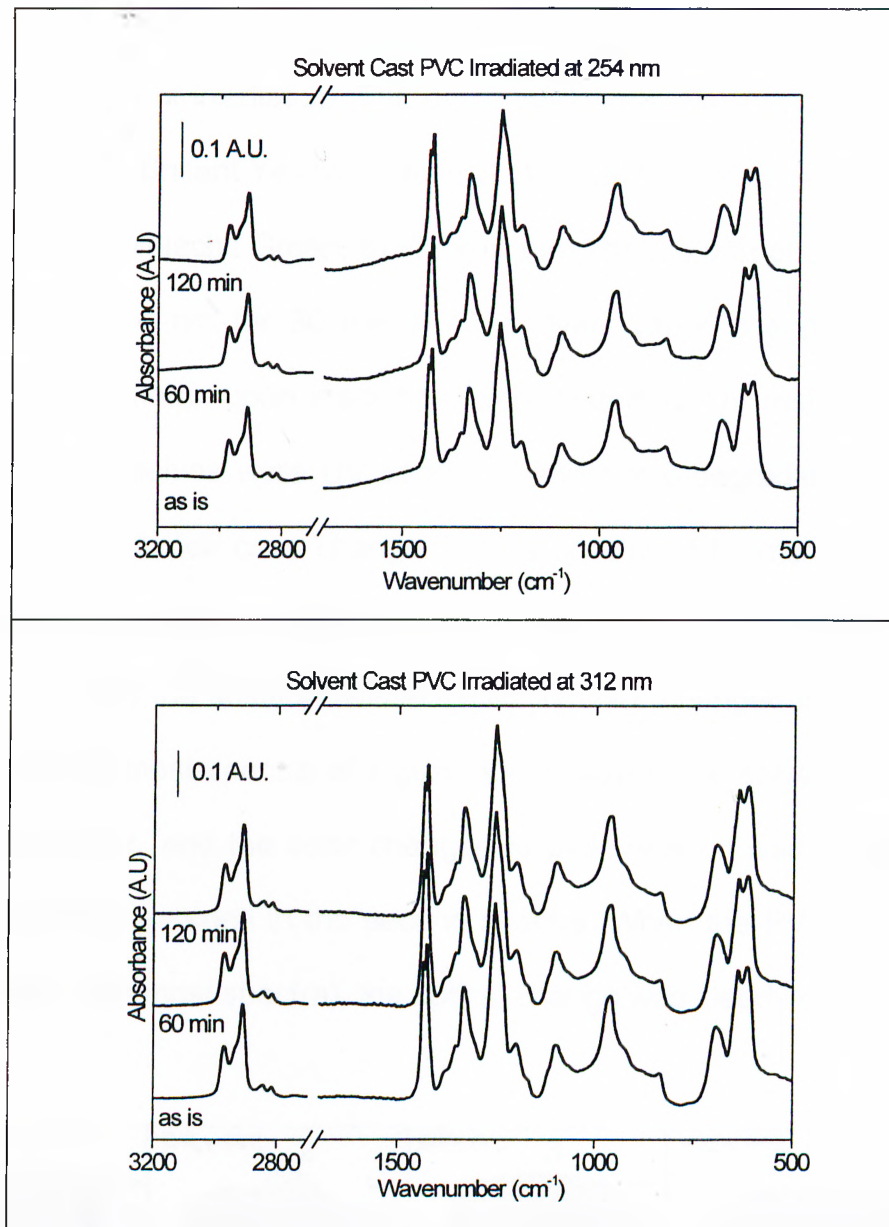


Figure 28. FTIR Spectra of PVC irradiated at 254 (top) and 312 (bottom) nm

3.2. *Better Utilisation of Degradation*

3.2.1. *Blends with pH Indicators*

For better utilisation of degradation, pH indicators were employed. Many pH indicators were blended with PVC and solvent cast films were

exposed to UV radiation. Figure 29 shows the optical changes of PVC/dye blends as a result of irradiation. The dyes used were; 1) Bromocresol Green; 2) Congo Red; 3) Brilliant Yellow; 4) Methyl Orange; 5) Bromocresol Purple; 6) Methyl Violet; 7) Malachit Green; 8) Fluorescein. The top part of each sample is exposed to 254 nm for 30 minute. The dyes, which changed color or intensity in PVC matrix upon irradiation, were tested for UV resistivity. Most of the dyes themselves were UV sensitive, and photo-degradation of PVC clearly accelerated their color change. Visible spectra of Bromocresol Green, as an example, are given in Figure 30. Bromocresol Green had a blue color in solution and when the solution was acidified its color changed to yellow, as seen in the right-most spectra of Figure 30. However, the solvent cast dye had a yellow color, and the color changed to pink, when it was exposed to 254 nm radiation, as seen in the second spectra. When the PVC/BG blend was irradiated (left-most spectra), the optical change was clearly catalysed.

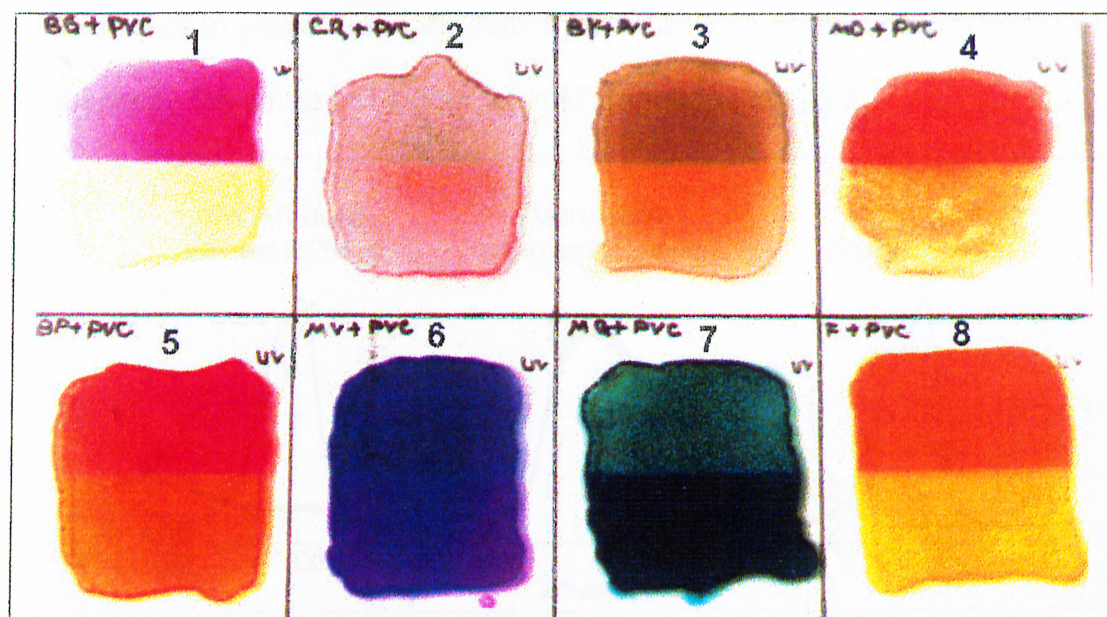


Figure 29. Irradiated PVC/dye blends

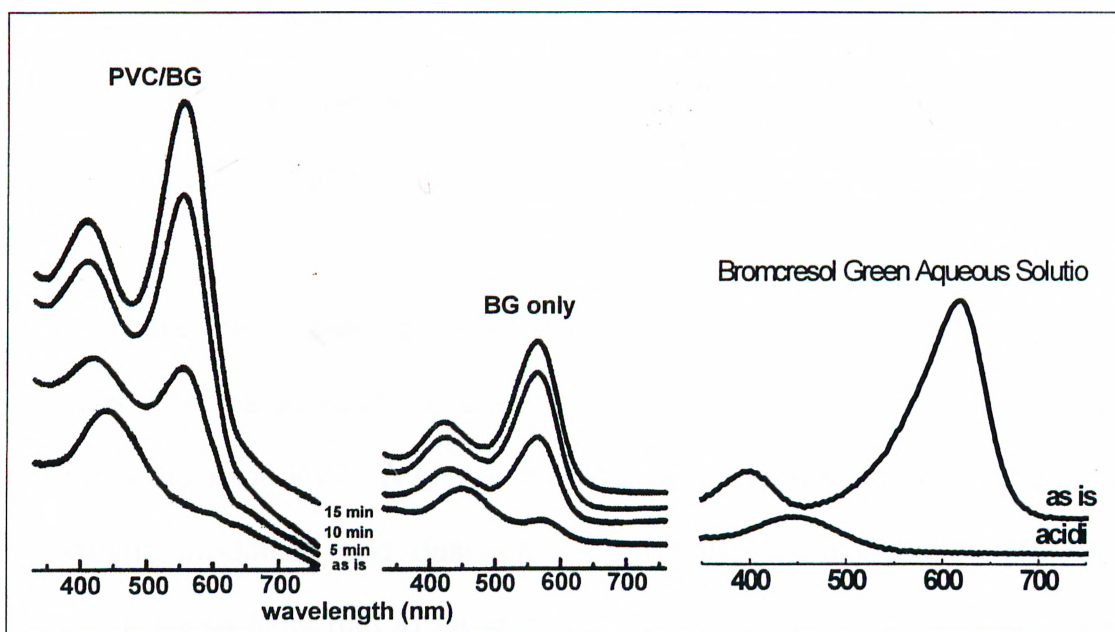


Figure 30. Visible spectra of Bromocresol Green as solution, as film, and as blend with PVC

One of the indicators used, Methyl Violet, had a blue color in the basic form and a yellow color in the acidic form, as shown in Figure 31. Surprisingly, the dye is resistant to UV radiation, as shown in the second spectra. The PVC/MV blend films, having originally a blue color, changed their color to yellow upon irradiation, with the loss of the 550 nm peak, which is exactly the same behaviour as in MV aqueous solution.

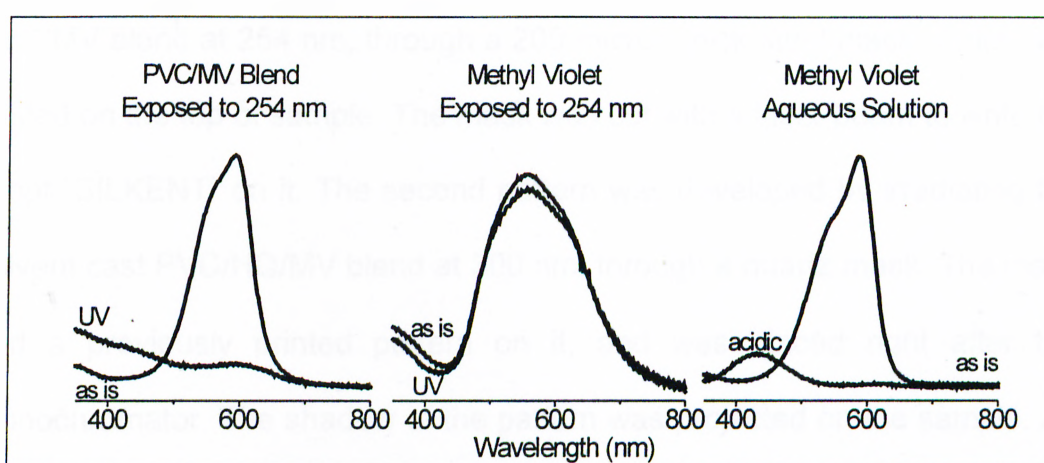


Figure 31. Visible Spectra of Methyl Violet, as solution, as film, and as blend with PVC

With this spectroscopic evidence, it is clearly demonstrated that, UV irradiation dehydrochlorinated PVC, and that an ACID-BASE REACTION took place in the blend of PVC with Methyl Violet.

There have been several studies for devising radiation sensing systems. For this purpose, several pH indicators were blended with various polymers including PVC. These blend films were exposed to different doses of gamma irradiation and dosimetric calibration was established [75-79]. However, these films had to be stored in the dark before using to increase reliability and lifetime. In addition, the possible damage of the indicator upon irradiation was always underestimated. The MV/PVC system is quite stable under daylight, and it is well established that the change is only due to polymer degradation. This system is a good candidate for dosimetric and/or lithographic purposes.

In Figure 32 and Figure 33, examples of lithographic utilisation are presented. The first pattern was imprinted by irradiating the solvent cast PVC/MV blend at 254 nm, through a 200 micron thick steel mask, which was placed on the top of sample. The mask was cut with a laser beam to write the script "BILKENT" on it. The second pattern was developed by irradiating the solvent cast PVC/HQ/MV blend at 300 nm, through a quartz mask. The mask had a previously printed pattern on it, and was placed right after the monochromator. The shadow of the pattern was projected on the sample. As seen from the scale bars, the first example has macroscopic dimensions, while the second has microscopic dimensions. The latter figure can be

scanned in the x-direction recording the absorbance at 600 nm, and Figure 33 also shows the fidelity of the printed pattern in terms of absorbance change in lateral direction.



Figure 32. Lithographic application of PVC/MV blend in macro scale

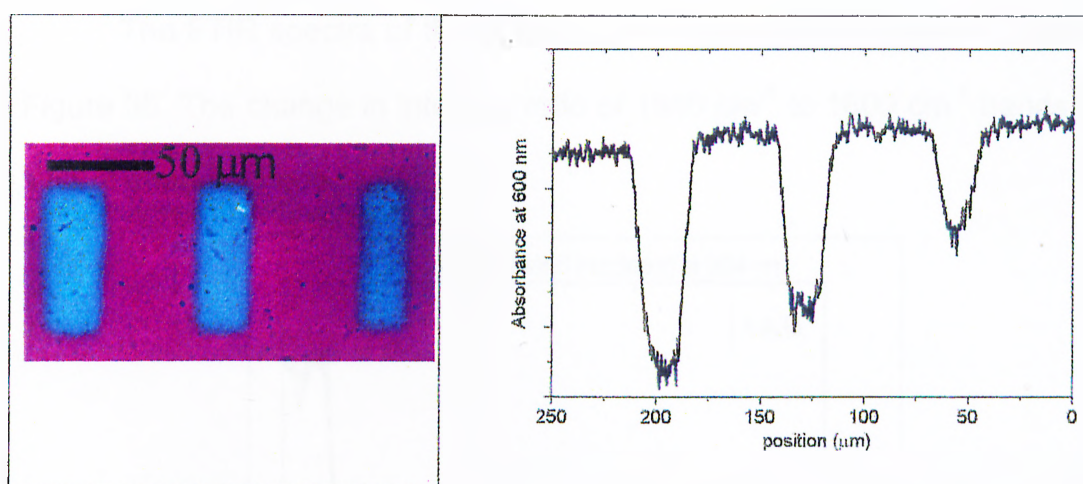


Figure 33. Micro scale lithographic pattern and its lateral absorbance change

3.2.2. Blends of PVC with Conducting Polymers

Conducting polymers were also used for better utilization of degradation. Basic forms of PANI and 2-Cl PANI were blended with PVC, and solvent cast films were exposed to UV radiation. Reversibility of the systems was tested by further exposure to NH_3 vapor.

2-Cl PANI showed higher solubility in THF compared to PANI, as expected due to the presence of Cl atom attached to the benzoid ring

structure. When the PVC/PANI and PVC/2-Cl PANI blends containing the same amount of the conjugated polymer were exposed to 254 nm UV radiation, the latter blend showed a very intense polaron band in contrast to the former as shown in Figure 34. This difference is also believed to reflect to the measured conductivities. Photo-degradation of PVC at this wavelength within the irradiation period of 2 hours does not yield polyenes, so the conductivity of the blends is totally attributable to doped PANI or 2-Cl PANI.

The FTIR spectra of the irradiated PVC/2-Cl PANI blend are shown in Figure 35. The change in intensity ratio of 1500 cm^{-1} to 1600 cm^{-1} bands is a sign of change in conductivity.

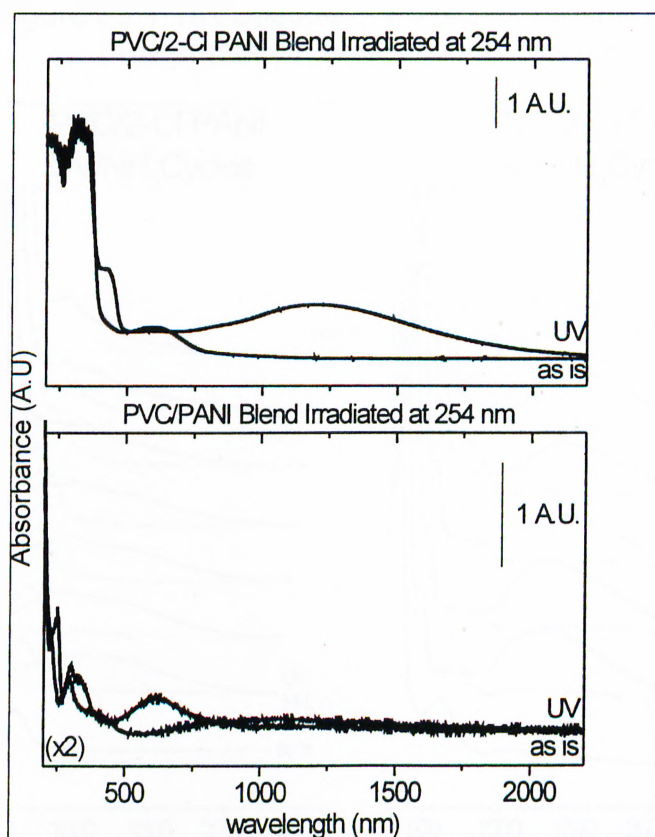


Figure 34. UV-Vis-NIR spectra of Irradiated PVC/PANI and PVC/2-Cl PANI blends containing equal amounts of conducting polymer

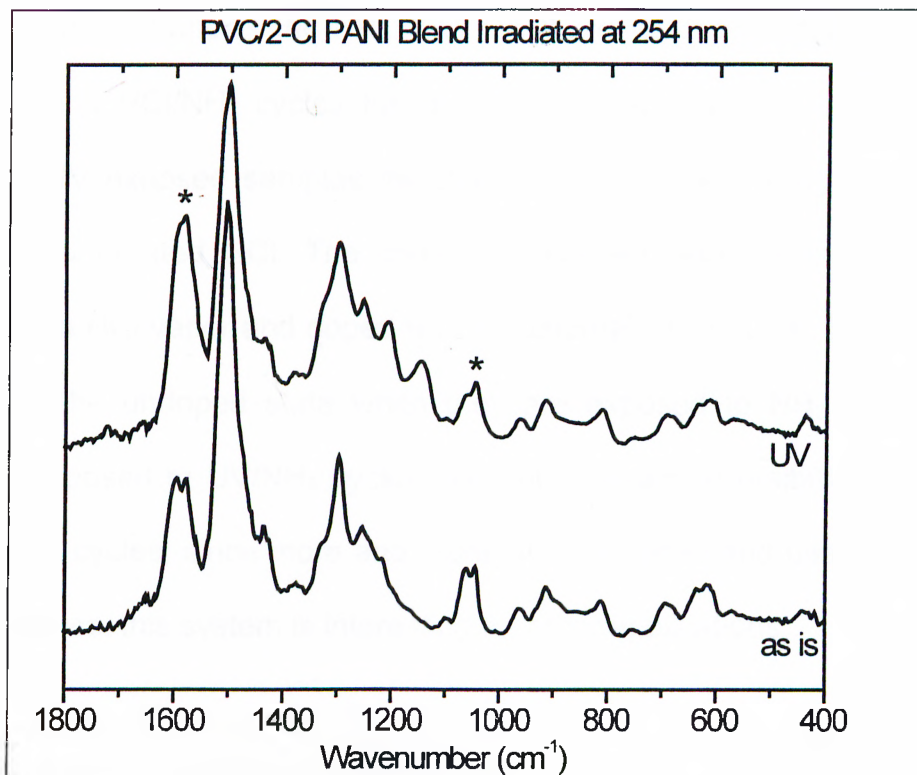


Figure 35. FTIR Spectra of PVC/2-Cl PANI Blend Irradiated for 2 hours at 254 nm

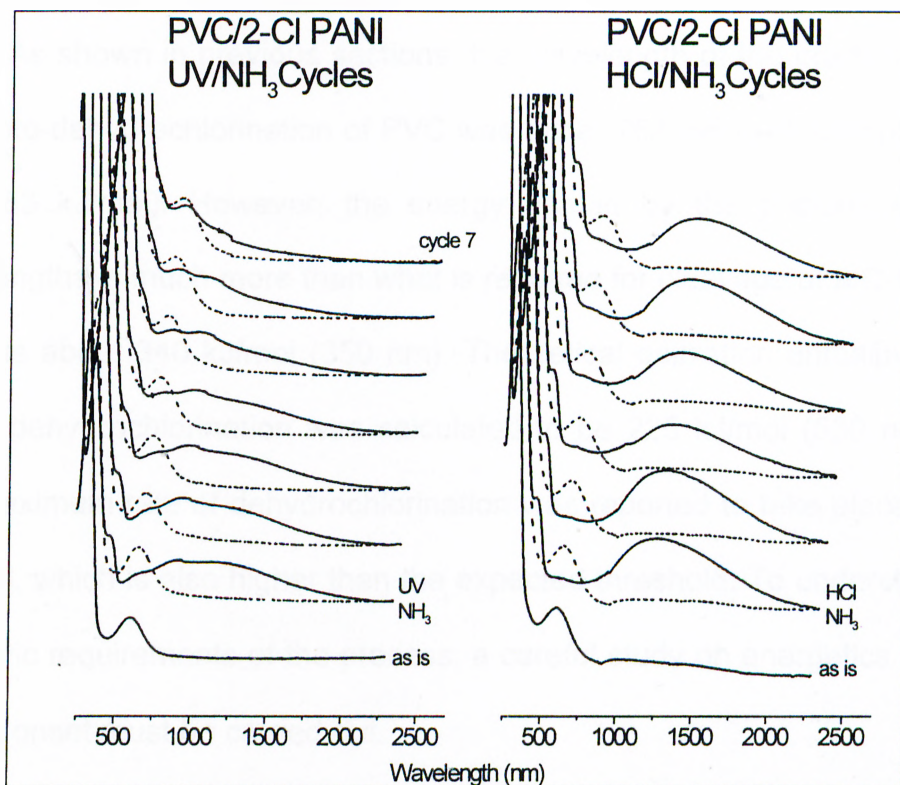


Figure 36. PVC/2-Cl PANI blends exposed to consecutive UV/NH₃ and HCl/NH₃ cycles

Figure 36 shows the PVC/2-Cl PANI blends exposed to consecutive UV/NH₃ and HCl/NH₃ cycles for comparison. Development of the polaron band in UV exposed samples indicates doping of the conjugated polymer with *in-situ* created HCl. The same is observed with the sample that is exposed to HCl vapor and doped with an external HCl source. Both samples return to the undoped state when they are exposed to NH₃ vapors. The system exposed to UV/NH₃ cycles can not maintain reversibility for a large number of cycles, since more and more HCl is created and used up in time. Nevertheless, this system is interesting for other applications.

3.3. Wavelength Tuning of PVC Photodegradation

As shown in previous sections, the wavelength of the irradiation used for photo-dehydrochlorination of PVC was either 254 nm (471 kJ/mol) or 312 nm (383 kJ/mol). However, the energy carried by the photons of these wavelengths is much more than what is required for cleavage of a C-Cl bond, which is about 340 kJ/mol (350 nm). Theoretical activation enthalpy of gas phase dehydrochlorination was calculated to be 225 kJ/mol (530 nm) [35]. The maximum rate of dehydrochlorination was reported to take place at 370 nm [16], which is also higher than the expected threshold. To understand the energetic requirements of the process, a careful study on energetics and the energy onset must be carried out.

As mentioned in previous sections, there are practical ways to monitor dehydrochlorination of PVC, such as incorporation of pH indicators or basic

forms of conducting polymers into PVC matrix. In the former case, the decrease in the dye peak, 550 nm for Methyl Violet, can be used to monitor the extent of dehydrochlorination and in the latter case, formation of a polaron band can be used to gauge dehydrochlorination, as shown in Figure 37. However, only PVC/MV systems, enable us to monitor polyenes, since the spectral window of 320-460 nm is not obscured.

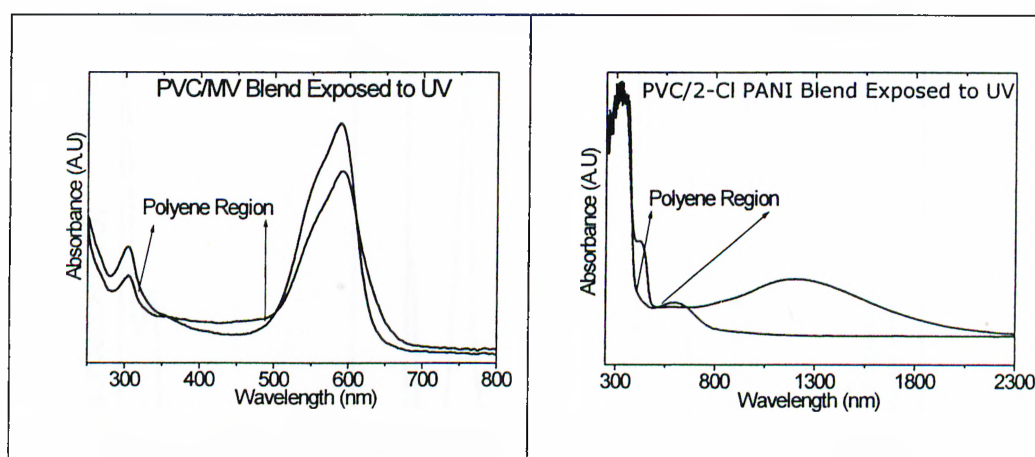


Figure 37. Dehydrochlorination monitoring tools

As concluded from HCl release, isolated double bonds are created in PVC chain, but no polyenes form, as a result of UV radiation of short duration. The result can be linked to very low quantum yield of the overall process, since PVC has no absorption bands in the spectral region of interest. This limitation could be overcome using a very intense radiation source such as a laser, and long polyenic sequences could be obtained [80].

Another approach is to introduce sensitizers into the polymer matrix, which absorb in the spectral region of interest, and irradiate the sample at the peak position of these impurities. For this purpose, hydroquinone, anthraquinone, and anthracene were blended with PVC, and the blends were

irradiated at their peak positions using monochromatic light. Figure 38 shows the UV spectra of the additives used in THF. Methyl violet was also introduced into the systems as the third component to monitor the extent of dehydrochlorination.

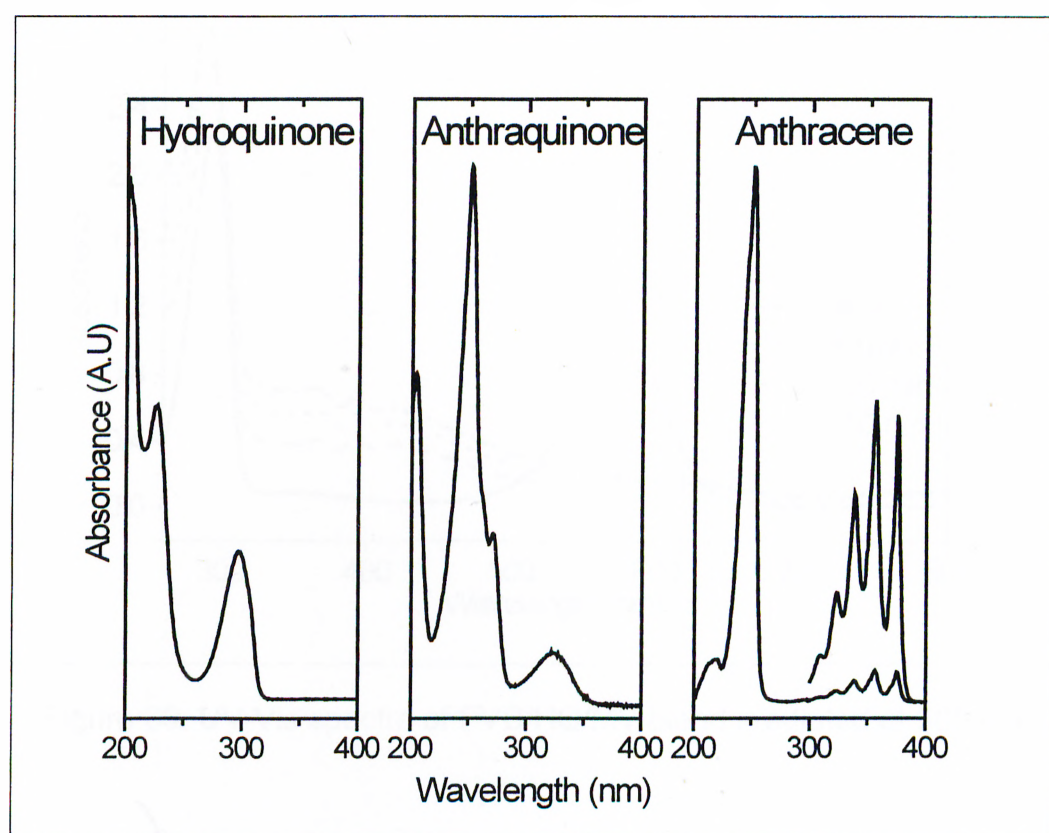


Figure 38. UV spectra of additives used

UV-Vis spectra of the PVC/HQ/MV blend irradiated at the peak position of hydroquinone, 300 nm, for 3 hours are given in Figure 39. The decrease in the MV peak intensity is an indication of dehydrochlorination. However, polyene formation (in 320-500 nm region), accompanied the first process in contrast to the system without HQ (Figure 37). Moreover, the HQ peak intensity did not change apart from the increasing background

absorption. This suggests that HQ simply acts as a sensitiser, and transfers the energy it absorbs to the PVC matrix.

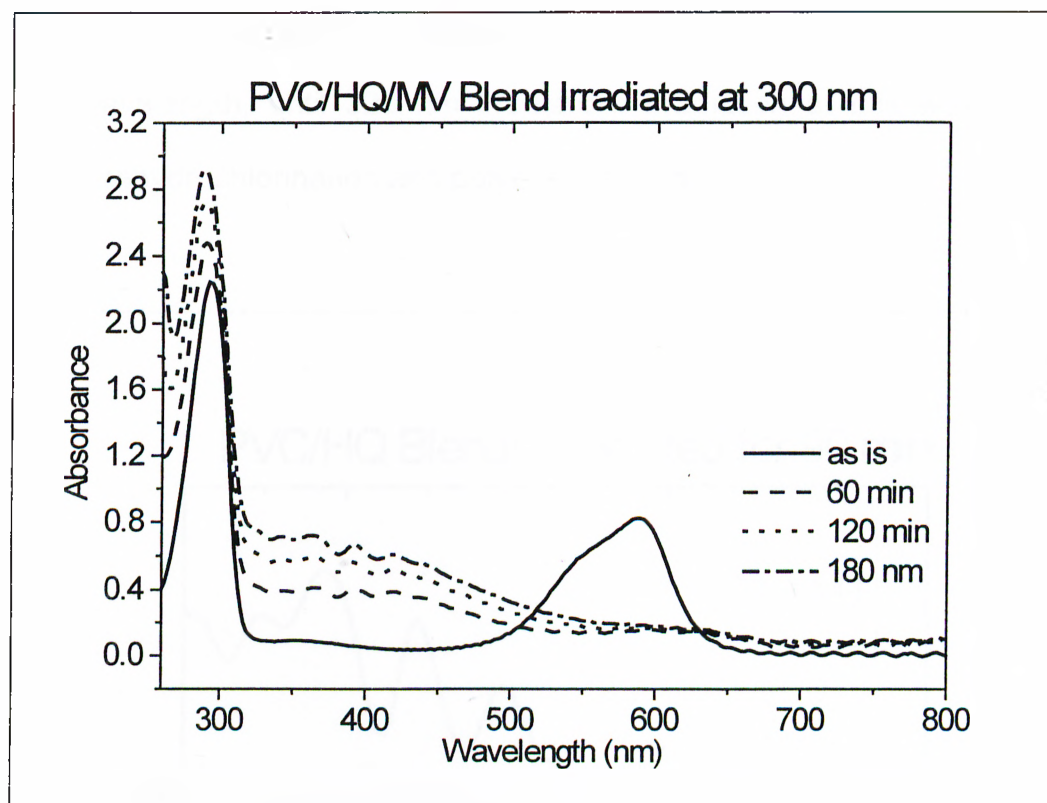


Figure 39. UV-Vis spectra of PVC/HQ/MV blend irradiated at 300 nm

When the PVC/HQ blends were irradiated for 90 minutes, at and slightly off the peak position, 300, 280, and 320 nm, chain length distribution of the polyenes varied as shown in Figure 40. The difference may arise from the wavelength of irradiation, together with the amount of the transferred energy, since the absorbance of HQ at 280 nm, 300 nm, and 320 nm are different.

The energy onset for the PVC/HQ system is near the peak position of HQ. Figure 41 shows the 20 minute irradiated PVC/HQ/MV blend with

wavelength starting from 600 nm down to 300 nm. The immediate decrease of the MV peak intensity after irradiation with 600 nm can be attributed to matrix relaxation and thickness change due to dissipated heat. After matrix was stabilised, no significant change in MV peak took place with irradiation at lower wavelength, until 320 nm irradiation. Irradiation at this wavelength, caused dehydrochlorination and polyene formation.

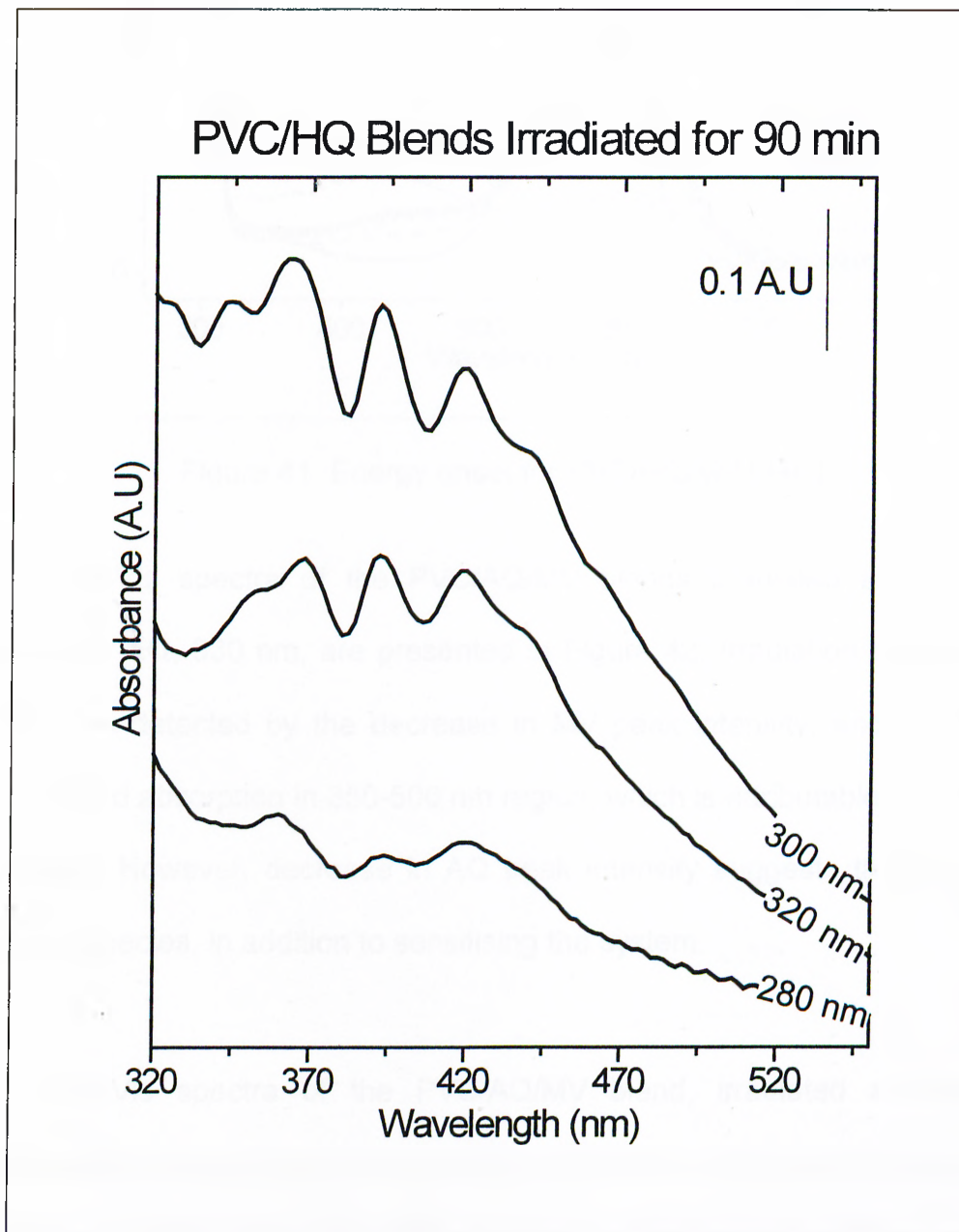


Figure 40. Effect of wavelength on polyene chain length distribution

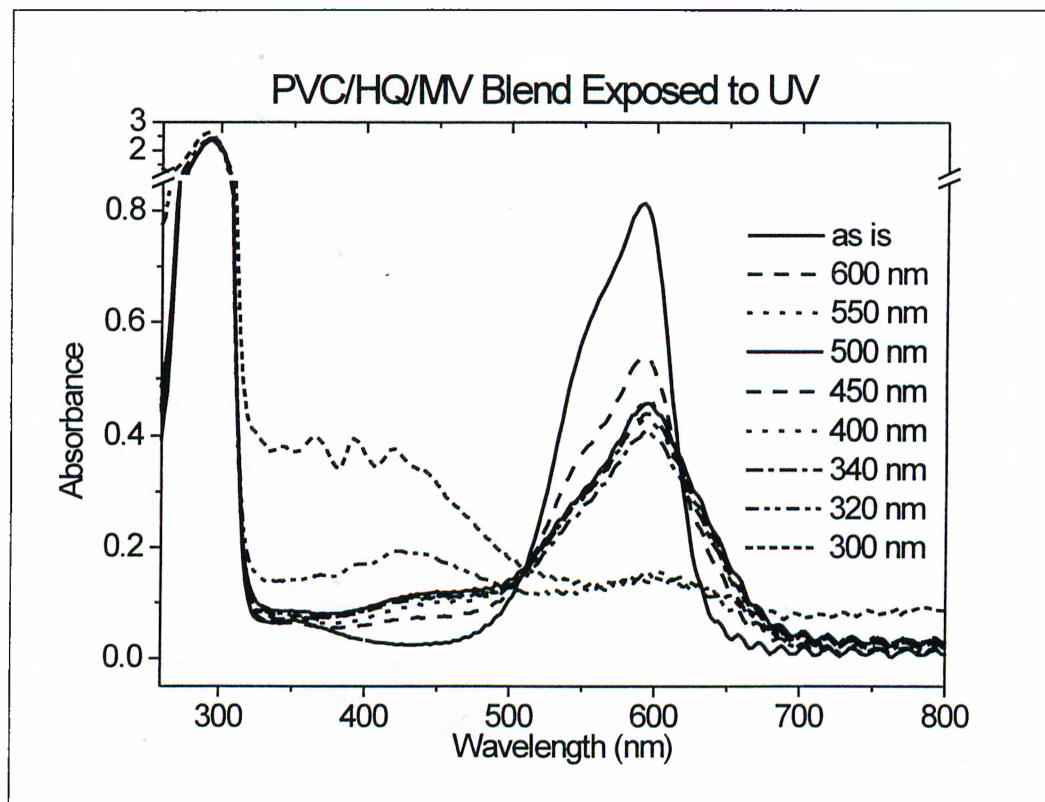


Figure 41. Energy onset for PVC/HQ/MV blend

UV-Vis spectra of the PVC/AQ/MV blends irradiated at the peak position of AQ, 330 nm, are presented in Figure 42. Irradiation caused HCl release as detected by the decrease in MV peak intensity, and increased background absorption in 350-500 nm region, which is attributable to polyene formation. However, decrease in AQ peak intensity suggests that AQ is a reacting species, in addition to sensitising the system.

UV-Vis spectra of the PVC/AQ/MV blend, irradiated at different wavelengths starting from 450 nm down to 300 nm for 30 minutes are shown in Figure 43. The AQ in the blend started to degrade at 400 nm, which coincides with the formation of polyenes. However, HCl release started at

375 nm, as understood from the decrease in MV peak intensity. The maximum decrease of MV peak intensity corresponds to 330 nm irradiation.

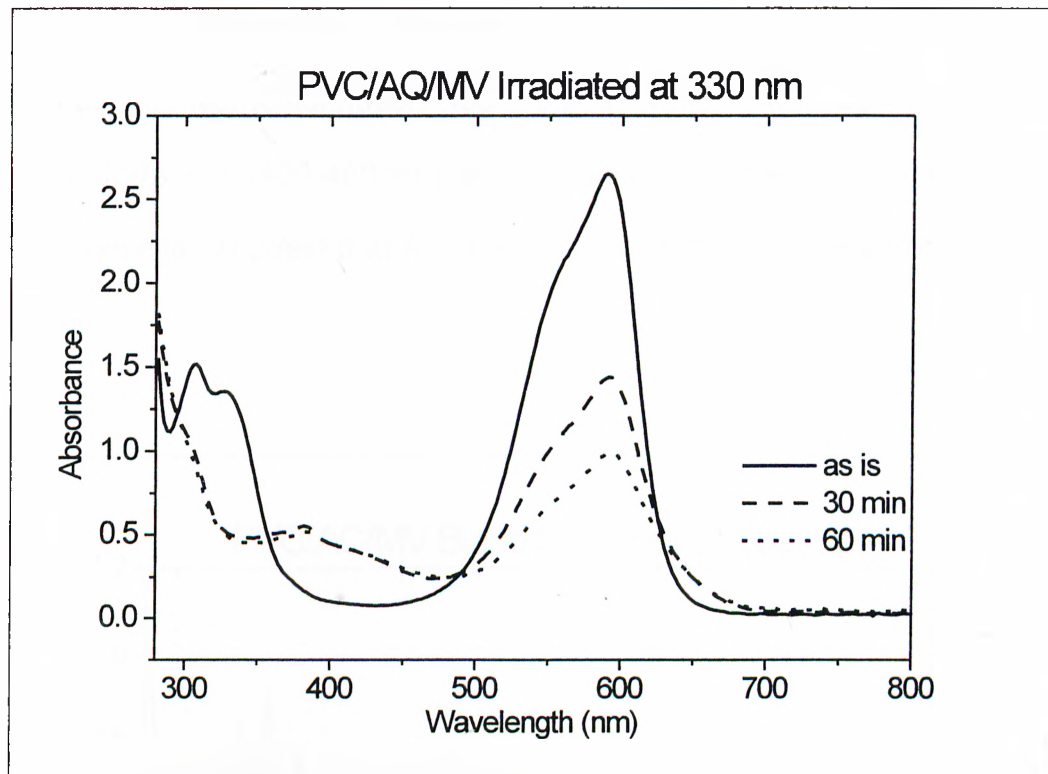


Figure 42. UV-Vis spectra of PVC/AQ/MV blend irradiated at 330 nm

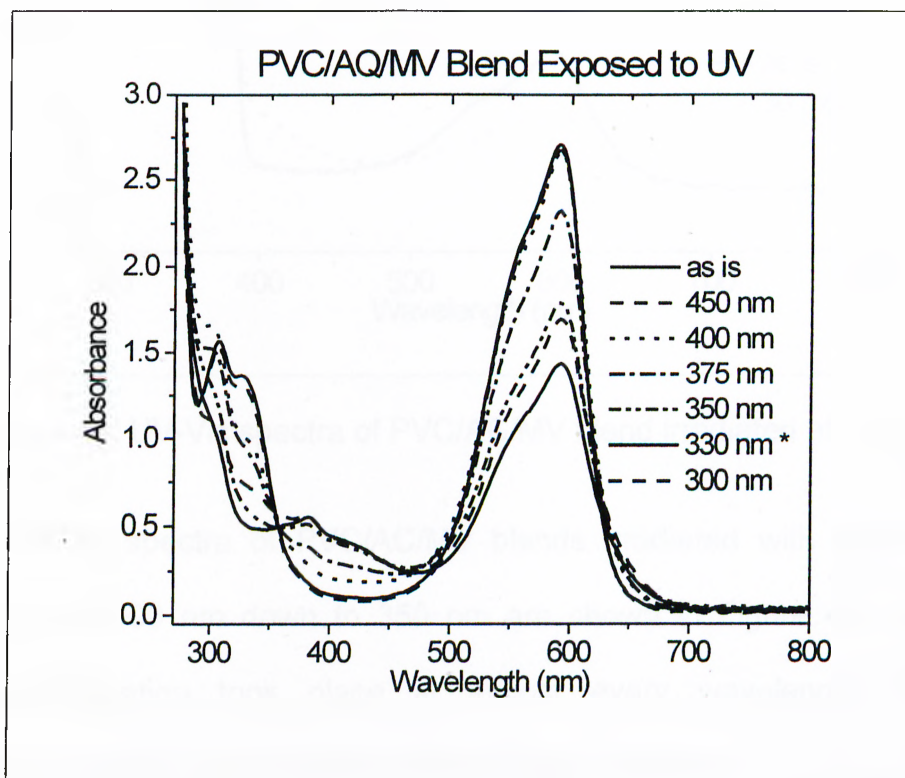


Figure 43. Energy onset for PVC/AQ/MV blend

UV-Vis spectra of PVC/AC/MV blends irradiated at peak position of AC, 382 nm, are shown in Figure 44. As the decrease in MV peak intensity indicates, dehydrochlorination took place, which was accompanied by polyene formation (400-480 nm), even within 30 minutes. Decrease in the AC peak intensities suggest that AC is also consumed in the dehydrochlorination reaction.

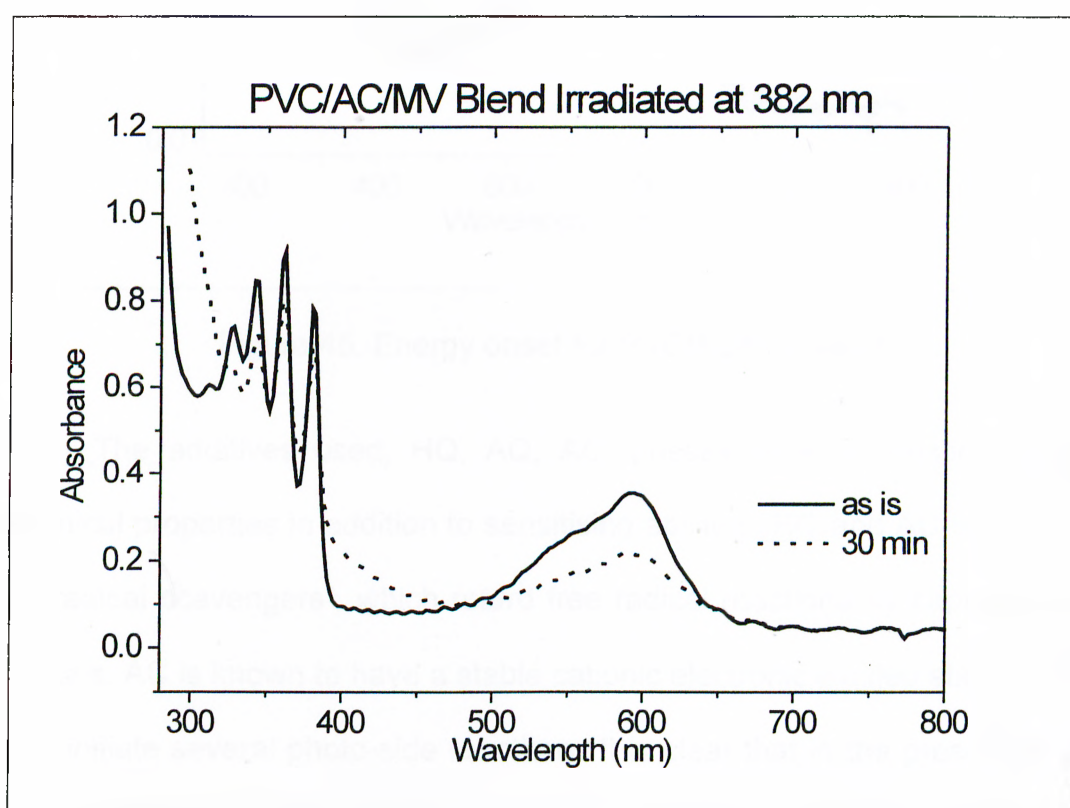


Figure 44. UV-Vis spectra of PVC/AC/MV blend irradiated at 382 nm

UV-Vis spectra of PVC/AC/MV blends irradiated with wavelengths starting from 700 nm down to 350 nm are shown in Figure 45. Although dehydrochlorination took place at almost every wavelength, polyene formation could only be monitored after 400 nm radiation.

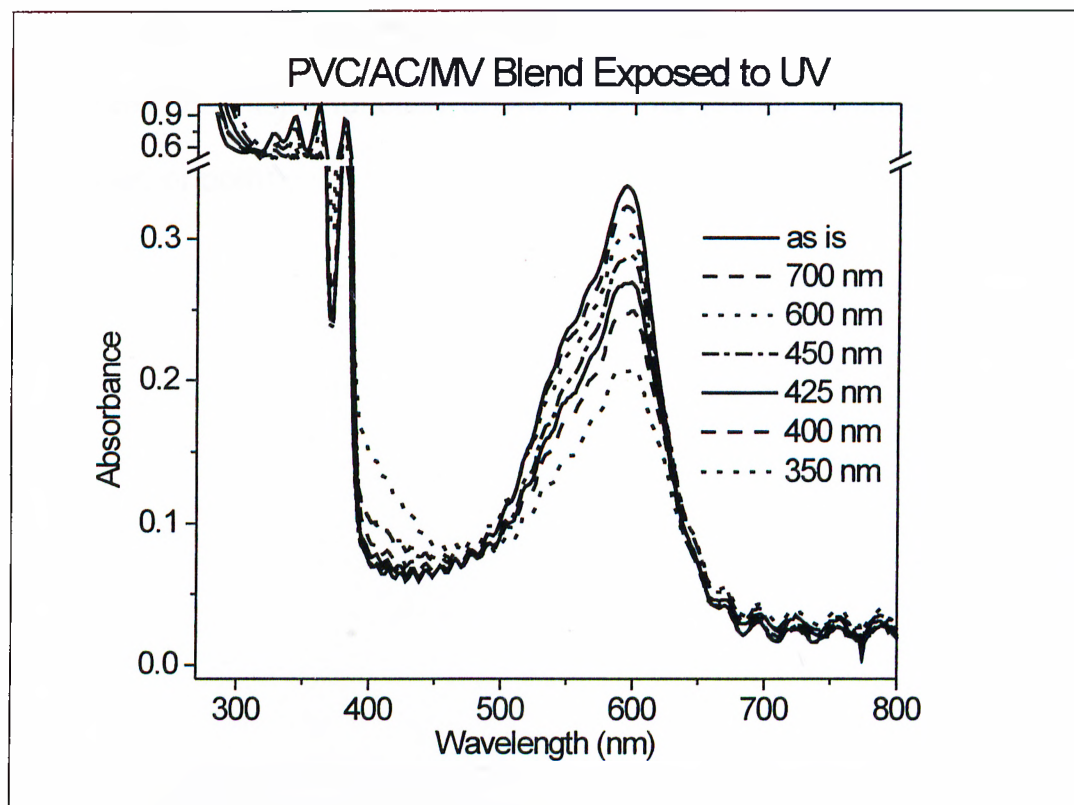


Figure 45. Energy onset for PVC/AC/MV blend

The additives used, HQ, AQ, AC, possess other interesting photochemical properties in addition to sensitising abilities. HQ and AC are known as “radical scavengers”, which retard free radical reactions by capturing the radicals. AC is known to have a stable cationic electronic excited state, which may initiate several photo-side reactions. It is clear that in the present study these additives functioned as energy transfer agents, but the possible side reactions were not fully investigated. However, with the help of these additives, the energy onset of photodegradation was lowered to almost the energy of a C-Cl bond (350 nm). The theoretical value of activation energy for dehydrochlorination (530 nm), with the expectation of somewhat lower wavelength due to solid matrix effects, may be realised using different sensitisers and/or combinations.

A suitable additive, which has an absorption in a different region than AQ and HQ, could be added to the PVC/AQ and PVC/HQ systems to understand the major function of AQ and HQ (either sensitiser or radical scavenger, or both).

4. CONCLUSION

Photodegradation of PVC with short wavelength UV radiation and monochromatic Xe radiation was investigated. Solvent cast PVC dehydrochlorinated when exposed to short wavelength UV radiation. However, polyene formation did not accompany this process, instead isolated double bonds formed. HCl release was monitored with the acid-base indicator, Methyl Violet, incorporated in the matrix.

The optical changes of Methyl Violet, incorporated into the PVC matrix, were mainly due to the capture of the acid released by PVC. This system, which involves a solvent free ACID-BASE CHEMISTRY, may be used for lithographic or dosimetric purposes. Basic forms of conducting polymers were blended with PVC, and electrical conductivity increases were induced by irradiation with short wavelength UV radiation. This system may lead to many novel applications.

In the last part of the study, sensitizers were added to the PVC matrix, to enable the tuning of the wavelength of photodegradation. Strong polyene formation accompanied dehydrochlorination as opposed to non-sensitized systems. With the help of sensitizers, the energy onset of photodegradation was reduced down to the theoretical C-Cl bond cleavage energy. The exact

mechanism of photosensitisation or the photo-side reactions require further studies with more sophisticated analytical systems and techniques.

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