

ANALYSIS OF UV INDUCED DEHYDROCHLORINATED PVC
(WITH HYDROQUINONE) USING DIRECT PYROLYSIS MASS
SPECTROMETRY (DPMS), TGA, UV/VIS-NIR AND FTIR TECHNIQUES

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MASTER OF SCIENCE

By

ERCAN AVCI

JULY 2003

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis of the degree of Master in Science

.....
Prof. Dr. Şefik Süzer (Principal Advisor)

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis of the degree of Master in Science

.....
Prof. Dr. Jale Hacaloğlu

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis of the degree of Master in Science

.....
Asst. Prof. Dr. Dönüş Tuncel

Approved for the institute of Engineering and Sciences

.....

Prof. Dr. Mehmet Baray

Director of Institute of Engineering and Science

ABSTRACT

ANALYSIS OF UV INDUCED DEHYDROCHLORINATED PVC (WITH HYDROQUINONE) USING DIRECT PYROLYSIS MASS SPECTROMETRY (DPMS), TGA, UV-VIS-NIR AND FTIR TECHNIQUES

ERCAN AVCI

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Supervisor: Prof. Dr. Şefik Süzer

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Poly(vinyl chloride) (PVC) degrades easily upon heat and light exposure via loss of HCl. The mechanism of this process is well understood, known as the zip mechanism and the dehydrochlorination results in conjugated segments, polyenes. It is also possible to utilize PVC polymer as an in-situ acid donor since the main degradation product is HCl. Addition of hydroquinone (HQ) into PVC matrix sensitizes the photodehydrochlorination of PVC at 312 nm.

In this study the effects of photodehydrochlorination on thermal and material properties of PVC were investigated using DPMS and TGA as well as UV-Vis-NIR and FTIR techniques. In addition, the photodegradation of PVC/PVAc blend, copolymer (PVC-co-PVAc) and PVAc were similarly investigated. Dehydrochlorination of the polymers resulting from UV-exposure were also investigated for doping of PANI in blends.

HCl evolution behavior of the UV dehydrochlorinated PVC exhibits a characteristic property which is different from the unirradiated ones. Both DPMS and TGA results confirms the sensitization of PVC photodehydrochlorination at 312 nm by hydroquinone (HQ) resulting in a temperature onset that is the lowest (140 °C). HQ assistance upon 312 nm UV exposure is not significantly observed in the copolymer. The low temperature

onset of UV-induced copolymer is a promising result to produce longer polyene chains, since polymer backbone starts to decompose after ca. 220 °C, using copolymer might be an alternative to PVC.

Keywords: Poly(vinyl chloride)(PVC), Poly(vinyl acetate)(PVAc), PVC-co-PVAc, hydroquinone, polyaniline, photodegradation, DPMS, TGA, UV-Vis-NIR, FTIR.

ÖZET

UV ETKİSİYLE DEHİDROKLORİNASYONA UĞRAMIŞ HQ İÇERİKLİ PVC'NİN DİREKT PİROLİZ KÜTLE SPEKTROMETRİ (DPMS), TGA, UV-VIS-NIR VE FTIR TEKNİKLERİYLE ANALİZİ

ERCAN AVCI

Kimya Bölümü Yüksek Lisans Tezi

Tez Yönericisi: Prof. Dr. Şefik Süzer

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Poli(vinil klorür) (PVC) ısı ve ışığa maruz kaldığında kolayca HCl kaybederek bozunur. Bu olayın mekanizması bilinmektedir ve zip (fermuar) mekanizması olarak adlandırılır. Dehidroklorinasyon sonucunda polien olarak adlandırılan konjüge yapıli parçacıklar oluşur. PVC'nin bozunmasında temel ürün HCl olduğundan, bu polimer 'in-situ' (yerinde) asit verici olarak da kullanılabilir. PVC matriksine hidrokinon (HQ) eklenmesiyle PVC polimerinin 312 nm de bozunması hızlanır.

Bu çalışmada DPMS ve TGA tekniklerinin yanında UV-Vis-NIR ve FTIR tekniklerini kullanarak fotodehidroklorinasyonun PVC polimerinin ısı ve malzeme özelliklerine etkileri incelendi. Buna ek olarak, PVC'nin yanında poli(vinil asetat) (PVAc)'ın, bu iki polimerin karışımlarının ve kopolimerlerinin foto bozunması ve bunların PANI ile karıştırılmış örnekleri önceki çalışmaya benzer olarak araştırıldı.

UV ışığına maruz kalmış PVC'den HCl çıkışı UV ışığına maruz kalmamış PVC'ye göre değişik bir karakter sergiler. Hem DPMS, hem de TGA PVC'nin 312 nm de

bozunmasının HQ katılımıyla hızlandığını doğrulayan sonuçlar vermiştir ve bu örnekler en düşük HCl bozunma başlangıç sıcaklığına sahiptir (140 °C). HQ'nun etkisi kopolimerin 312 nm de bozunmasında sıradışı bir farklılık sergilememiştir. UV etkisiyle bozunmuş kopolimerin düşük bozunma başlangıç sıcaklığına sahip olması, uzun konjüge yapılı polienlerin elde edilmesi için ümit verici olabilir ve polimer iskeleti yaklaşık 220 °C'den sonra parçalanmaya başladığından, bu kopolimer PVC'ye bir alternatif olabilir.

Anahtar Kelimeler: Poli(vinil klorür), Poly(vinil asetat)(PVAc), PVC-ko-PVAc, hidrokinon, polianilin, foto bozunma, DPMS, TGA, UV-Vis-NIR, FTIR.

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1. INTRODUCTION

1. 1. Poly(vinyl chloride) (PVC)

Poly(vinyl chloride) (PVC) is undoubtedly among the most frequently used plastics; it is widely applied in many branches of industry and building. It is an amorphous polymer, nevertheless its stiffness at ambient temperature is due to the attraction between electronegative chloride atoms and electropositive hydrogen atoms of neighboring chains. Its advantages are comparatively high chemical resistance, low production cost, and an almost universal possibility of application as pastes, lattices, solutions, films, boards, various extruded or molded pieces etc. [1].

However, the basic disadvantageous property of polymers and copolymers of vinyl chloride is its low resistance to the effects of heat and light. After a certain time, these effects lead to extensive changes in mechanical, optical and electrical properties of PVC [2-5].

1. 2. Polymer Degradation

In the classical chemistry, the term degradation means breaking down of structure. As related with polymer science, it means the decrease in molecular weight of polymer. There are two general types of polymer degradation processes:

i-) Random degradation: In this process, chain rupture or scission occurs at random points along the chain, leaving fragments which are usually large compared to a monomer unit.

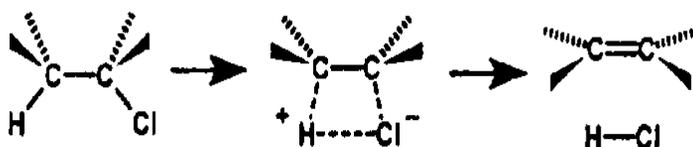
ii-) Chain depolymerization: It involves the successive release of monomer units from a chain end.

These two types may occur separately or in combination, may be initiated thermally or by ultraviolet light, oxygen, ozone, or other foreign agent. It is possible to differentiate the

two processes. For example, molecular weight drops rapidly as random degradation proceeds but may remain constant in chain depolymerization. [6]

1. 2. 1. Thermal Degradation of PVC (Pyrolysis)

A slow thermal decomposition of PVC, characterized by the release of hydrogen chloride, takes place at comparatively low temperatures (about 100°C). The elimination of HCl leads to the formation of conjugated polyenes.



If another HCl molecule is eliminated, a new double bond conjugated with the preceding one is formed. In this manner, dehydrochlorination leads to formation of a system of conjugated double bonds in the PVC molecule. The light absorption in the UV region of such conjugated systems is shifted toward longer wavelengths with increase in the number of double bonds. When five to seven number of double bonds is reached, the absorption is seen at visible region, so that the decomposition can be followed by color change; yellow through orange, red, red-brown, until it is completely black.

At temperatures up to 200-220 °C, hydrogen chloride is the only volatile product of the thermal degradation of PVC. At higher temperatures the C-C bonds are cleaved, and various hydrocarbons can be detected among the gaseous products, such as benzene, ethylene, propylene, and butylene.

If the thermal degradation of PVC is carried out in air, oxygen attacks both the original polymer and the polyene systems arising from it and various oxygen-containing groups such as OH, CO, and COOH [2-4].

Ping Xu *et al* [2] studied molecular defects in four suspension-polymerized PVC samples and their thermal dehydrochlorination rates in light and dark quantitatively. The rate of thermal dehydrochlorination of PVC in dark related to the labile chlorine atoms (particularly internal allylic chlorine atoms). On the other hand, the rate of photo-thermal dehydrochlorination of PVC under UV light is related to the carbonyl allylic groups and double bonds (particularly terminal double bonds).

Dadvand *et al* [7] have used pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) to assess the thermal degradation behavior of polymers containing chlorine. The total ion current diagram of PVC holding the temperature at 600 °C shows that benzene is a pyrolysis product with a retention time longer than that for HCl as shown Figure 1. At higher temperatures the polyacetylene-type backbone, remaining after the comparatively fast loss of HCl from the polymer, degrades to give a wide range of low-MW hydrocarbons, largely unsaturated. Their findings also support the proposed mechanism [8] that claims HCl product molecule can participate in the formation of a transition state which leads to formation of another HCl molecule (autocatalytic effect), as shown in the reaction scheme1 below.

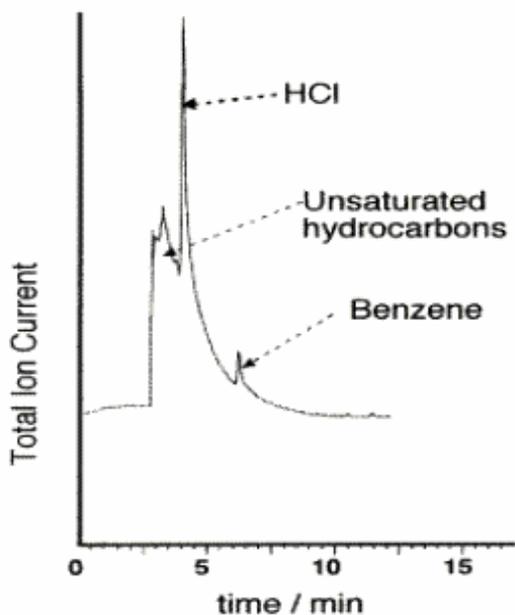
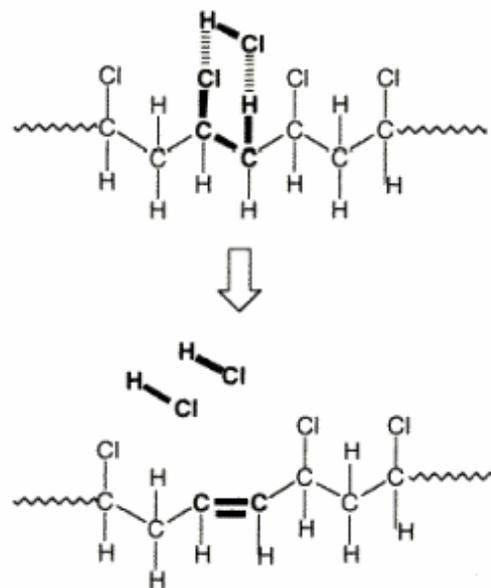


Figure 1: PVC pyrolysis at 600 °C.



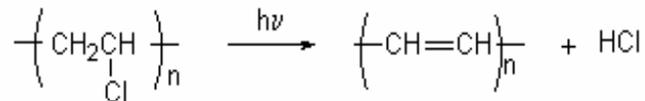
Scheme.1

It is well-known that thermal degradation of PVC is complicated by the catalytic effect of evolving HCl. In one study, Troitskii *et al* [9] developed a theory about autocatalytic thermal degradation of PVC in the presence of HCl as the branched chain reaction with the degenerated branching of the chain. The role of thermally excited states of the polyenes and polyenyl carbocations in the degenerated branching of chain is considered. It is concluded that at 180-200 °C polyenes having eight or more conjugated double bonds are highly reactive. Reactivity of polyenyl carbocations is greater because energy for excitation of them in the triplet state is less than that of polyenes. As a result, it can be assumed that in the autocatalytic thermal degradation of PVC in the presence of HCl, reactions with participation of polyenes and polyenyl carbocations excited in the triplet state make the principal contribution to the degenerated branching of chain.

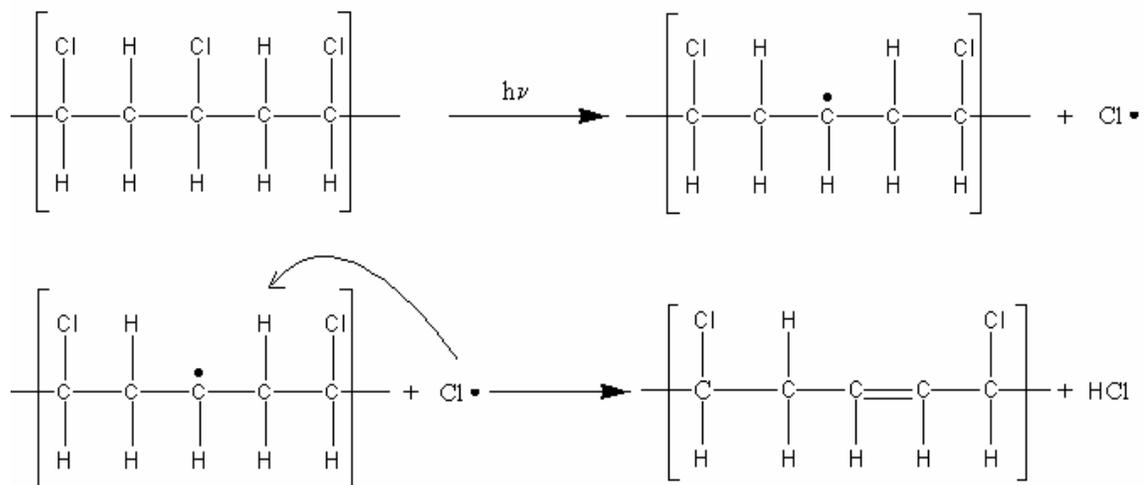
In the thermal degradation of PVC, the reaction of intramolecular cyclization of polyenes having $n > 3$ (n : number of conjugated double bond) is the most probable reaction of termination of dehydrochlorination chain. The reactions of intra- and intermolecular cyclization lead to a decrease of n in formed polyenes. It has been shown that the average length of kinetic chain of PVC is equal to 8-15, but the average value of n in formed polyenes, which has been determined by the use of absorption spectra of degraded PVC, is equal to 3-10. Thus, in thermal degradation of PVC the reaction of cyclization decreases the concentration of long polyenes and increases the concentration of short ones [9].

1. 2. 2. Photodegradation of PVC

Since PVC contains only, C-C, C-H, and C-Cl bonds it is not expected to absorb light of wavelength longer than 190-220 nm. However, it is a fact that free radicals are formed when PVC is irradiated with UV and even with visible light. The light instability of PVC causes some structural abnormalities like in thermal degradation. The decay mechanism of PVC under energetic light is the following:



Like in thermal decomposition, in this process, hydrogen chloride is evolved and polyenes are also formed. Color develops; chain scission and crosslinking occur. Any mechanism offered to explain these phenomena must recognize that they occur at room temperature. It is a bit hard to believe that such a mechanism holds at room temperature, from the fact that PVC is stable for years in the dark but degrades rapidly in sunlight [2,5]. It is believed that ultraviolet light catalyzed oxidation has a short induction period. Oxidation seems to be the main mechanism in light degradation; also, that oxidative attack depends on an initial dehydrochlorination to provide points on the chain susceptible to oxidation. It is also proposed that light acting on a photosensitive molecule can produce a radical. It has been suggested that initiation and propagation step reactions in the photodegradation of PVC are similar to the following [10]:



Scheme.2

1. 2. 2-a) Photostability of PVC

The theory and practice of PVC stabilization are connected with the development of the polymer degradation theory. It is well known that thermal degradation proceeds in two ways:

- (1) HCl elimination from any part of the polymer chain with the formation of isolated C=C bonds,
- (2) formation of the sequences of conjugated C=C bonds resulting from the dehydrochlorination of the sequences of the VC units, activated by the carbonyl allyl groups.

The stability of polymer molecules can only be enhanced by decreasing the rate of polyene formation. In principle, the decreasing rate of HCl elimination with the formation of polyenes can be associated with the substantial increase in the thermal stability of the active centers of PVC dehydrochlorination such as carbonyl allyl groups. This process can occur in two ways:

- i*) Disruption of conjugation in the initial active centers of PVC dehydrochlorination, i.e., C=O and/or C=C bonds
- ii*) Replacement of labile Cl atoms in $-\text{C}(\text{O})-(\text{CH}=\text{CH})_n-\text{CHCl}-$ groups ($n \geq 1$) by more thermostable groups [11].

Li Jian *et al* [5] discussed the structural changes in PVC chains brought about by photodegradation. The length of conjugated polyenes are $n=2-4$ and do not change with the reaction temperature or irradiation time either in air or in nitrogen. However, the content of polyenes increases and the content of carbonyl groups increases with increasing irradiation time and temperature in air.

1. 2. 2-b) Photo-yellowing:

Yellowing is essentially a consequence of dehydrochlorination of polymer chains in the presence of light. Unlike the virgin resin, processed PVC compounds contain chromophoric impurities such as polyene sequences formed as a result of thermal degradation during processing. These moieties absorb short wavelength ultraviolet light, undergoing “zip” dehydrochlorination to yield long polyene sequences. When the sequence length exceeds about 8, visible yellowing of the vinyl occurs.

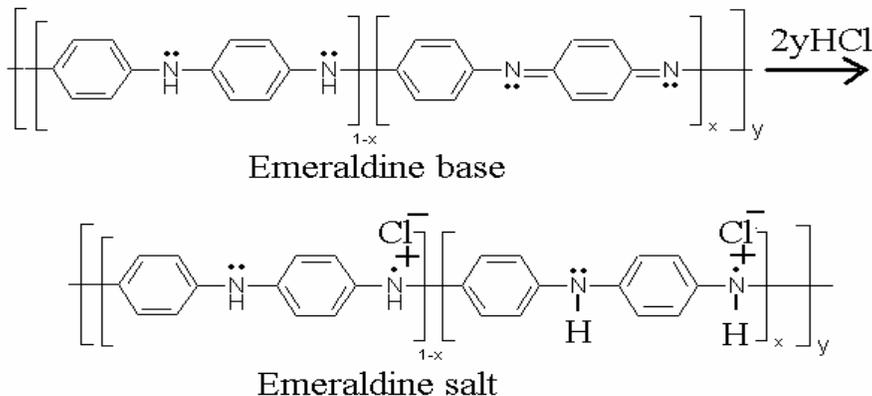
The prevention of uneven yellowing and subsequent chalking due to sunlight is an important consideration in the design of rigid PVC formulations for applications. Andrady *et al* [12] studied on the yellowness index of polymer samples under different monochromatic light sources. 280, 300, 320, 340 nm wavelengths result in increase in yellowness index of PVC samples. At higher wavelengths of 400 and 500 nm, the samples undergo photobleaching resulting in a decrease in yellowness index. Light stability of PVC can be dramatically improved by adding a light screener, rutile titanium dioxide (TiO₂).

1. 3. Aim of the Study

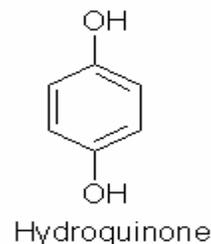
Numerous investigations have been carried out and reported on PVC. Photodehydrochlorination and thermal decomposition processes are investigated and documented [2-5]. Although majority of the previous investigations has focused on stabilization of PVC, some have also tried to benefit from this degradation, since it is possible to utilize the main degradation product (HCl) as an in-situ acid donor [13-18].

In a previous study, utilization of PVC dehydrochlorination process was reported [13]. In this study, they reported that electrical conductivity of PVC and PANI (Polyaniline) blend films, prepared in nonconducting (basic) form increases 3-4 orders of magnitude (from less than 10⁻⁶ S/cm to 10⁻³-10⁻² S/cm) under γ -rays or UV exposure. The reason of

the increase in conductivity was attributed to dehydrochlorination (loss of HCl) of PVC, which oxidizes (dopes) PANI in PVC matrix (Scheme 3). This was proved by XPS, UV-vis-NIR and FTIR spectroscopic techniques. Further exposure of the films to gaseous NH₃ made a reversible effect to decrease conductivity to some extent by reducing (undoping) partially the oxidized centers.



Scheme 3



Scheme 4

In a similar study, Sertova *et al* reported that base form of polyaniline (emeraldine base, EB) behaves as trap of evolved HCl from PVC. Here, PVC is used as a donor of HCl. As a result, the conductivity of polyaniline increases [14].

In this respect, the aim is to maximize dehydrochlorination. Along these lines, S. Suzer *et al* have later reported that PVC exhibits an appreciable dehydrochlorination under 312 nm UV light when it is mixed with 10 % (w/w) hydroquinone, HQ (Scheme 4) where 312 nm corresponds to the absorption maxima of hydroquinone. Normally, PVC does not absorb at 312 nm, however exposure to 312 nm radiation of PVC-Hydroquinone blends resulted in an extensive dehydrochlorination and formation of polyenes. The detailed mechanism of this process is not well-understood [15].

The aim of this study is to obtain complementary chemical/structural information on the UV induced dehydrochlorinated PVC (with hydroquinone) by using direct pyrolysis mass

spectrometry (DPMS), thermogravimetric analysis (TGA), FTIR and UV-Vis spectroscopic techniques.

1. 4. Conducting Polymers, (PANI)

Traditionally, organic substances, including polymers, are insulators. During the past 25 years, however, a new class of organic polymers has been devised with high ability to conduct electrical current. The conductivity of intrinsically insulating polymers can be enhanced by about 10-15 orders of magnitude into the metallic or semiconducting range by doping [19].

Conducting polymers have attracted considerable attention because of their electrical and optical properties and many potential applications such as energy storage, electromagnetic interference shielding, photoelectronic device, sensor, and etc. It is well-known that organic conductive materials are generally difficult to be processed.

Polyacetylene (PAC) and polyaniline (PANI) represent two very different classes of conducting polymers. The former is doped to metallic state by redox processes involving either partial oxidation or partial reduction of the pi-system; the latter, in emeraldine oxidation state, is doped by a non-redox process involving protonation of the polymer in which the total number of electrons associated with the polymer is unchanged.

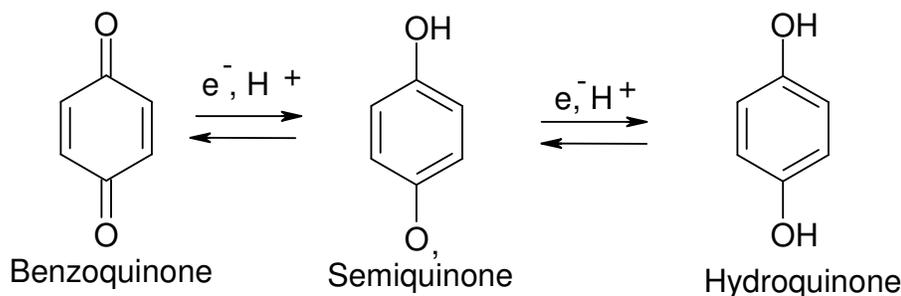
Conductivity of polyacetylene, $(CH)_x$, is determined by a variety of parameters including number of defects in the polymer chain, the degree of alignment of the polymer chains, the type of dopant and method of doping.

Polyaniline (PANI), in its doped, conducting form (Emeraldine Salt, ES) is not soluble or processable when compared to its undoped, non-conducting form (Emeraldine Base, EB). Several attempts have been made to improve the processibility of conducting polymers. For example, it can be blended with a number of conventional polymers, thus leading to

materials with high electrical conductivity and high mechanical strength [20]. Kang *et al* [21] reported that the electrical conductivity of polyanilines doped with HCl decreases upon exposure to oxygen and increases reversibly upon evacuation. The former situation represents the reduction in the concentration of polarons due to the spin-spin interaction of oxygen with paramagnetic polarons, generated by HCl doping process and the latter the reduction in the mobility of polarons due to the partial localization of delocalized polarons. Therefore, it was concluded that the decrease in conductivity comes from the reduction in concentration and the mobility of polarons, the charge carriers for electrical conductivity. It was also found that the time scale for the diffusion of oxygen molecules was much longer than that for the spin-spin reaction of oxygen with polarons. Thus, the small decrease in electrical conductivity may be associated mostly with the reduced mobility of polarons by localizing reaction instead of reduced polaron concentration.

1. 5. Role of Hydroquinone at Photodegradation of PVC

It is well established that hydroquinone (HQ) undergoes electrochemical oxidation to benzoquinone (BQ) in aqueous media according to the reaction shown in Scheme 5. This equilibrium reaction has been used for pH measurements because the potential for



Scheme 5. Oxidation of hydroquinone to semiquinone and then benzoquinone.

the reaction exhibits a pH dependence of 60mV/pH with a proton involved for each electron transfer. Shim *et al* [22] studied the reduction of BQ to HQ. They found that in buffered solution the reduction is a two-electron process however in unbuffered solution

the reduction is one electron process. It was also explained that during the electrochemical reduction of BQ to HQ, first, electron transfer being the main process, second was the protonation of the radical anion. Using electronic spectroscopy one can monitor the oxidation of HQ to BQ.

Suzer *et al* [15] demonstrated that photo-dehydrochlorination can be effectively sensitized by incorporating hydroquinone into PVC blends containing methyl violet. In Figure 2 the spectroscopic changes as a result of different UV-irradiation are shown. Although pure PVC is not influenced greatly when it is exposed to either 254 or 312 nm UV radiation for 120 minutes, a blend containing 10 % (w/w) hydroquinone undergoes extensive dehydrochlorination and polyene formation when exposed to 312 nm UV radiation that corresponds to absorption maxima of hydroquinone. The dramatic sensitization by hydroquinone was clearly shown by of using methyl violet that is converted to acidic form in the blend.

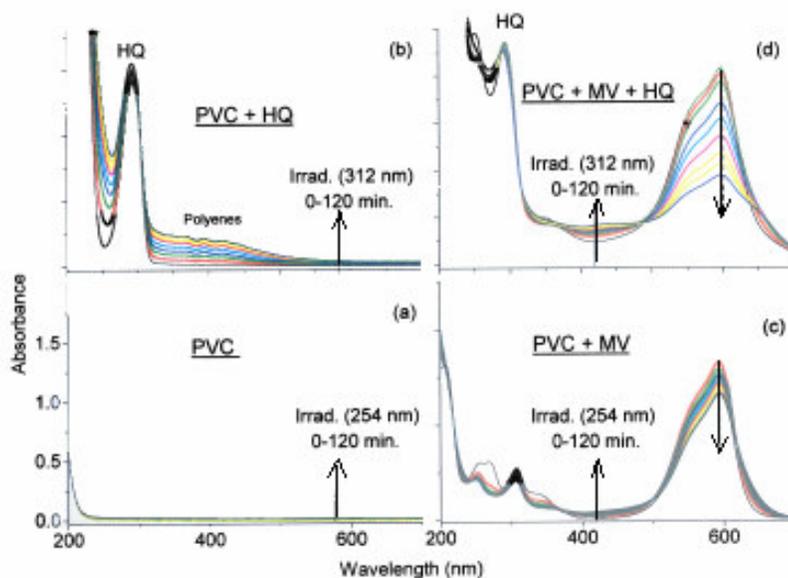
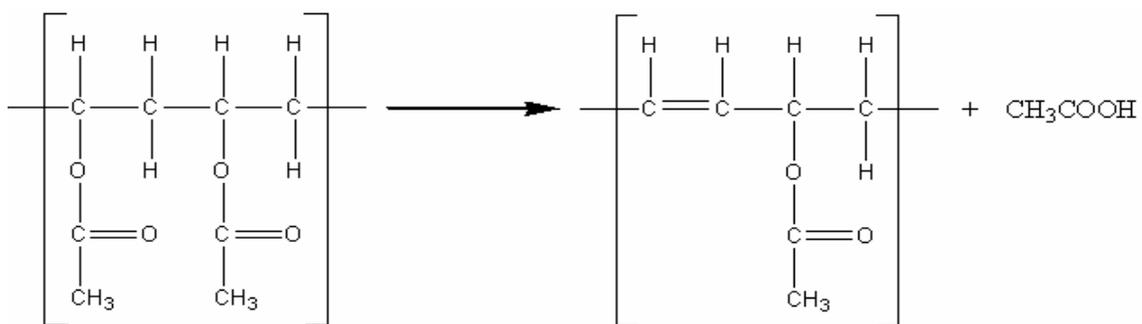


Figure 2: UV/Vis-NIR spectra recorded every 15 min for 2 h.

1. 6. PVAc / PVC (Blends, Copolymers) with PANI

Polymer blending is to mix two or more polymers together, which is a well-established strategy for achieving specific physical properties, without the need to synthesize new polymers. This process can lead to obtain new materials having properties of both components. However, some physico-chemical properties of polymer in blends are unpredictable and non-additive. In numerous cases the synergism or antagonism of properties are observed [23,24]

Commercial vinyl polymers such as poly(vinylchloride) (PVC) and poly(vinylacetate) PVAc are extensively studied because of their broad applications in industry. Major uses of PVAc are water-based paints, adhesives, and substrate for poly(vinyl alcohol) production [24]. Structure of PVAc and its degradation as a result of heat and light is given in Scheme 6.



Scheme 6. PVAc structure and its degradation reaction, which is similar to PVC degradation.

Zhang *et al* [26] studied the viscometry of PVAc/PVC blends in various solvents. The intermolecular interactions between PVC and PVAc in solution are greatly associated with the solvent. In either THF (tetrahydrofuran) or DMF (N,N'-dimethylformamide), repulsive intermolecular interactions between PVC and PVAc exist. On the contrary, in MEK (methyl ethyl ketone), attractive intermolecular interactions exist between them.

Tremendous research has been carried out to improve the conductivity and processibility of PANI by forming interpenetrating polymer networks (IPNs), copolymers, composites and blends. Synthesis and characterization of PANI/crosslinked polyvinylacetate (PVAc) semi-IPNs were concerned due to that the solubility parameter of PVAc is close in value to that of aniline (Hildebrand parameter δ of aniline is $21.1 \text{ MPa}^{1/2}$, and δ of PVAc is $20 \text{ MPa}^{1/2}$). The conductivity of semi-IPNs increases with increasing content of PANI and increasing acidity used during the polymerization of PANI. The conductivity of the semi-IPN is 0.13 S/cm , with the highest PANI content of $19.3 \text{ wt } \%$ [26].

The influence of ultraviolet irradiation ($\lambda=254 \text{ nm}$) on PVC thin films modified by addition of small amount ($1\text{-}10 \text{ wt.}\%$) of poly(vinyl acetate) (PVAC) was investigated by FTIR, UV-Vis and solid state ^{13}C -NMR spectroscopy. It was found that PVAC decelerates PVC photodegradation, photocrosslinking and photooxidation leading to carbonyl groups formation. This retarding effect caused by PVAC presence in PVC can be explained by fast reactions of low molecular degradation products (e.g. radicals, peroxides) formed in PVAC phase with the macroradicals and macromolecules in both polymers. Moreover, PVAC can protect PVC photodamage owing to absorption of harmful UV-radiation by carbonyl groups [24,27]. They also investigated the radiation stability of PVC/PVAc blends using AFM technique. Addition of small amount of PVAc to PVC films influences its photostability. After exposure of polymer blends to UV irradiation (254 nm) some surface defects appear and photo-crosslinking occurs. UV-irradiation of pure PVC leads much higher surface roughness comparing to irradiation of blends [19].

The pyrolytic stability of PVC-co-PVAC was investigated by Grassie [28] *et al* and it was concluded that the introduction of PVAC reduces the thermal stability of PVC and it becomes least stable at $40 \text{ wt. } \%$ PVAC in the copolymer. For the copolymers, the degradation rate constants are higher and the activation energies are lower compared to that of the homopolymers. This clearly indicates that the copolymers are less stable than the homopolymers. A proposed reason was that addition of vinyl acetate changes the polarity of the chain and enhances rapid elimination of $\text{CH}_3\text{COOH} / \text{HCl}$.

1. 7. Mass Spectrometric Analysis

Mass spectrometry (MS) is a powerful analytical technique used to identify unknown compounds, quantify known materials, and determine the structural and chemical properties of molecules. Mass spectrometry is now almost 90 years old and used in all branches of chemistry, in physics, geology, environmental, agricultural and space research and so on.

A mass spectrometer is an instrument that measures the masses of individual molecules that have been converted into ions, i.e., molecules that have been electrically charged. Formation of gas phase sample ions is an essential prerequisite to the mass sorting and detection processes that occur in a mass spectrometer. The gas phase ions are sorted in the mass analyzer according to their mass-to-charge (m/z) ratios and then collected by a detector. In the detector the ion flux is converted to a proportional electrical current. The data system records the magnitude of these electrical signals as a function of m/z and converts this information into a mass spectrum [29-30].

A mass spectrum is a graph of ion intensity as a function of mass-to-charge ratio. Mass spectra are often depicted as simple histograms as shown in Figure 3. This record of ions and their intensities serve to establish the molecular weight and structure of the compound being mass analyzed. For example, Figure 3 shows a mass spectrum of the simple molecule carbon dioxide, CO_2 .

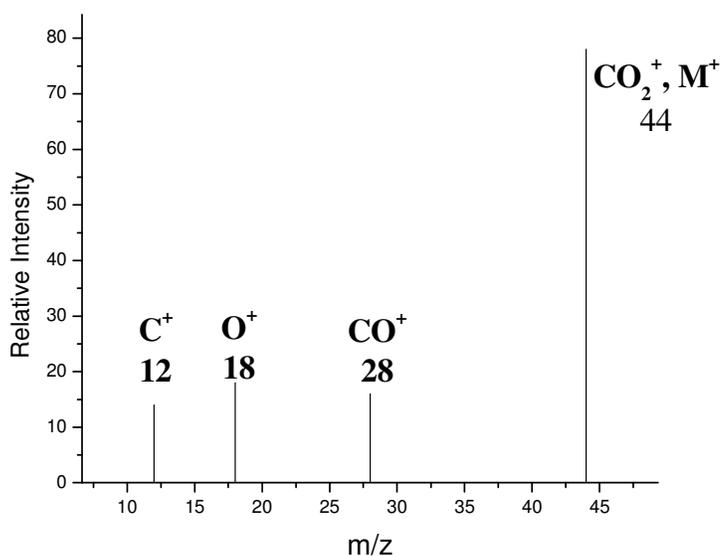


Figure 3: Mass spectrum of carbon dioxide, CO₂. Molecular ion is seen at m/z 44.

In this example, all the ions are positively charged (it is possible to generate and detect negative ions as well). The ionized CO₂ molecule (or molecular ion) appears at m/z 44. Since the ionization process breaks up or fragments some of the CO₂ molecules, a fraction of the ions appear in the spectrum at m/z values less than the m/z value that corresponds to the molecular mass of CO₂. Cleavage of a carbon-oxygen bond in the molecular ion to produce ionized carbon monoxide or ionized atomic oxygen result in the fragment ions at m/z 28 and 16; loss of two neutral oxygen atoms results in an additional fragment at m/z 12 for carbon. The molecular ion is designated as M⁺ or CO₂⁺ and the fragment ions are designated as CO⁺, O⁺ and C⁺ [30].

1. 7. 1. Basic Requirements for a Successful Analysis

- a-) A high vacuum environment (10^{-4} to 10^{-8} torr) must be supplied,
- b-) The sample must easily be transformed to the gas phase,
- c-) The gaseous sample molecules can be ionized by energetic electrons (20-70 eV),

d-) The peak of each component must be discriminated from the others. Since mass-to-charge ratios are tried to be found, different ions which have the same m/z values can not be identified easily, for example CO and N₂ which both have 28 m/z value.

1. 7. 2. Direct(-Indirect) Pyrolysis Mass Spectrometry

Pyrolysis means the thermal degradation of a complex material in an inert atmosphere or a vacuum. The detection of ions produced from large molecules (polymers) can only be possible after production of volatile fragments. Pyrolysis causes molecules to volatilize and also to cleave at their weakest points. DPMS is one of the most useful techniques for the detection of large fragmented molecules. It prevents the problem caused by fast recondensation polymerization. As a difference from the indirect pyrolysis, by this technique, unstable volatile fragments can be recorded. The advantages of this technique are the rapid detection of pyrolysis products, detection of high molecular weight products and the determination of primary degradation products. These pyrolysis products are indicative of the polymer degradation pathways and the polymer structure. In this technique the sample may be inserted as a solid, but it is preferable to dissolve it first in a solvent. The sample size should be 1.0 μg or less to avoid contamination of the ion source [31-33].

1. 8. TGA Technique

Thermogravimetry is one of the oldest thermal analytical procedures and has been used extensively in the study of polymeric systems. The technique involves monitoring the weight loss of the sample in a chosen atmosphere (usually nitrogen or air) as a function of temperature. It is a popular technique for evaluation of thermal decomposition kinetics of polymeric materials and hence provides information on thermal stability and shelf life. However, it is probably best known for its ability to provide information on the bulk composition of polymer compounds [34].

Thermogravimetric analysis is a useful method to detect different volatile substances as temperature changes slowly. TGA and DPMS techniques are thought as complementary of each other. However, the drawback is that the pressures are different at each environment. One is highly vacuumed; the other is at atmospheric conditions. This difference affects the degradation process of complex substances, such as polymers. In TGA technique, as the thermal degradation of a polymer occurs, recondensation of pyrolysate is more possible compared to in DPMS technique. This drawback may not affect so much to interpret the results if this difference is taken into account carefully.

1. 9. Infrared Spectroscopy (IR)

Infrared spectroscopy is an excellent technique for identification of pure organic and inorganic compounds whether they are in the form of a simple compound or a complex mixture of polymers. Each material, provided that it is infrared active, produces a unique infrared spectrum and it is this property of a material that allows us to identify it. With the exception of a few homonuclear molecules, such as O₂, N₂, and Cl₂, all molecular species absorb infrared radiation.

IR is a less satisfactory tool for quantitative and qualitative than its ultraviolet and visible counterparts because the narrow peaks that characterize infrared absorption usually lead to deviations from Beer's law. The most important advances in infrared spectroscopy have come about with the introduction of Fourier-transform spectrometers. This technique improved the quality of infrared spectra and minimized the time required to obtain data. [35,36].

1. 10. UV-Vis Spectroscopy

UV/Vis spectroscopy is most frequently used for quantitative analysis of various compounds that have absorbance in the UV-Vis range. Many heavy metal complexes

absorb in the visible region, and various organic compounds with double bonds absorb in the UV-Vis range. Increasing conjugation causes a shift of observed peaks from the vacuum UV toward the visible end of the spectrum. This means that the technique can occasionally be used to give structural clues for unknown compounds (qualitative analysis). UV-Vis spectra are typically observed as broad peaks that cover several nanometers. The wide range of vibrational states that the molecules may be the cause these broad peaks. Fine structure may be observed in certain solvents or in the vapor phase, where many possible vibrational modes are suppressed. [37,38].

1. 11. Previous Studies

Birer *et al* [18] have studied the UV induced changes in PVC composites by using UV-Vis, FTIR and XPS techniques. In acidic form of PVC/PANI blends, the strong polaron band around 600 nm is the fingerprint of electrical conductivity. This band is blue shifted in the basic form of the blend. It is also verified by FTIR spectra that electrical conductivity increases as the free carrier absorption band around 1600 cm^{-1} develops. The same group has also studied PVC films containing methyl violet. The blend films were prepared by dissolving PVC and the basic dye (methyl violet) in a 10:1 weight ratio in freshly distilled tetrahydrofuran (THF). The films were exposed to 254 nm UV irradiation. It was demonstrated that a process similar to the indicator color change in an aqueous media can also be induced within the PVC matrix by the action of light. It was also proposed that this process can be utilized for lithographic purposes.

Degradation of PVC has been reexamined in the light of DT-DSC-TG techniques up to a temperature of $1000\text{ }^{\circ}\text{C}$ by Chatterjee *et al* [39]. Four distinct stages of degradation have been identified. The first stage, up to a temperature of $185\text{ }^{\circ}\text{C}$, is essentially eventless with no thermal change or mass loss. The second stage, spans up to $375\text{ }^{\circ}\text{C}$, are primarily endothermic dehydrochlorination to some polyene residue, and also weakly exothermic decomposition of hydroperoxide groups possibly to carbonylallyl groups. Tertiary chlorine and allylic chlorine sites together with carbonylallyl sites initiate zip-like dehydrochlorination of PVC. The third stage of degradation starts after $375\text{ }^{\circ}\text{C}$, and

involves structural reorganization, such as crystallization, isomerization, crosslinking and aromatization. The fourth stage generally occurs beyond 500 °C, is only poorly understood and perhaps involves structural breakdown of the residue from the third stage.

Slapak *et al* [40] determined the pyrolytic degradation kinetics of virgin-PVC and PVC-waste by analytical (TGA) and computational methods. The analytical method proved to be too inaccurate for determining the reaction order unambiguously. Numerical modeling of the degradation curves proved to be more accurate for the determination of the kinetic parameters. It was also reported that increasing heating rate shifts the thermogravimetric curves to higher temperatures due to the fact that reaction time decreases and conversion is never in equilibrium.

Accelerated photodegradation of PVC was studied by Torikai *et al.* [41]. It was investigated that both main-chain scission of PVC and degradation product formation is accelerated under the longer wavelength radiation (>290 nm) (simulating terrestrial sunlight) by shorter wavelength pre-irradiation. The reactions in this process are dependent on the pre-irradiation time and the threshold wavelength for main-chain scission of PVC shifts to longer wavelength on pre-irradiation.

Guo *et al* [42] investigated that polyene films containing certain amounts of poly(ethylene glycol)s (PEG) catalyst is extensively dehydrochlorinated by aqueous potassium hydroxide. The molar mass of the PEG used as phase transfer catalyst is ranged from 200 to 800 g/mol. The results of elemental analysis and UV-Visible, Fourier Transform-infrared (FT-IR) and FT-Raman spectra indicate that the polyene films obtained from these systems are polyacetylene-like and contain relatively long conjugated sequences. The highest conversion at room temperature is measured to be about 90 %. The conductivity of iodine-doped polyene films is found to be as $10^{-2} \text{ S cm}^{-1}$.

In a different study, PVC was treated with ethanol, trimethylaluminum, and dibutyltin maleate in order to substitute labile chlorine. The degradation behavior of the modified samples was compared with that of an ordinary suspension PVC and PVC obtained by

anionic polymerization [43]. All modified samples and anionic PVC showed the same behavior when degraded in pure nitrogen. It was also observed that rate of dehydrochlorination decreased and polyenes became shorter. Degradation in HCl atmosphere resulted in higher dehydrochlorination rate and longer polyenes for all samples with improved heat stability. The results showed that the polyene sequence distribution depends on the presence of HCl in the sample during thermal degradation.

Vymazal [44] *et al* reported a study on thermal degradation of PVC at 180 °C in air in the presence of Ba, Cd and their combination. In the presence of Cd stearate, dehydrochlorination proceeds at many sites giving rise to relatively short polyenes. In the presence of Ba stearate, the number of degradation sites is smaller, but long sequences are formed, causing the coloration of the polymer. In synergistic combinations of Ba/Cd stearates, both these mechanisms may operate.

Thermal degradation of both PVC and PVAc polymers follows a two-step degradation mechanism involving chlorine or acetate radical removal followed by polyolefinic backbone breakage. In the first stage of PVC up to around 600 K, the degradation is mostly due to dehydrochlorination leaving polyene structure. In the second stage, up to around 750 K, the structural degradation of the polyene backbone occurs, leading to the evolution of various aromatic compounds like benzene, toluene, naphthalene, indene, anthracene, o-xylene, and various chlorobenzene. Since poly (vinyl chloride) and poly (vinyl acetate) have structural similarity, PVAc also undergoes in two stages. In the first stage of PVAc thermal degradation up to 650 K, acetic acid is released followed by a second stage up to 750 K in which the breakage of the backbone occurs [45].

Sivalingam *et al* [46] studied role of metal oxides on the thermal decomposition of poly (vinyl chloride) (PVC) and poly (vinyl acetate) (PVAc) and their blends investigated by thermogravimetry (TGA). While the degradation of PVAc was mildly affected by the presence of metal oxides, the degradation of PVC was greatly influenced by metal oxides. Blends of PVC-PVAc were obtained by solution blending by dissolving the polymers in tetrahydrofuran (THF). Scanning electron microscopy (SEM) and TGA

showed complete miscibility of polymers in the blend. The first stage degradation of the blend was greatly influenced by the presence of PVC and metal oxides suggesting that hydrochloric acid liberated from PVC influenced the decomposition behavior of PVAc. The second stage degradation (olefinic breakage) of the blends was mildly affected by the metal oxides and the breakage was similar to pure polymers.

2. EXPERIMENTAL

2. 1. Preparation of Samples

The polymers, which were used in our studies, were purchased from Aldrich and used without further purification.

Main chemicals that were used are:

- Poly(vinylchloride) (PVC), inherent viscosity 1.02, Mn=60 000 and Mw=106 000
- Poly(vinylacetate) (PVAc), Mw=167 000
- PVC-co-PVAc (86 % VC, 14 % VAc), Mn=27 000
- Polyaniline (PANI (EB)),
- Hydroquinone (HQ),
- Tetrahydrofuran (THF) (distilled over KOH).

The polymers were dissolved in THF (Carlo Erba) solution. THF contains 0.05% hydroquinone to prevent peroxide formation. Therefore, THF is distilled in the presence of KOH to remove the impurities and hydroquinone. PVAc blend solutions were prepared in the co-polymer mass ratio that is 86 to14 (PVC/PVAc). HQ was mixed with the polymers as 10 % (w/w). The films were prepared by casting the solutions on polypropylene sheets. Although PVC is good at making films on glass, the films containing PVAc can only be prepared on polypropylene sheets. In order to achieve free-standing films a minimum of 24 hours casting time was employed. After formation of uniform films, TGA, UV-Vis-NIR and FTIR spectroscopic investigations are carried out.

2. 2. DPMS

The direct pyrolysis mass spectrometry (DPMS) instrument in our laboratory basically consists of a direct insertion pyrolysis probe and a heater/temperature controller unit, which was constructed in our laboratory. The mass analyzer is a Finnigan 4000

quadrupole (0-1000 amu) mass analyzer and a personal computer is used for instrument-control, data acquisition (together with data manipulation) and deriving the heater/temperature controller. The software was written in visual basic.

In DPMS studies, sample size should be kept as small as possible, only enough to obtain the desired information should be used. Using small samples will help to keep the vacuum system clean and the background low. Thin films (ca. 10 μg) on stainless steel plates were cast from prepared polymer solutions. The plate is set on the direct insertion probe. Data are collected as probe is heated. Typical DPMS spectra are shown below in Figure 4.

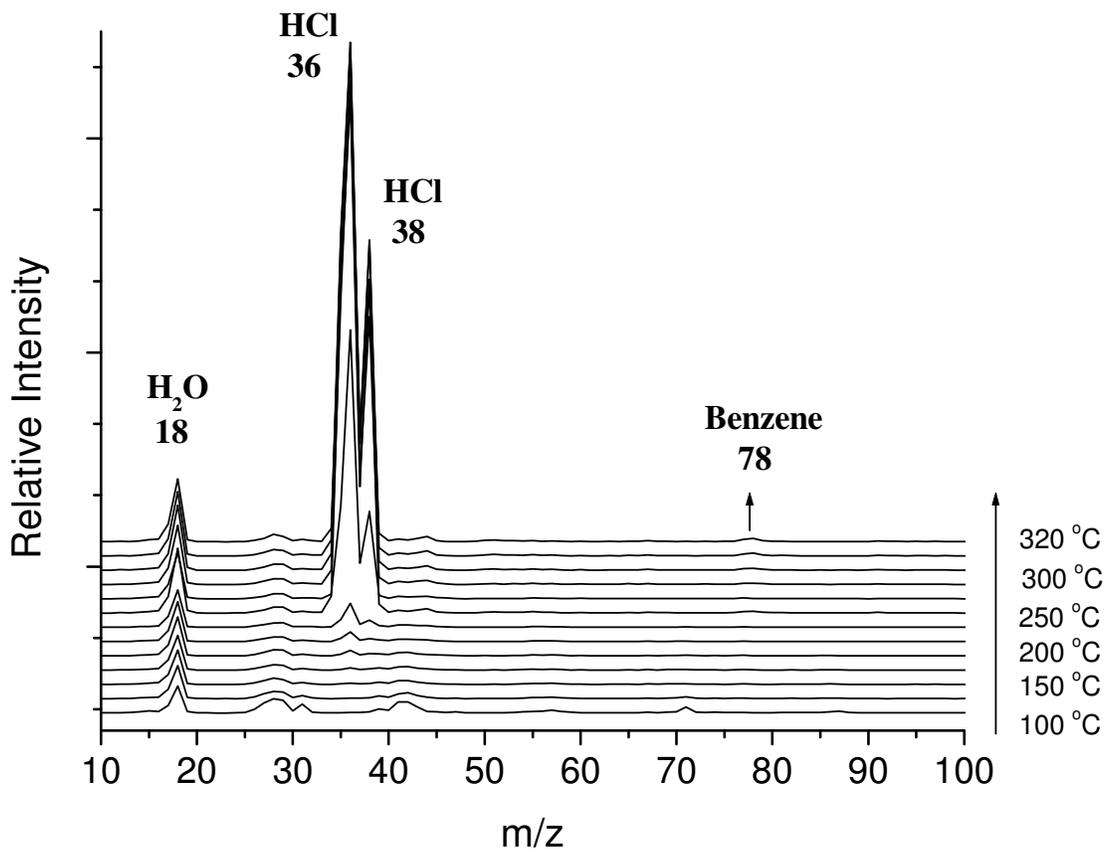


Figure 4: Mass spectra of PVC as is at elevated temperatures

More specifically, after the sample film was inserted onto the end of the high temperature probe of the mass spectrometer, it was first heated to 80 °C and kept at that temperature for 10 minutes to eliminate the solvent and other volatiles, then heating continued up to 300 °C with approximately 13 °C/min heating rate (the temperature profile and two mass spectra are shown in Figure 5). Approximately one mass spectrum (0-170 amu) was recorded per minute. The main peaks are of HCl and Cl in different isotopic masses, H₂O and benzene at this temperature. All the other peaks including water are all resulting from background gases.

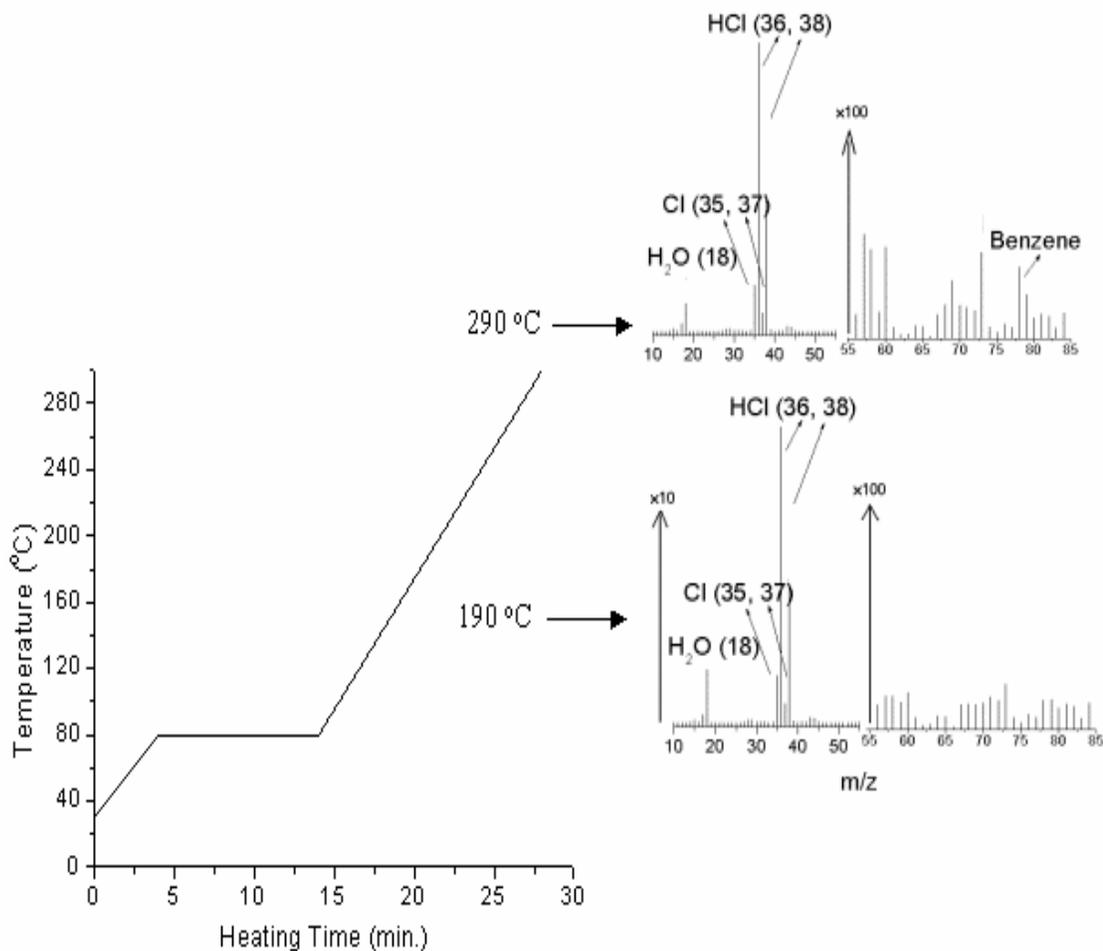


Figure 5: Heating profile and two mass spectra of PVC as-is at 190-290 °C in DPMS.

In our DPMS studies, the vacuum pyrolysis behavior of polymers is examined by plotting intensity of particular masses that are recorded during pyrolysis versus temperature. Figure 6 illustrates the change of intensity of HCl (36) detection from PVC and acetic acid (60) from PVAc.

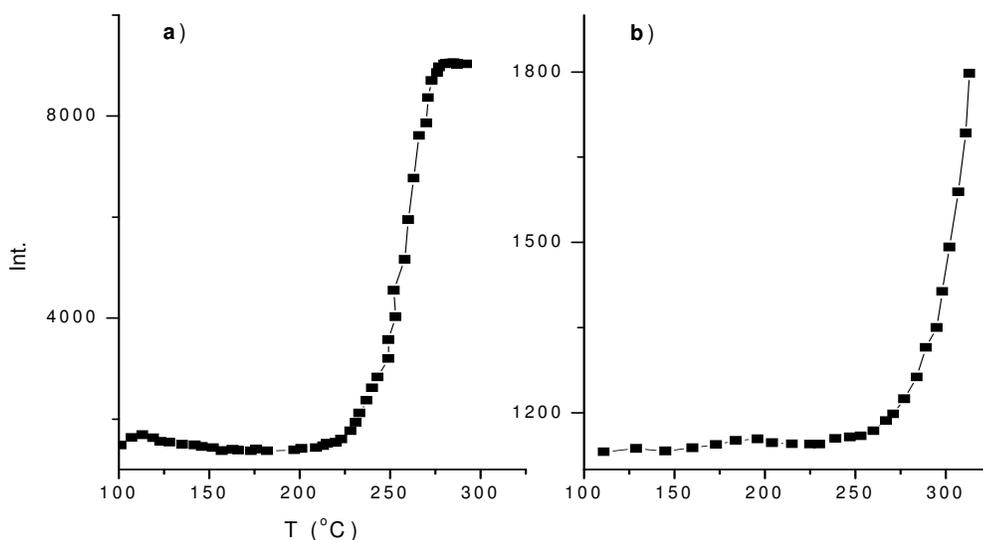


Figure 6: DPMS study. HCl (36) detection from pyrolysis of PVC (a), Acetic acid (60) detection from pyrolysis of PVAc (b).

2. 2. 1. The Heater/Temperature Controller

This unit, which was constructed in our laboratory, is used to generate controllable electrical current to heat (to volatilize) the sample and to record the temperature of the probe. It mainly consists of an amplifier, a transformer and other electronic elements. The amplifier amplifies the tiny output voltage from the J-thermocouple. The temperature calibrations were made several times against an automatic temperature controller (Harrick). The schematics of the electrical circuits in the heat control unit can be seen in Figure 7 a, b.

Figure 7 a: Heater Circuit

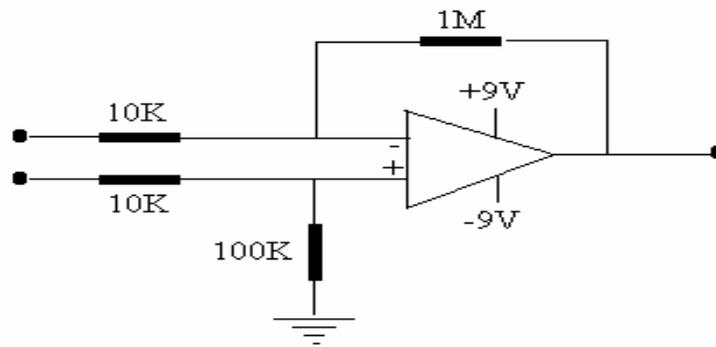
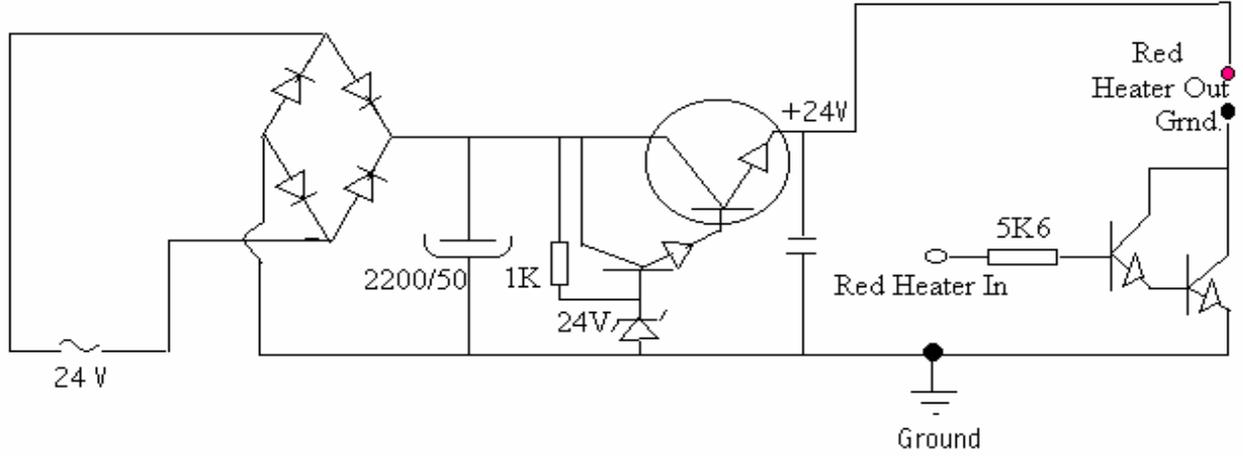


Figure 7 b: The thermocouple Amplifier

2. 2. 2. Linearity of the Heating Rate

In this part of study, the pyrolysis behavior of polymer samples were examined at different heating rates. Different heating rates were set by changing the input voltage to the probe. The constant voltage can supply almost a linear increase of temperature with time in samples as shown in the Figure 8.

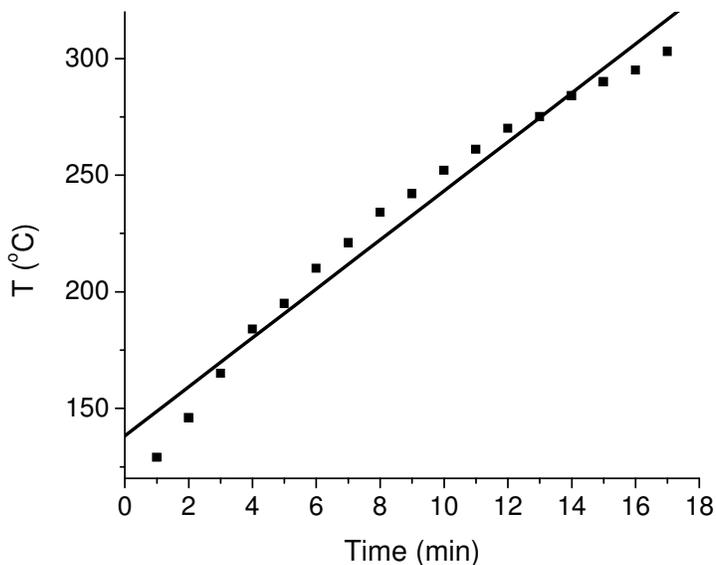


Figure 8: The change of probe temperature with time in DPMS at a heating rate of ~ 11 $^{\circ}\text{C}/\text{min}$.

2. 3. Photodegradation

Irradiation to induce photodegradation in the films are carried out with a low-pressure mercury lamp ($7\text{mW}/\text{cm}^2$) emitting a single line at 254 nm and/or a low-pressure fluorescent filter coated lamp ($8\text{mW}/\text{cm}^2$), that emits mostly at 312 nm. The samples were exposed to these lamps in different durations (1–12 h).

2. 4. TGA

Thermal decomposition studies were carried out in a TGA (Setaram, TG DTA/DSC) under inert flowing nitrogen atmosphere at the heating rate of 5 K/min. The free-standing solvent cast polymer films were 25-30 mg and placed in an aluminum crucible. All the runs were carried out between 40 °C to 330 °C. The following is an example for the TGA curve of PVC.

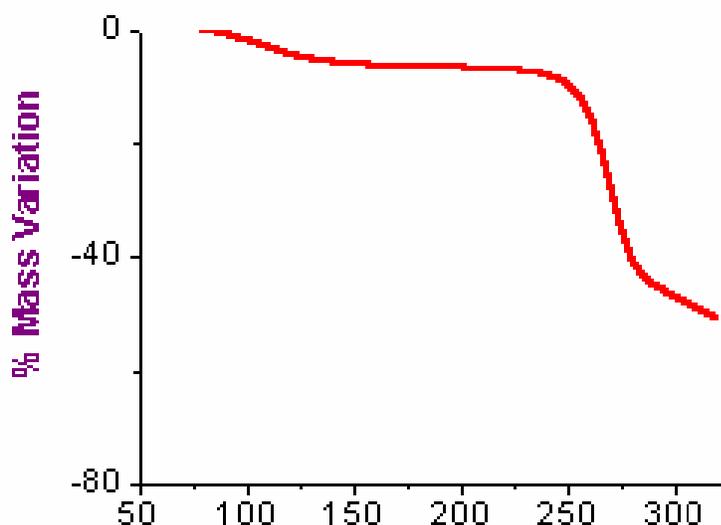


Figure 9: TGA result of PVC.

2. 5. UV-Vis Spectroscopy

The UV-Vis Spectra of the samples are recorded with a Varian Cary 5 Spectrophotometer. Cary 5 is a double beam spectrophotometer working in a range of 190-3200 nm. The instrument is equipped with interchangeable deuterium/tungsten sources, a reflection grating monochromator, and a photomultiplier detector.

2. 6. FTIR

The IR spectra of the samples were recorded with a Bomem Hartman MB-102 model FTIR spectrometer. The spectra were taken with the total number of scans 128 and a resolution of 2 cm^{-1} .

The FTIR spectrum of PVC is given in Figure 10. The spectrum of PVC does not indicate any significant quantity of impurity that should be considered carefully. The bands at 2976 cm^{-1} and 2910 cm^{-1} are result from the C-H stretching of CHCl and C-H stretching of CH_2 , respectively. At 1425 cm^{-1} , one can easily see the CH_2 deformation. Also C-H deformation of H-C-Cl can be seen at 1330 cm^{-1} . The peak at 1099 cm^{-1} is due to C-C stretching. 966 cm^{-1} shows the CH_2 rocking. Finally, there is a strong peak of C-Cl stretching at $600\text{-}700\text{ cm}^{-1}$.

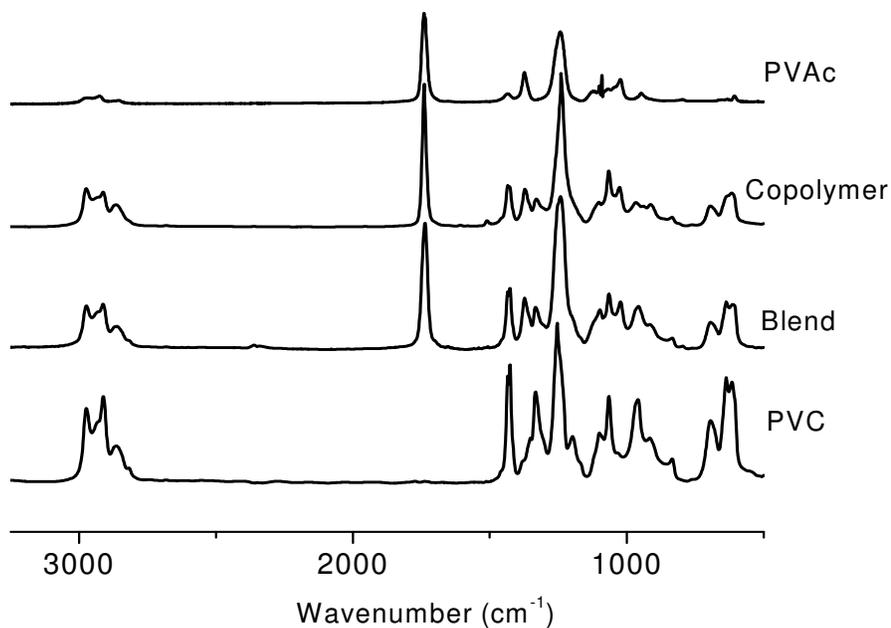


Figure 10: FTIR spectra of PVC, blend of PVC/PVAc, PVC-co-PVAc, and PVAc.

The FTIR analysis was also conducted for PVAc, PVC/PVAc blend, and PVC-co-PVAc films as shown in Figure 10. The main peaks corresponding to the wave numbers 2964, 2866, 1434, 1371 cm^{-1} are for different modes of vibration of CH_2 and CH_3 . The peaks at 1740 and 1240 cm^{-1} are due to $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bands, respectively, suggesting the acetate structure of PVAc.

The FTIR spectra of basic form of PANI are given in Figure 11. The change in the intensity of 1600 cm^{-1} and 1500 cm^{-1} peaks show the protonation of the imine nitrogens. In this transformation the insulating base (EB) form is converted to the conducting salt

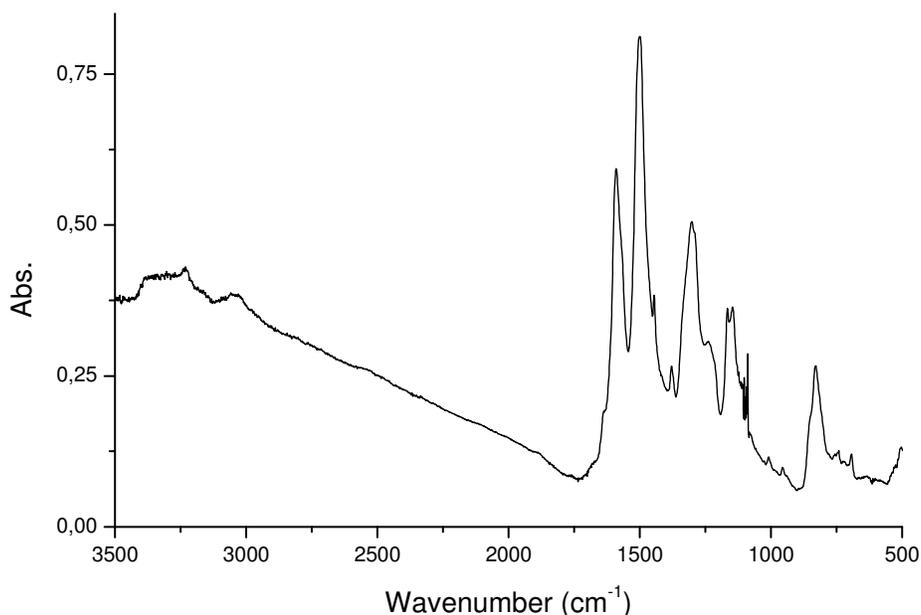


Figure 11: FTIR spectra of PANI base.

(ES) form. Aromatic ring, N-H deformation and $\text{C}=\text{N}$ stretching give absorptions in 1600 – 1450 cm^{-1} region. In general, the N-H deformation band is very weak and even unobservable. The band at 1510 -1500 cm^{-1} is mainly due to the benzenoid ring (B) stretching in PANI. A band near 1587 cm^{-1} is related to quinoid (Q) structure in PANI. The band in this aromatic region can be attributed to Raman active $-\text{C}=\text{C}-$ ring-stretching vibration. These normally infrared-inactive modes become infrared active when the

protonation induces conformation changes in the polymer chain, i.e. when polarons or bipolarons are produced, resulting in symmetry breaking along the chain. Accordingly, both 1587 and 1510 cm^{-1} peak positions change during HCl doping. Beside, upon addition of HCl, the relative intensity of 1587 to 1510 cm^{-1} decreases and shift to lower frequencies by about 10 cm^{-1} .

The bands at 1160 and 1140 cm^{-1} can be assigned separately: 1160 cm^{-1} to the intrinsic structure and 1140 cm^{-1} to a vibrational mode of B-NH⁺=Q or B-NH⁺-B structure, which is formed during the protonation. This indicates the existence of positive charges on the chain and the distribution of the dihedral angle between the quinone and benzenoid rings. It increases with the degree of doping of the polymer backbone.

The main absorption band for intrinsic PANI is located at 830 cm^{-1} . Substitutions can be seen from the assignments. 1220, 1105, 1010 and 830 cm^{-1} stand for 1,4-substitution, 1115, 1060, 960, 995 and 850 cm^{-1} for 1,2,4-substitution and 740 and 690 cm^{-1} for 1,2-or mono-substitution. 810 cm^{-1} corresponds to C-Cl stretching [46].

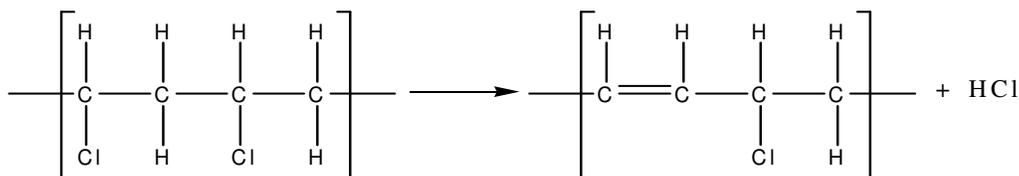
3. RESULTS & DISCUSSIONS

3. 1. Photodegradation of PVC and PVC/HQ(Hydroquinone)

3. 1. 1 DPMS Investigations

3. 1. 1-a) Pyrolysis Behavior of Pure PVC at Different Heating Rates

Direct pyrolysis mass spectrometry (DPMS) is an established technique for thermal analysis of polymers. The advantage of this technique is the rapid detection and determination of primary pyrolysis products that are indicative of the polymer degradation pathways and polymer structure. Dehydrochlorination is the most important thermal reaction (Scheme 7) that occurs in the pyrolysis of PVC.



Scheme 7: Dehydrochlorination reaction of PVC in pyrolysis. The evolved HCl in different isotopic masses at m/z 36, 38 can be detected by DPMS.

Thermal degradation of PVC in a broad range of temperatures (up to 1000 K) is essentially a two-step process [3]. The first step (up to the 600 K) mainly involves dehydrochlorination of the polymer and formation of macromolecules with conjugated double C=C bonds. Up to this temperature, HCl is the main volatile product (96-99.5%), the amount of other products being very low (1-3%) including benzene and some other hydrocarbons. The second step involves degradation of dehydrochlorinated product with cracking to low hydrocarbons of linear or cyclic (aliphatic and aromatic) structure. Essentially, the temperature change at these steps can shift depending on the rate of pyrolysis and the pressure of environment. Figure 12 demonstrates the thermogravimetric curves for the pyrolysis of PVC powder in nitrogen atmosphere at several heating rates [40].

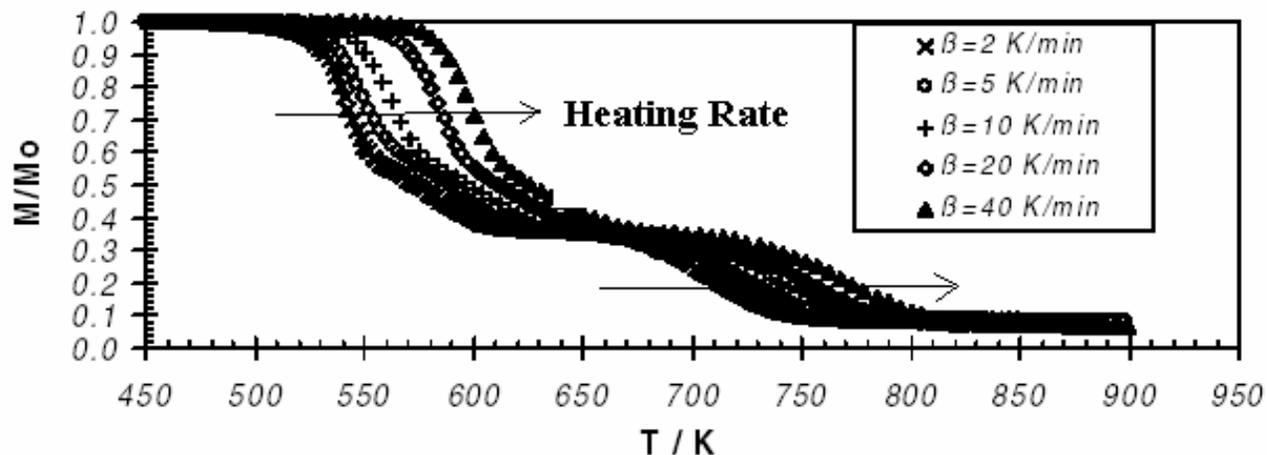


Figure 12: Thermogravimetric curves of PVC: relative mass loss versus temperature at a range of heating rates in a nitrogen atmosphere [40].

Similarly, in DPMS studies, pyrolysis behavior of polymers also changes depending on the heating rate. Figure 13 shows HCl (m/z 36) ion current change during the pyrolysis of PVC. Samples were first heated to 80 °C, and kept at that temperature for 10 minutes before ramping the temperature at three different rates (9, 12, 14 °C/min). The reason for shifting the curves to higher temperatures with increasing heating rate is a consequence that the reaction time decreases. In order to achieve activation energy, that is the minimum energy for a completed reaction, a certain amount of energy must be deposited to the sample. This is possible only with a shift of temperature onset in the pyrolysis process. Therefore, in all of the following, heating of the pyrolysis probe was carried out with a fixed rate in order to achieve reproducible results.

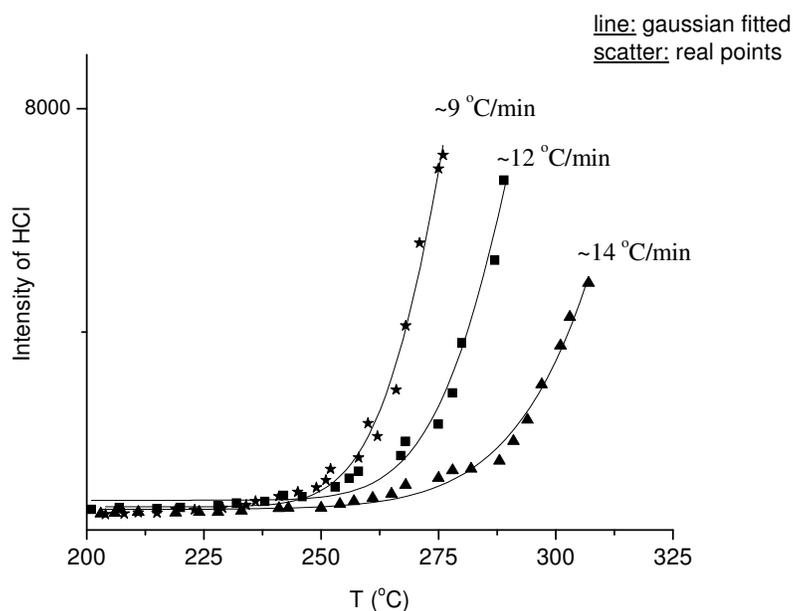


Figure 13: Experimental and fitted (Gaussian) data obtained for evolution of HCl (at m/z 36) from pure PVC at different heating rates.

3. 1. 1-b) Photodegraded PVC

The evolution of the volatile thermal decomposition products of polymers can be monitored by mass spectrometry. The specific objective is to assess the temperature at which the onset of degradation is detectable. Defining a specific temperature onset is somewhat artificial, because degradation does not suddenly start to occur at a precise temperature. For instance, from Figure 13, it is evident that there is a relatively small temperature region in which the degradation is first seen at the detection limit and then escalates rather quickly, and it is convenient to have some measure of this temperature region. This alternative method has been used in order to specify more precisely the details of the variation in thermal behaviour of light induced samples with temperature.

Two main thermal decomposition products of the polymers, HCl (at m/z 36) and benzene (at $m/z=78$), have been studied by recording their mass spectra as a function of temperature.

Figure 14 summarizes the pyrolysis behavior of PVC, UV decomposed PVC with hydroquinone, and PVC exposed to 312 and 254 nm light sources at a constant 8 °C/min. heating rate where the intensity of the ion currents at different masses are plotted against temperature. This summary figure depicts several interesting behavior of the samples which can be correlated with their material and/or thermal properties.

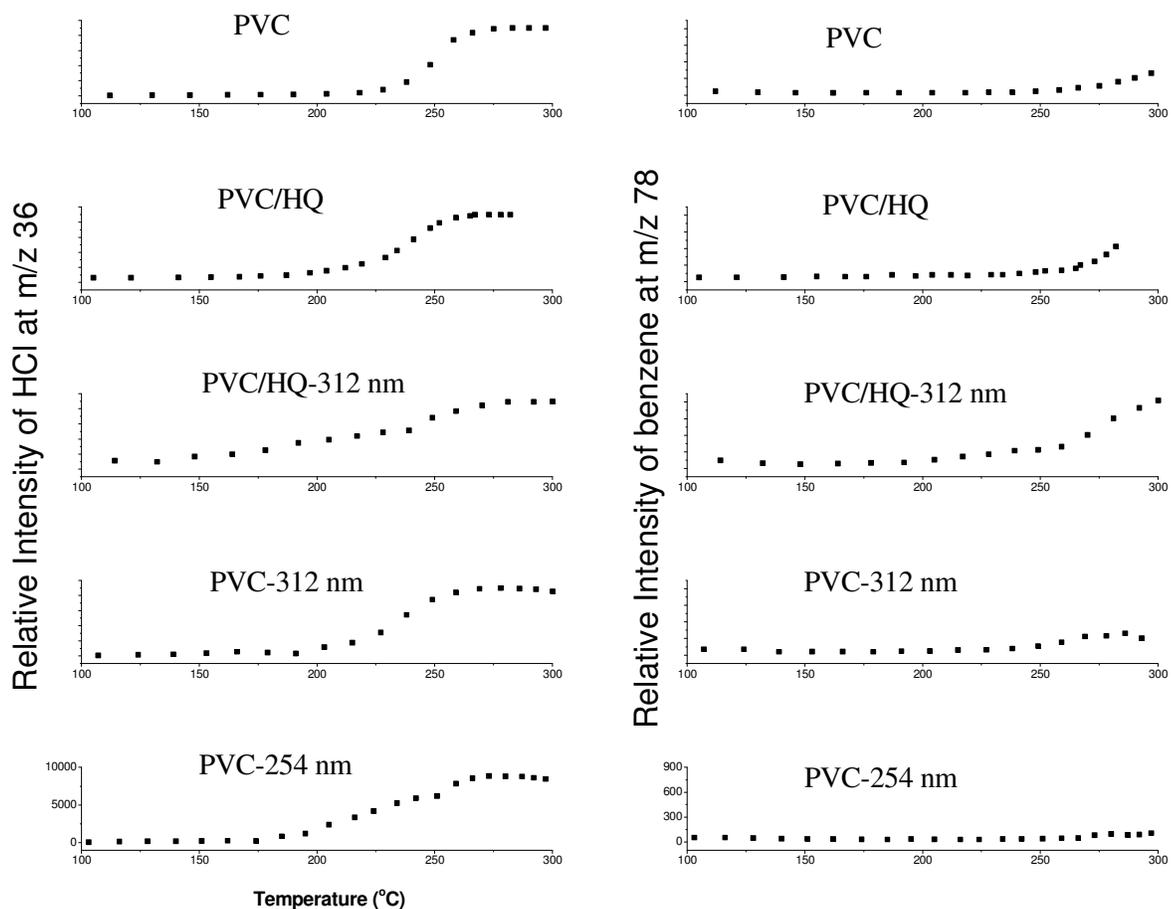


Figure 14: MS ion curves obtained for HCl at m/z 36 and benzene at m/z 78 from different PVC samples.

In Figure 15-a, HCl evolution from two different samples, pure PVC and PVC containing hydroquinone after 10 h irradiation with 312 nm light, are shown together. This figure indicates that dehydrochlorination of irradiated PVC (with HQ) starts to take place at much lower temperatures (around 150 °C), but pure PVC cannot be decomposed until the temperature reaches 250 °C, after which it starts to decompose rapidly. It can also be observed that the effect of radiation at 312 and 254 nm is not so significant compared to PVC/HQ (312 nm). Evolution of HCl from UV-induced samples (without HQ) starts at slightly lower temperatures compared to pure PVC.

The most abundant volatile product in PVC thermal degradation, other than HCl, is benzene. Benzene formation is a relatively low-temperature process with parallel HCl elimination. At high temperatures, this process is inhibited by polymer crosslinking. Benzene formation is an intramolecular cyclization process (backbiting route) of the polyene chain. The reaction is essentially initiated as the chain ends [47]. In our DPMS study formation of benzene (C_6H_6 , $M_w=78$) has also been monitored as an indicator. Temperature onsets and extent of detected ion current of benzene in our samples do not exhibit significant differences with the exception of UV (312 nm) exposed PVC/HQ blend. In this sample, benzene starts to be detected at lower temperatures (~200 °C) compared to the other samples (~250 °C) (Figure 15-b).

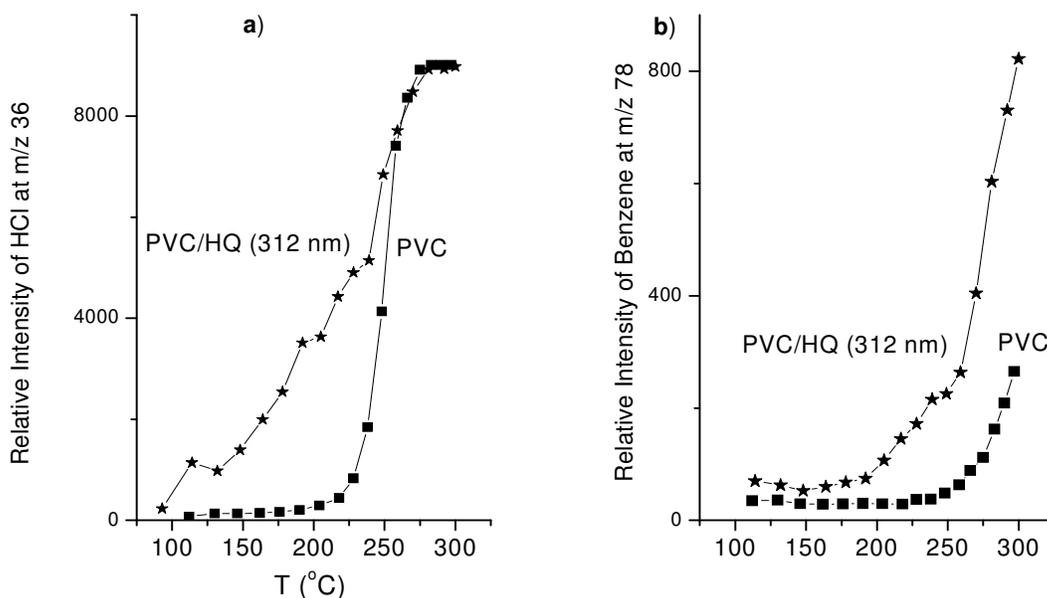


Figure 15: HCl (a) and Benzene (b) detection in UV-Induced PVC (312 nm, 10 h).

Influence of hydroquinone on the photothermal degradation of PVC:

The potential of a polymer for light-induced degradation is determined by its ability to absorb photons of suitable energy and availability of photochemical pathways to utilize the absorbed energy for chemical reactions. Most polymers can absorb ultraviolet (UV) radiation of $\lambda < 300$ nm [48], while those with chromophores such as carbonyl groups and unsaturated centers can absorb even longer wavelengths of (UV) radiation. PVC contains only C-C, C-H, and C-Cl, bonds and is therefore not expected to absorb light of wavelength longer than 300 nm [49]. The fact that free radicals are formed after irradiation of longer wavelength indicates that some kinds of chromophores must be present in the polymer matrix.

The DPMS molecular mass ion profiles of the volatile reaction products are monitoring the course of the photothermally induced reactions. The ion curves of the two main products, i.e. HCl and benzene are displayed and compared. The shift of the temperature onsets of dehydrochlorination and benzene formation in UV-induced PVC (with HQ) (Figure 15-a,b) may now be interpreted by two ways:

i) The heat instability of PVC must be caused by structural abnormalities formed during UV irradiation. These abnormalities may be chain scission of polymer backbone and polyene formation as a result of dehydrochlorination and photo-oxidation.

ii) Polymer matrix might have captured some of the HCl molecules generated during the UV exposure. In the course of pyrolysis, these molecules start to escape from polymer matrix at low temperatures.

3. 1. 2. TGA Study

Thermal degradation of PVC can mainly be considered as a two-step process. The first step (at about 400–600 K) account for about 60% of the total weight loss (the percentage of molecular weight of HCl to in monomer unit of PVC is 58.4) Degradation products are HCl (96–99%) and unsubstituted aromatics, mainly benzene and anthracene (1–3%). The residue has a polyene-like structure. Dehydrochlorination of PVC starts at a relatively low temperature. From previous studies of the isothermal degradation of PVC, it can be concluded that not all chlorine atoms are equally strongly bonded to the carbon backbone. The propagation reaction is believed to be a zipper reaction, autocatalysed by HCl [9]. The second step involves pyrolysis of the polyene structure, yielding mainly alkyl aromatics.

Sensitization of photodehydrochlorination of PVC by hydroquinone (HQ) was already investigated by Suzer et al. [15]. In our DPMS study we also demonstrated that the temperature onset for dehydrochlorination of UV-induced (312 nm) PVC/HQ composite is much lower than that of pure PVC. TGA technique is a supportive alternative to DPMS. Therefore, we also studied on UV-induced photodegradation mechanism of PVC using TGA technique. In TGA study, we concentrated on the weight loss behavior of PVC and its HQ composite in the first step of degradation (up to 330 °C). Thermogravimetric analysis of PVC, PVC/HQ (10/1 w/w) and their UV-induced forms (312 nm, 10 h) has been carried out in an atmosphere of nitrogen at a heating rate 5 °C/min. The free-standing solvent cast polymer films were 25-30 mg and placed in an aluminum crucible. All the runs were carried out between 40 °C to 330 °C. Figure 16

demonstrates the relative mass loss of the samples with increasing pyrolysis temperatures. TGA curve of pure PVC exhibits two stages of considerable mass loss. The first stage occurs between about 80 °C – 130 °C that comes from of volatile substances (THF, etc.). During the second stage, starting from about 240 °C dehydrochlorination of PVC and degradation to other volatile products like benzene formation occurs. The mass variation in PVC/HQ composite, which is exposed to the 312 nm UV source 10 hours, exhibits a very similar degradation pattern to the pyrolysis behavior of UV exposed PVC-HQ mixture in DPMS study (Figure 15-a). It is obvious that DPMS and TGA results are consistent with each other.

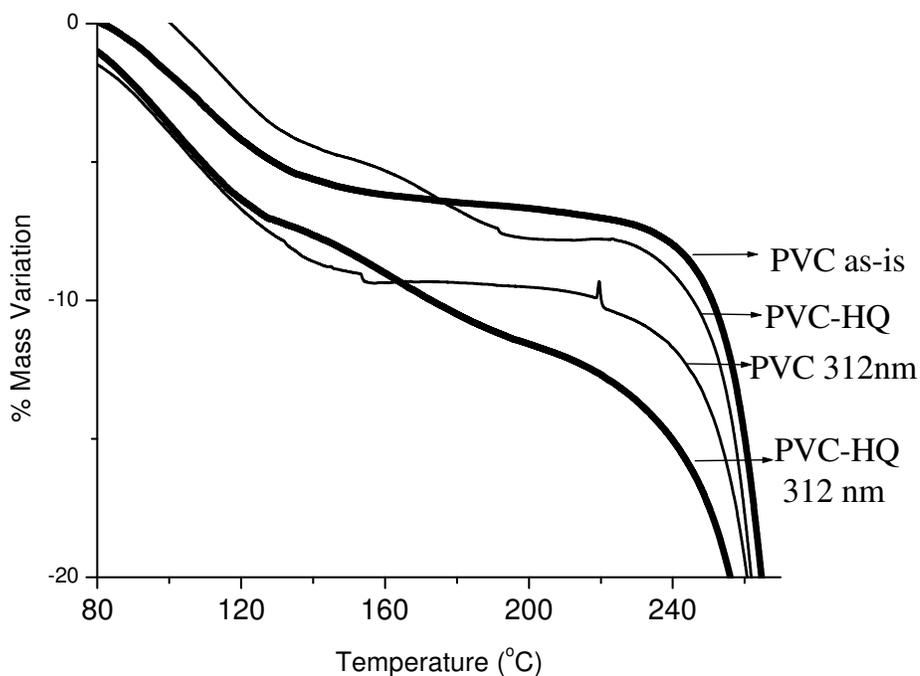


Figure 16: TGA curves of PVC, PVC/HQ and UV-induced forms (312 nm, 10 h).

3. 1. 3. UV-Vis-NIR Investigations

PVC dehydrochlorination process can also be monitored using UV-Vis spectroscopy. The photodehydrochlorination in PVC under UV irradiation leads to the formation of polyene segments with different number of conjugated double bonds. The presence of these

polyenes in polymer chains is responsible for coloration of PVC. The most important consequence of exposure of PVC to UV is the light-induced yellowing phenomenon, whereas the pure polymer does not absorb ultraviolet radiation wavelength that is greater than 250 nm.

As it is shown in Figure 17, PVC dehydrochlorinates significantly when exposed to the 312 nm UV light in the presence of hydroquinone. Without HQ there is no significant dehydrochlorination of PVC at 312 nm. The wavelength interval between 300-520 nm belongs to the produced polyenes [47]. Polyene formation can obviously be seen from the plot of PVC/HQ mixture exposed to 312 nm UV source for 10 hours. These findings reinforces our findings using DPMS and TGA techniques.

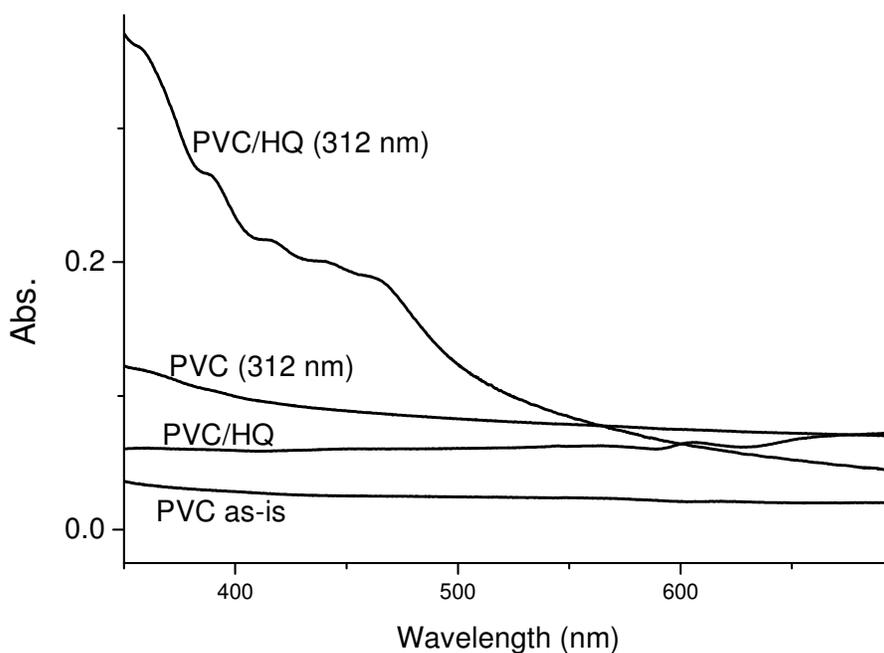


Figure 17: UV-Vis spectra of PVC, PVC/HQ and their UV-induced forms irradiated at 312 nm, for 10 h.

3. 2. Photodegradation of PVC, PVAc and PVC/PVAc (blends, copolymers)

The popular, simple and cheap method of polymer modification is blending two or more components with different properties. Even by the introduction of a small amount of one polymer into the matrix of the second, one can drastically change the behaviour of such composition. Kaczmarek *et al* reported that incorporation of PVAc decelerates photodegradation and photooxidation of PVC [27]. Copolymerization is also another alternative method to obtain some synergistic properties from two different polymers. Although a copolymer often has superior physical properties to either of the related homopolymers, the thermal stability is often impaired. The pyrolytic stability of PVC-co-PVAc was investigated by Grassie *et al* [28] and it was concluded that introduction of PVAc reduces thermal stability of PVC and it becomes least stable at around 40 wt.% PVAc in the copolymer.

In this part, we report our investigations of the photodegradation mechanism of PVAc and PVC/PVAc (blends, copolymers) as a possible alternative to PVC.

3. 2. 1 DPMS Investigations

i) HCl Evolution

Three different chloride containing polymer samples were used; PVC, a blend of PVAc and PVC (with 14/86 mass ratio), and PVC-co-PVAc (same composition as the blend). Samples were prepared in the same mass ratio and deposited onto the stainless steel plates by using micropipette (100 μ L) to make comparable films. We have found that DPMS studies are very sensitive to the overall sample weight which affects the relative intensity of detected pyrolysates and also to reach the saturation point in our measurements. Some of the samples were exposed to UV light (254 nm) during 10 hours. In order to get reproducible results, experiments were repeated at least three times. Reproducibility in the temperature scale is within 20 K. The results are given in Figure

18. Accordingly, it can be stated that non-irradiated PVC and blend samples do not exhibit any significant variation. However, the temperature onset of the copolymer is lower than that of other unirradiated ones. This result confirms the lower thermal stability of copolymer compared to PVC. Besides, UV-induced samples always start to dehydrochlorinate at much lower temperatures. Among them, the copolymer starts to give hydrogen-chloride molecules at the lowest temperature around 140 °C.

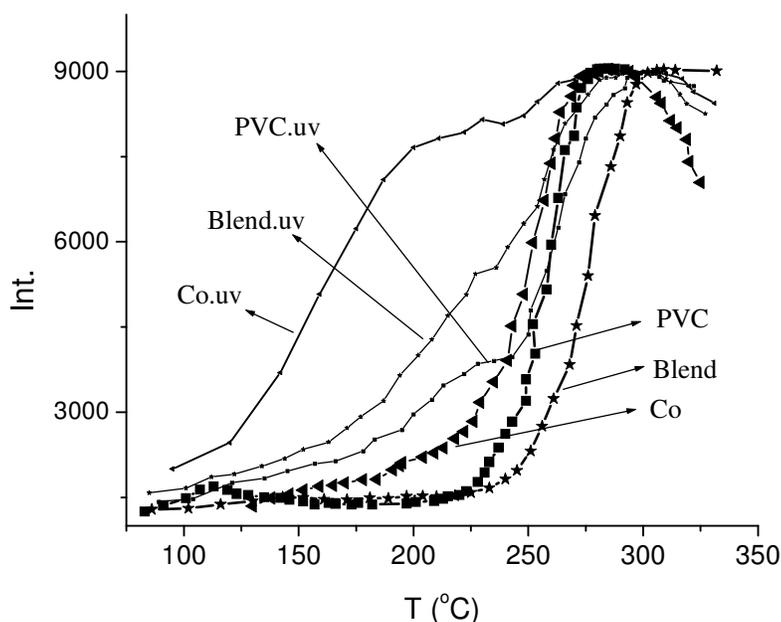
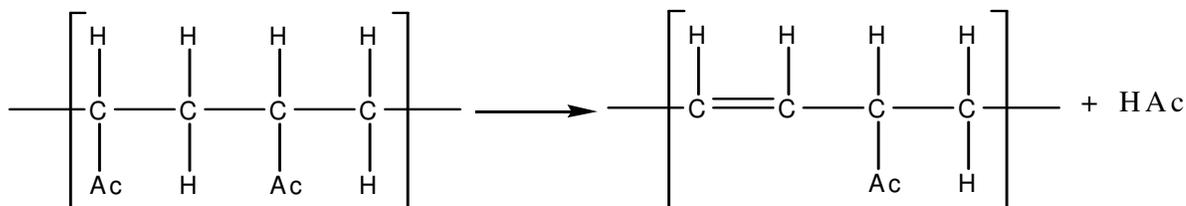


Figure 18: HCl evolution from UV induced (254 nm, 10 h) and unirradiated chloride containing samples.

ii) Acetic Acid Evolution

In the pyrolysis of acetate containing polymers, acetic acid (HAc, $M_w=60$) is also evolved. The evolution of acetic acid also leads to the formation of conjugated polyenes. The reaction mechanism is very similar to that of PVC (Scheme 8). However, the DPMS

behavior for the detection of acetic acid from PVAc, PVC-co-PVAc, and the blend exhibits a completely different route compared to HCl detection in the previous work (Figure 19).



Scheme 8: Pyrolysis reaction of PVAc leading to evolution of acetic acid and polyenes.

Polyvinylacetate: Acetic acid detection from irradiated and unirradiated PVAc does not exhibit appreciable differences. These samples follow nearly the same path at elevated temperatures. UV light may have changed the amount of acetic acid to some extent during exposure, but this difference cannot be detected by DPMS.

Copolymer: UV-induced copolymer samples start to decompose at around 275 °C to release acetic acid (60), whereas unirradiated ones give acetic acid at lower temperature (~240 °C). Besides, the extent of released pyrolysate (acetic acid) can be roughly compared by comparing the areas under the related curves. It is obvious that non-irradiated copolymer samples release much more acetic acid compared to radiated ones, which indicates that evolution acetic acid diminishes to some extent by UV-exposure.

Blend: The effect of UV exposure on blend of PVC and PVAc is not so a different within the error range of our DPMS measurements. It is possible that small variations in the overall mass can lead to the corresponding result, which is unavoidable.

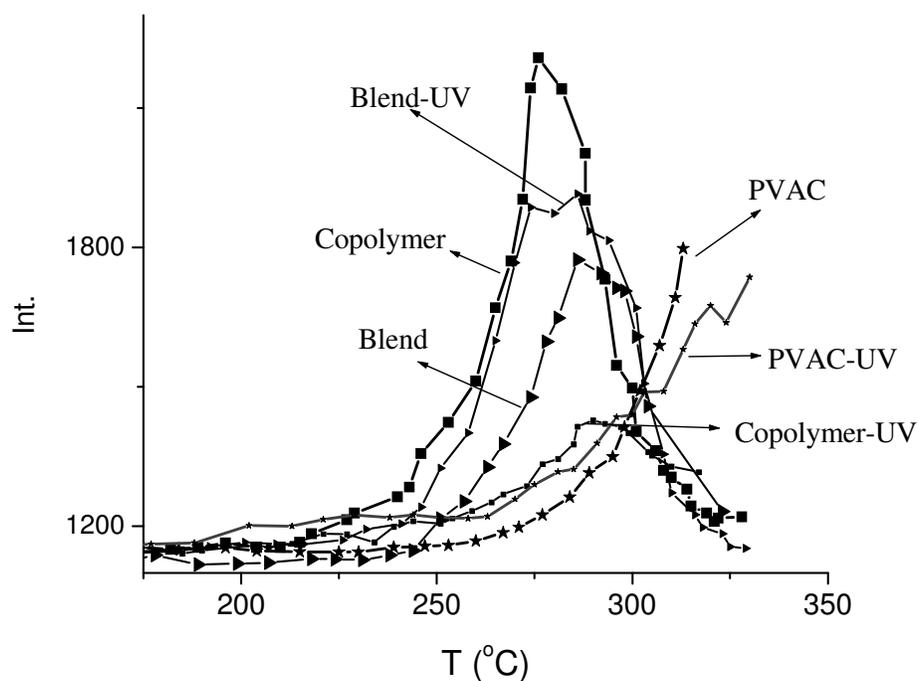


Figure 19: Acetic acid (CH_3COOH , 60) evolution from UV induced (254 nm, 10 h) and as-is acetate containing samples at elevated temperatures in DPMS.

Two general conclusions can be drawn from these degradation profiles:

i-) Dehydrochlorination temperature onset of UV-induced (254 nm) in the copolymer is much lower than that of corresponding PVC and PVC/PVAc blend. Beside, the lower thermal stability of copolymer has also been detected using DPMS technique. A proposed reason was that addition of vinyl acetate changes the polarity of the PVC chain and enhances rapid elimination of $\text{CH}_3\text{COOH}/\text{HCl}$ [28].

ii-) Acetic acid ion current profiles are completely different from dehydrochlorination profiles. In UV-induced (254 nm) chloride containing polymers dehydrochlorination temperature onsets are lower than that of unirradiated ones, whereas, in UV-induced acetate containing polymers temperature onsets of acetic acid detection are higher than that of unirradiated ones.

3. 2. 2. UV-Vis-NIR Investigations

3. 2. 2- a) UV-exposed Polymers (254 nm)

The following plots (Figure 20) demonstrate the spectroscopic changes of polymers (PVC, PVC-co-PVAc, PVC/PVAc blend, and PVAc) by the effect of UV radiation (254 nm, 10 h). The comparison between the spectra of UV-irradiated and non-irradiated displays the small increase in 300-500 nm region, which is the characteristic of existence of polyenic structures. This situation is more obvious in copolymer and PVAc. Hence, it is proven that polyvinylacetate release acetic acid to generate polyenic structures similar to the behavior of PVC.

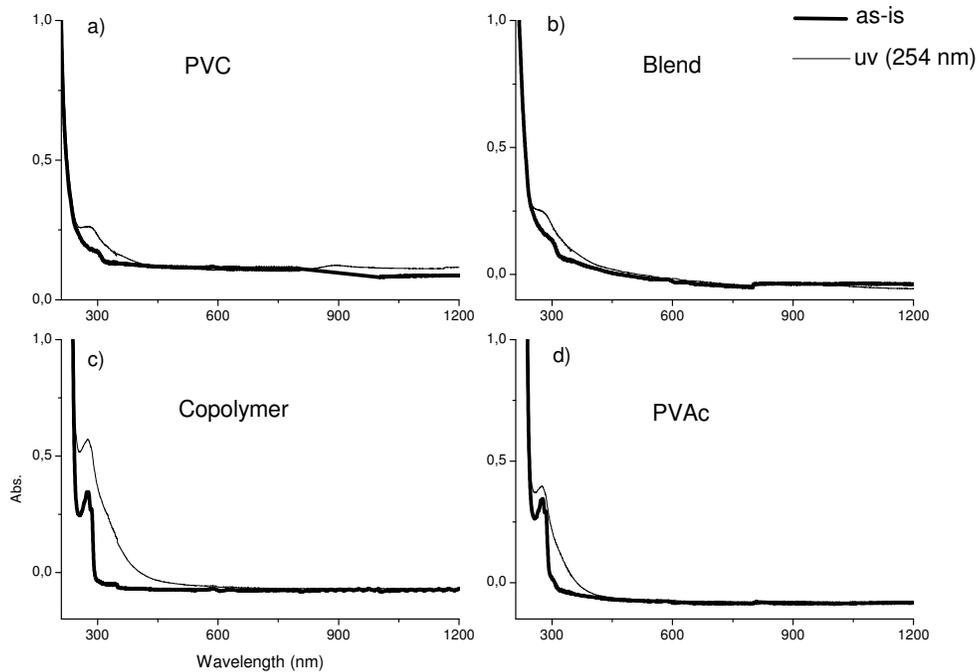


Figure 20: UV-Vis spectra of (a) PVC, (b) PVC-PVAc Blend, (c) PVC-co-PVAc and (d) PVAc before and after 10 hours 254 nm UV-exposure.

3. 2. 2-b) UV-exposed Polymers (312 nm) incorporated with HQ

The UV-Visible spectroscopic changes occurred in HQ incorporated PVC, PVC/PVAc (Blend), Copolymer samples after 10 hours 312 nm UV exposure as shown in Figure 21.

i-) *PVC*: As it is shown in Figure 21-a, PVC dehydrochlorinates significantly when exposed to the 312 nm UV light in the presence of hydroquinone and polyenes are formed.

ii-) *PVC/PVAc Blend*: The UV-Vis-NIR spectra of PVAc blended PVC (Figure 21-b) demonstrate no significant difference from PVC samples. The sensitization role of HQ is also observed upon UV- exposure in blend/HQ composite.

iii-) *PVC-co-PVAc*: After UV exposure, the sensitization role of hydroquinone is also observed in copolymer samples (Figure 21-c). On the other hand, one of the similarities between copolymer and PVC is that polyene formation in HQ blended copolymer under UV-exposure is as much as in irradiated PVC/HQ blend. Polyene formation in copolymer film upon exposure of 254 nm light is also observed in our previous works (Figure 21-c). The excess polyene formation in copolymer most probably comes from release of acetic acid, not only from dehydrochlorination because upon UV exposure (254 nm) a considerable amount of polyenic structures are formed in PVAc films (Figure 20-21-d).

iv-) *PVAc*: PVAc films do not exhibit similar behavior with PVC in terms of extent photodehydrochlorination of HQ blended PVC films (Figure 21-d). PVAc is slightly influenced by HQ upon 312 nm UV-exposure. Formation of polyenes (slightly) upon UV irradiation (254 nm and 312 nm) in PVAc indicates the evolution of gaseous acetic acid similar to the process in photodehydrochlorination of PVC.

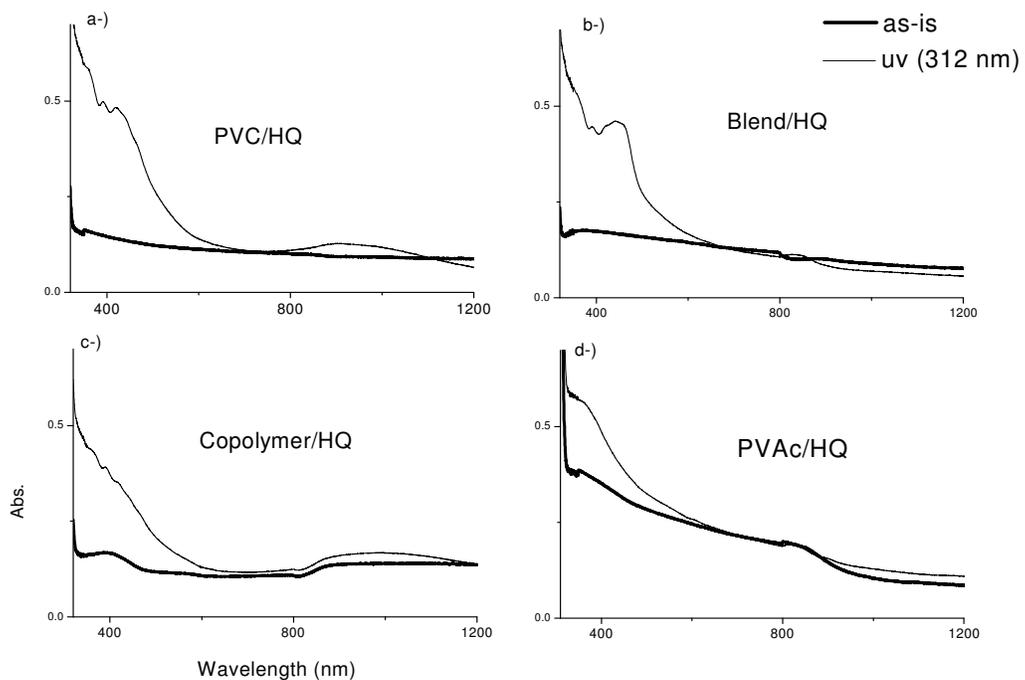
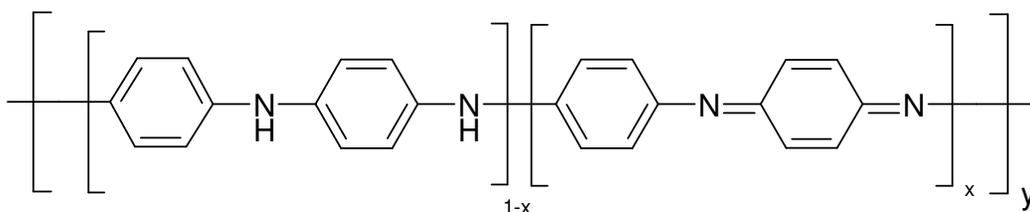


Figure 21: UV-Vis spectra of (a) PVC, (b), Blend (PVC/PVAc) (c) Copolymer, and (d) PVAc and Hydroquinone (HQ) before and after 10 hours 312 nm UV-exposure.

3. 3. PANI Blended Polymers

Polyaniline (PANI) in its doped, conducting form (emeraldine salt, ES) is not soluble or processable, in contrast to its undoped, non-conducting form (emeraldine base, EB). Doping is important method for changing the electronic properties especially increase of conductivity of the resulting product. Protonation of PANI can be carried out by wet and/or vapor harsh acid treatment. The general formula for the PANI is shown in Scheme 9.



Scheme 9: Reduced and oxidized form of PANI (EB, $x=0.5$).

It has been found that PANI is most conductive in its green state, emeraldine form, which corresponds to a value of $x=0.5$. In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depends on its oxidation state and on the pH of the aqueous acid [49]. Dehydrochlorination of PVC resulting from UV-exposure can also be utilized for doping of PANI in PVC/PANI blends. This kind of doping process can occur as a result of trapping of in-situ created HCl molecules by PANI(EB).

3. 3. 1. DPMS Investigations

3. 3. 1-a) Photodegradation of PVC/PANI Blends

PVC and PVC/PANI blend films were exposed to UV irradiation (254 nm) for 10 hours. The vacuum pyrolysis behavior of these samples are compared with unexposed ones as shown in Figure 22. It can firstly be stated that UV-induced samples have lower

temperature onsets (~ 150 °C) compared to unirradiated ones. Dehydrochlorination of PVC exhibits a sharp increase around 240 °C and PANI has no effect on PVC during pyrolysis. In addition, in-situ doped PANI/PVC blend dehydrochlorinates at ca. 40 K higher temperature compared to PANI/PVC.

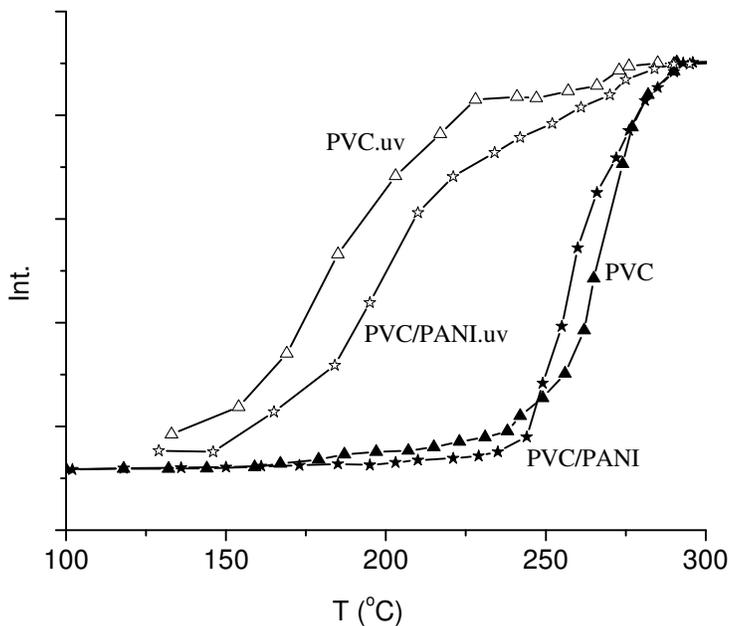


Figure 22: Evolution profile of HCl at m/z 36. PVC and PVC-PANI samples exposed to UV irradiation (254 nm, 10 h).

3. 3. 1-b) HCl Vapor Exposure

We also carried out external HCl vapor exposure of blended polymers to compare the two protonation types, in-situ and external. The MS ion curve of acid exposed PANI for the HCl evolution (Figure 23) exhibits two temperature onsets; the first one is around 150 °C, but the second of around 260 °C is more significant.

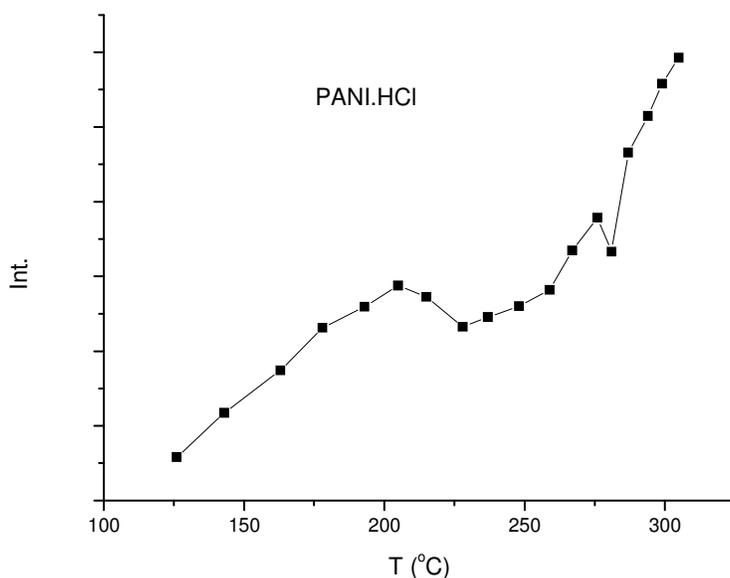


Figure 23: Evolution profile of PANI obtained for HCl at m/z 36 exposed to HCl vapor for 10 h.

An important difference between in-situ and external doping is observed as shown in Figure 24-a. During UV-exposure PANI is doped but simultaneously polymer structure is decomposed. Therefore, its degradation in pyrolysis starts at lower temperature compared to the externally doped PVC/PANI blend. This is most probably related to the damaging ability of HCl against UV exposure. Accordingly, the HCl vapor can not damage PVC as much as UV exposure.

The effect of acid exposure to PVC is interesting that dehydrochlorination starts at low temperatures (~ 140 °C) (Figure 24-b). This result might be attributed to autocatalytic dehydrochlorination of PVC in the presence of HCl. Besides, it is expected that PVC and PANI blend, exposed to HCl vapor, exhibits a synergism of separate PVC and PANI (HCl vapor exposed) samples.

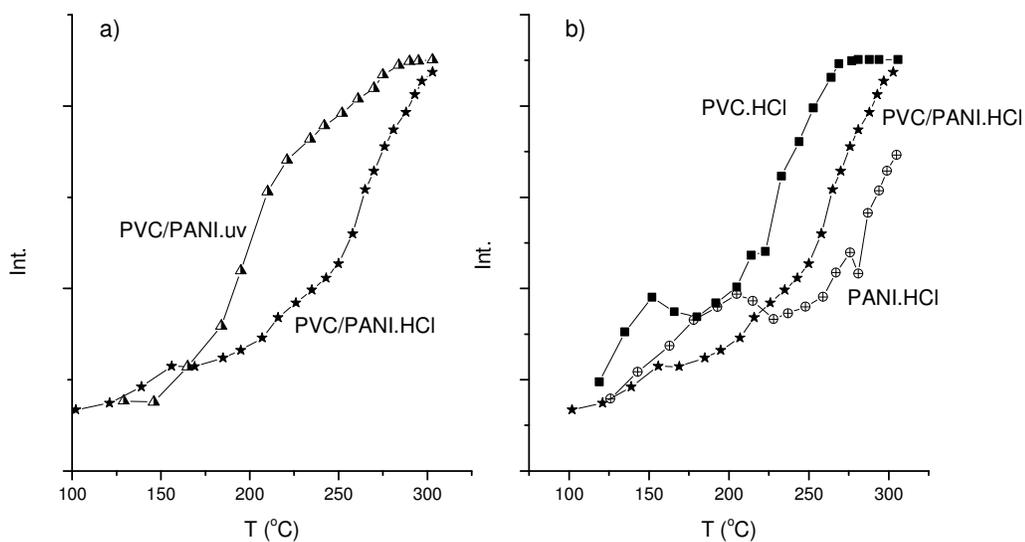


Figure 24: Evolution profile of HCl at m/z 36. PVC and PVC-PANI samples exposed to HCl vapor for 10 h.

3. 3. 1-c) Photodegradation of Copolymer/PANI Blends

The HCl evolution from PVC-co-PVAc and its blend with PANI (EB) upon 254 nm UV exposure for 10 hours exhibits similar behavior similar to previous PVC/PANI study (Figure 25). Dehydrochlorination in UV induced copolymer and copolymer/PANI blend starts at lower temperature (~ 120 °C) compared to the unirradiated ones (~ 180 °C). In addition, UV induced copolymer has a lower (ca. 40 K) temperature onset compared to UV induced Copolymer/PANI blend.

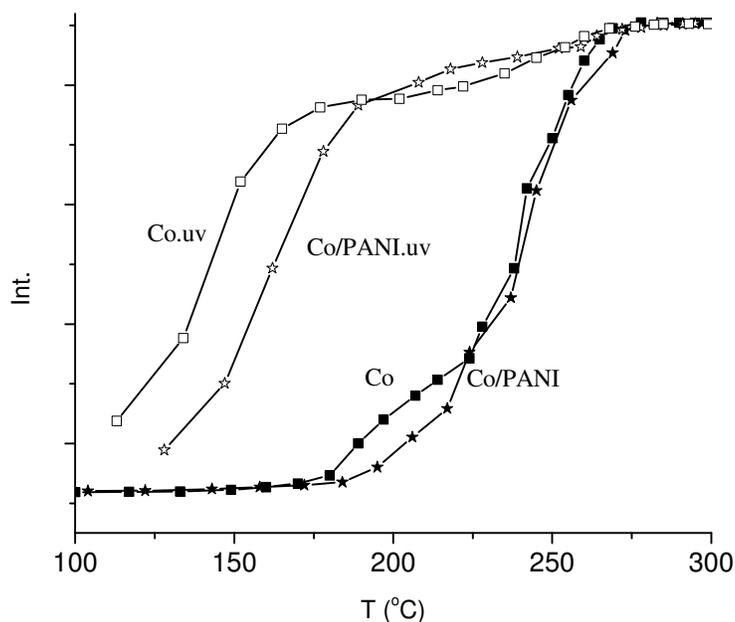


Figure 25: HCl (36) detection in DPMS. Copolymer and Copolymer-PANI samples exposed to UV (254 nm) or HCl vapor during 10 h.

3. 3. 1-d) HCl Vapor Exposure

Copolymer samples were also exposed to HCl vapor for 10 hours (Figure 26). The results are close to the results of the previous PVC study. However, the increase in dehydrochlorination is very sharp around 140 °C. In addition, there is no significant difference between in-situ and external doping as shown in Figure 26-a. Besides, the synergistic property between copolymer and PANI can also be observed for the system. HCl intensity from acid exposed Co-PANI blend is almost equal to the sum of HCl detection from acid exposed PANI and the copolymer.

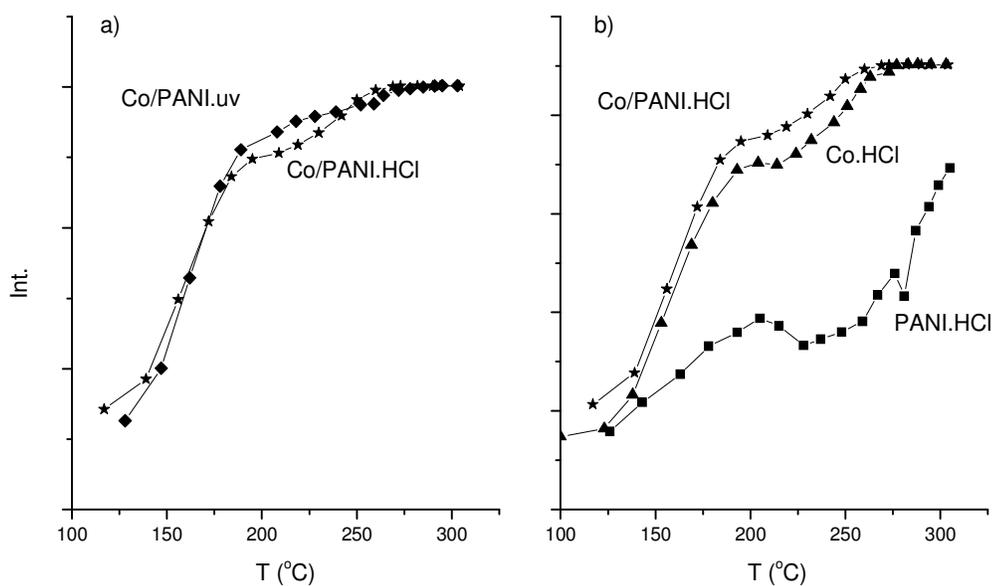


Figure 26: HCl (36) detection in DPMS. Copolymer and Copolymer-PANI samples exposed to UV (254 nm) or HCl vapor during 10 h.

3. 3. 1-e) A Summary of DPMS Results

The DPMS results of studied polymers can be summarized illustratively as shown in Figure 27 where the temperature onsets of HCl (36) and/or acetic acid (60) detection are depicted.

- i) Dehydrochlorination of acid vapor exposed PANI starts at low temperatures (~130 °C) but the main temperature onset is around 260 °C, which is higher than temperature onset of PVC.

Features common to all of the samples

- ii) HCl vapor exposed and UV exposed PVC or copolymer samples start to release HCl molecules at lower temperature compared to untreated ones.
- iii) The effect of PANI addition is observed in UV induced polymer/PANI blends as a shift of temperature onset to higher temperatures (~40 K). However, the same thing does not occur in unirradiated PANI blends.

Differences between samples

- iv) The low thermal stability of copolymer is confirmed. The temperature onset (starting temperature of HCl evolution) belong to UV induced copolymer has the lowest value.

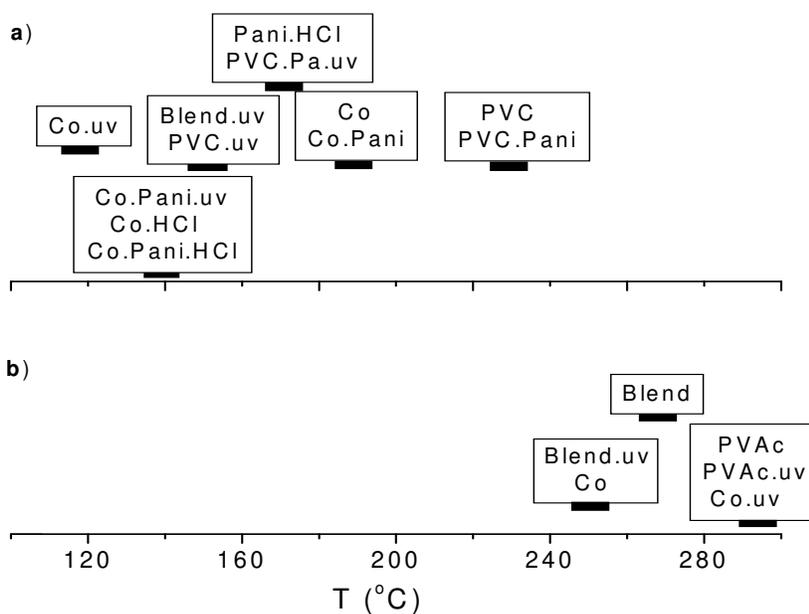


Figure 27: The illustrative temperature onsets of as-is, UV-induced and acid vapor exposed PVC, PANI, copolymer (Co), PVC/PVAc blend and PVAc. (a) HCl (36), (b) CH₃COOH (60) detection.

3. 3. 2. UV-Vis-NIR Investigations

Doped form of Polyaniline (PANI), which is the conducting form (Emeraldine Salt, ES), can be obtained by protonation of the imine nitrogen atoms in emeraldine base by HCl molecules. The structural change can be monitored by UV-Vis-NIR spectroscopy. Figure 28 illustrates UV-Vis-NIR spectra of insulating and salt form of PANI. The conducting form of PANI has a large polaron band, however the base form does not have any absorption in that region (500-1200 nm).

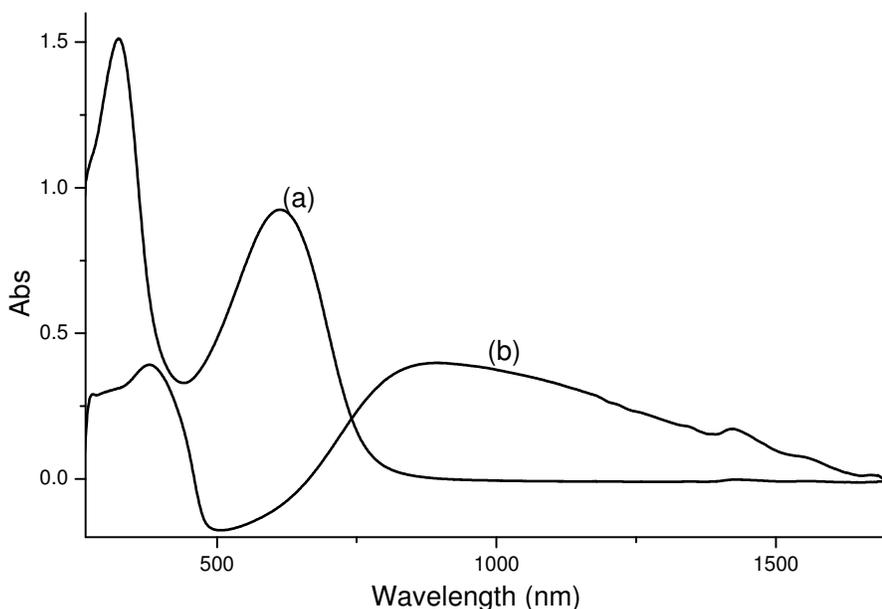


Figure 28: UV-Vis-NIR spectra of PANI base (a) and salt (b).

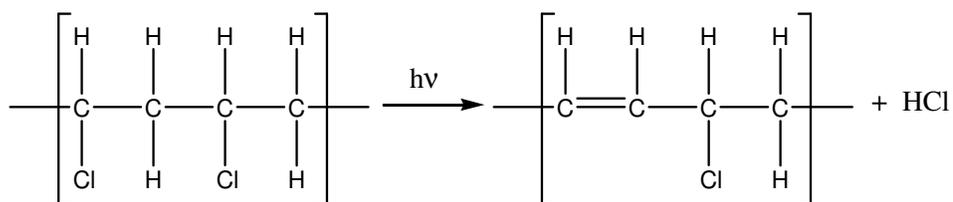
3. 3. 2-a) UV-exposed Polymers

All of the polymers blended with PANI (EB) exhibit a characteristic behavior of doping process upon UV (254 nm) irradiation as shown in Figure 29. The freshly prepared dark blue films have absorption bands centered around 600 nm and a strong transition around 300 nm (similar to PANI) which is indicative of the undoped form of the PANI (EB). The 600 nm band shifts to longer wavelengths upon exposure to UV and films become green,

indicative of the doped salt form PANI (ES). The same result is not observed in PVAc films.

From all these spectroscopic results it can be clearly stated that the in-situ generated HCl from chloride-containing polymers is captured by basic form of polyaniline in the matrix. However, PVAc matrix does not exhibit such a behavior. Accordingly, the acetic acid molecules from the acetate containing polymers as a result of UV exposure are not trapped by PANI (EB) in the same manner. Hence, the small easily broken and diffusive HCl molecules are unique in this sense.

The overall process can be described as follows:



Scheme 10: Doping of PANI.

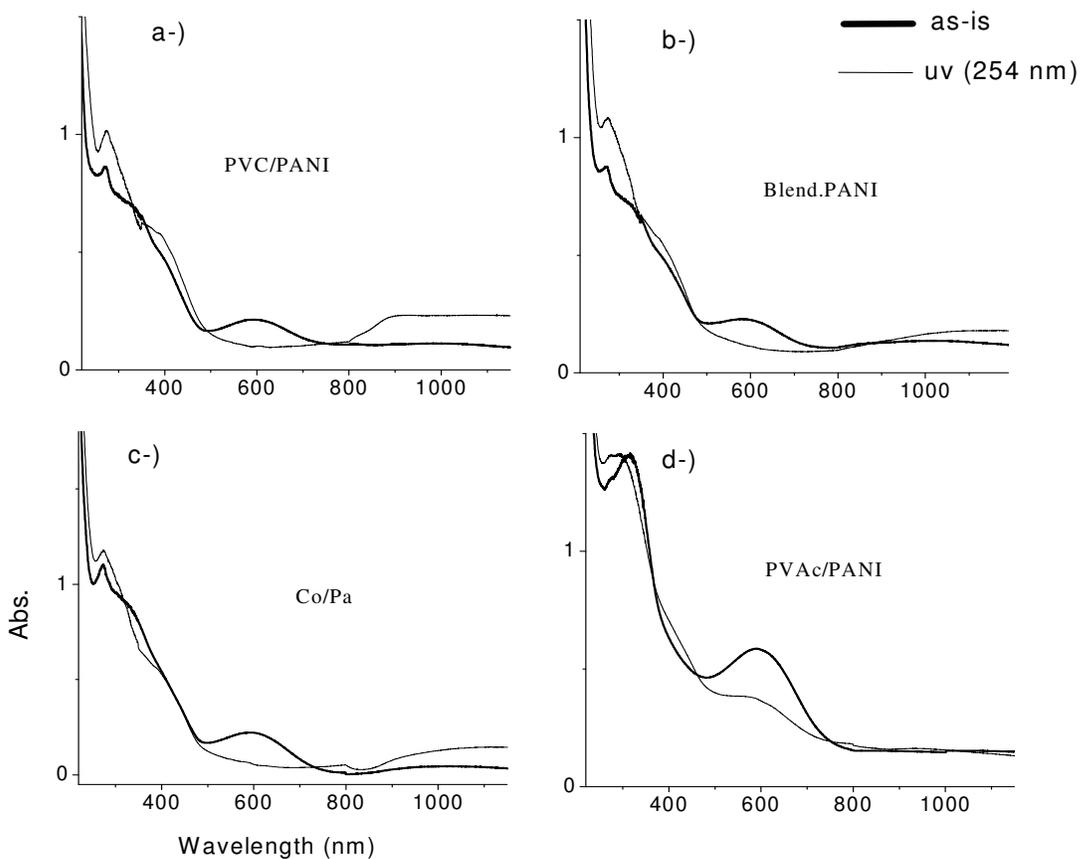


Figure 29: UV-Vis spectra of PANI blended (a) PVC, (b) PVC-PVAc Blend, (c) PVC-co-PVAc and (d) PVAc exposed to 254 nm irradiation for 10 hours.

3. 3. 2-b) HCl vapor-exposed Polymers

In this part, the doping process were studied using external (HCl) vapor source. The spectral changes upon HCl doping are given in Figure 30. Prepared free-standing polymer films were exposed to HCl vapor for 10 hours. Development of polaron band in all samples indicates doping of PANI externally.

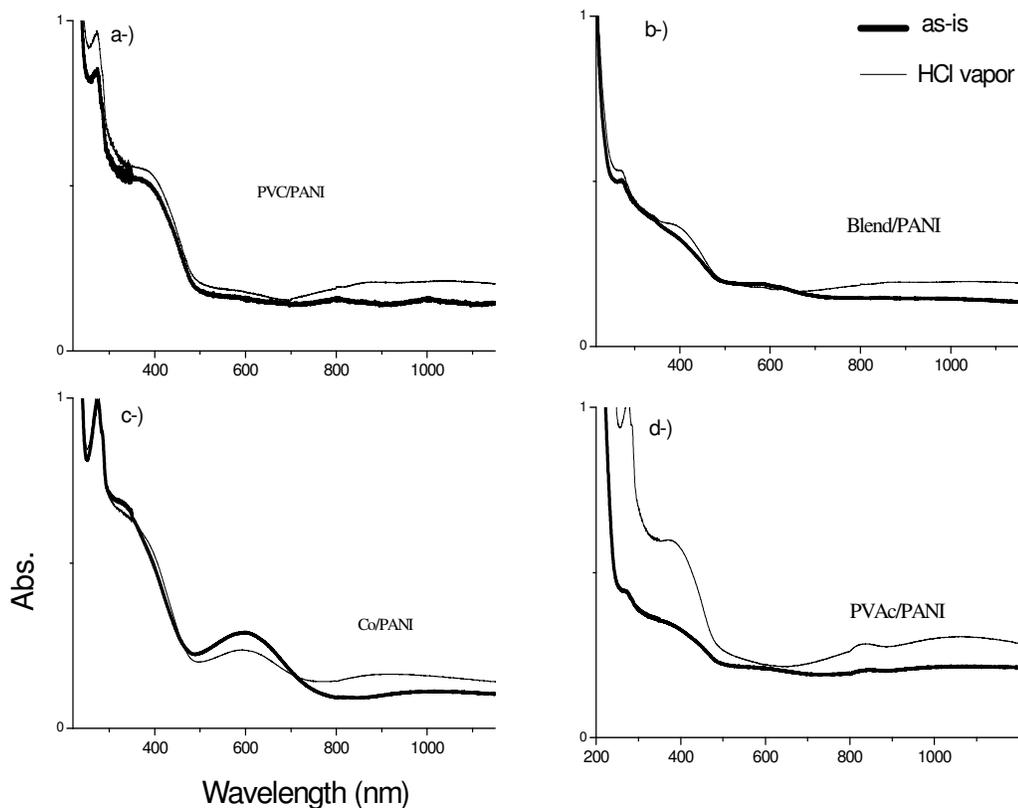


Figure 30: UV-Vis spectra of (PANI blended) (a) PVC, (b) PVC/PVAc Blend, (c) PVC-co-PVAc and (d) PVAc exposed to HCl vapor for 10 hours.

3. 3. 2-c) HQ Incorporated Polymers

PANI blended polymers (PVC, copolymer, PVC/PVAc blend, and PVAc) incorporated with HQ (1/10 w/w) were also investigated upon UV exposure (312 nm) for 10 hours. The optical changes upon HQ incorporation and UV exposure to all polymers are illustrated in Figure 31. The increase after UV exposure in 500-1200 nm region, which belongs to large polaron band, indicates doping of PANI with the externally incorporated HCl (Figure 31-a,b,c). However, there is no change in polaron band in PVAc since acetic acid is not trapped by PANI.

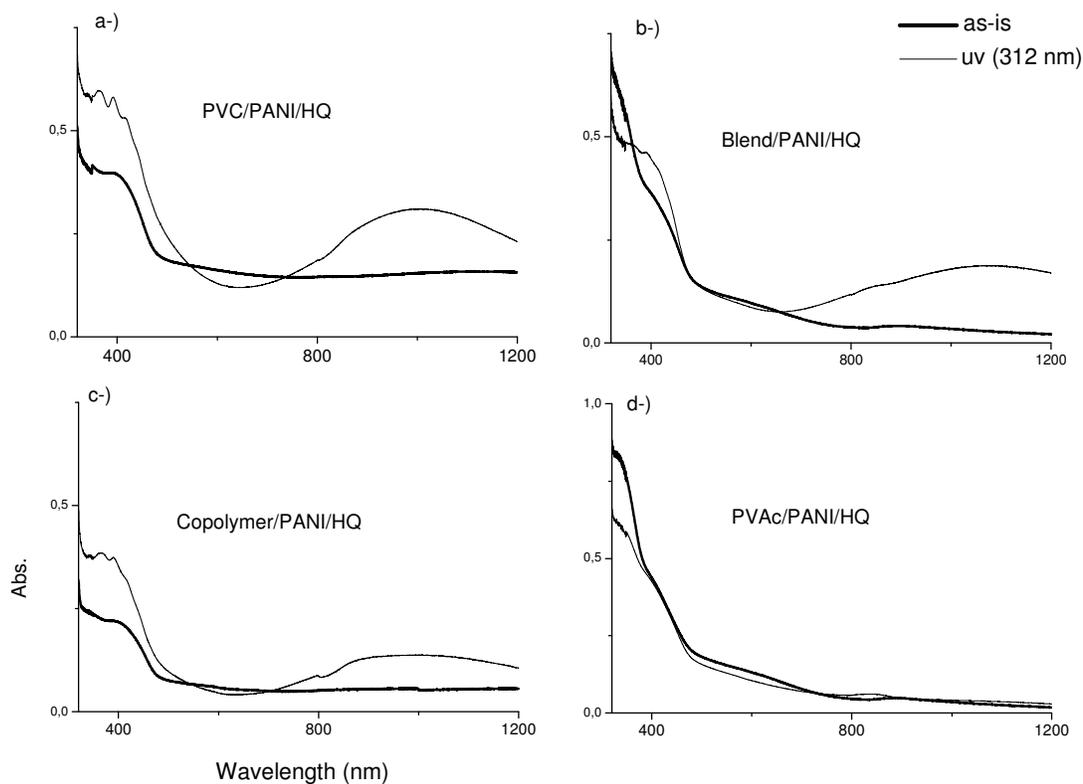


Figure 31: UV-Vis spectra of (a) PVC, (b), Blend (PVC/PVAc) (c) Copolymer, and (d) PVAc blended with PANI and/or HQ before and after 10 hours 312 nm UV-exposure.

3. 3. 3. FTIR Investigations

The infrared spectroscopy can be conveniently used to study the interconversions of polyaniline. The IR investigation of polymers (PVC, copolymer, PVC/PVAc blend) containing PANI were carried out. The spectra are in agreement with previously reported results [46]. Upon protonation of PANI, it is expected that characteristic changes in 2700-1800 cm^{-1} polaron band and also the red shift in 1600-1500 cm^{-1} benzenoid and quinoid region as shown in Figure 32.

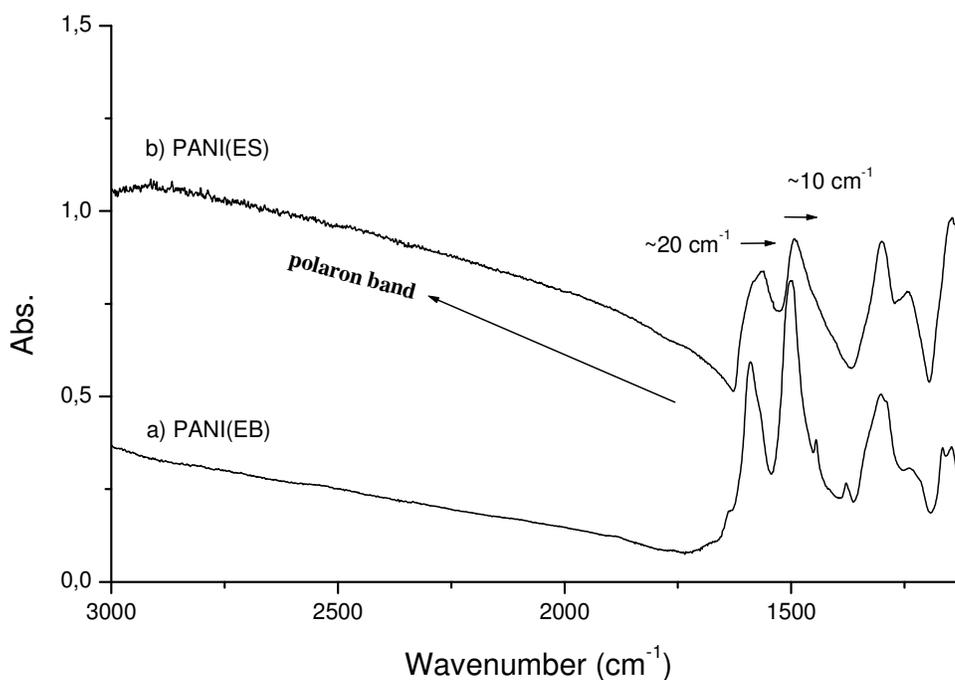


Figure 32: FTIR spectra of PANI base (a) salt (b).

3. 3. 3-a) UV-Induced (254 nm) Polymers

The observable spectral changes after UV exposure (254 nm, 10 h) in chloride containing polymers occurs as a red-shift (ca. 10 cm^{-1}) in 1510 and 1587 cm^{-1} bands and polaron band as shown in Figure 33. It is again very difficult to indicate any spectral change in PVAc/PANI blend upon irradiation.

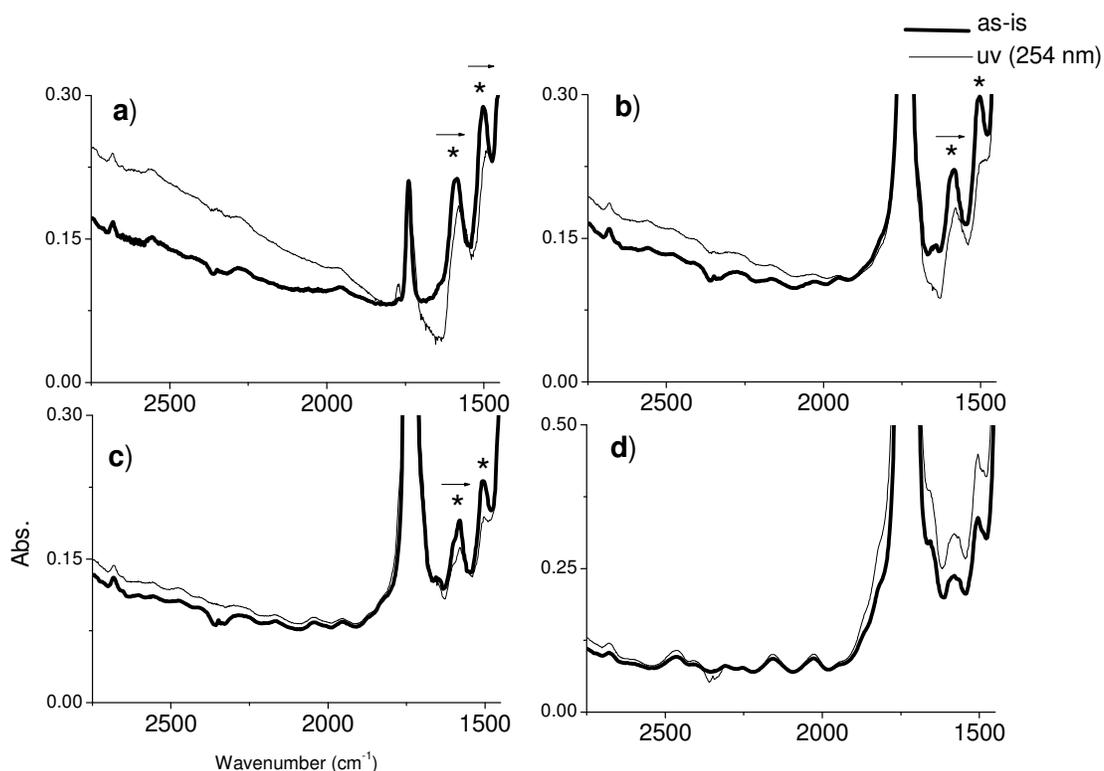


Figure 33: FTIR spectra of PANI blended polymers before and after UV-exposure (254 nm, 10 h), PVC (a), Blend (PVC/PVAc) (b), copolymer (c), PVAc (d).

3. 3. 3-b) HQ Incorporated Polymers

i-) HCl Vapor Exposed Polymers

Figure 34 shows the IR spectra of polymers containing PANI and HQ before and after HCl vapor exposure for 10 hours. All samples exhibit appreciable changes in favor of protonation of PANI upon acid vapor exposure. The increases in polaron band is higher in PVC compared to others. In these spectra, to observe the change in PANI 1510 cm^{-1} is very difficult due to the overlap with HQ band. In PVC sample the red shift (ca. 15 cm^{-1}) is observed around 1587 cm^{-1} peak.

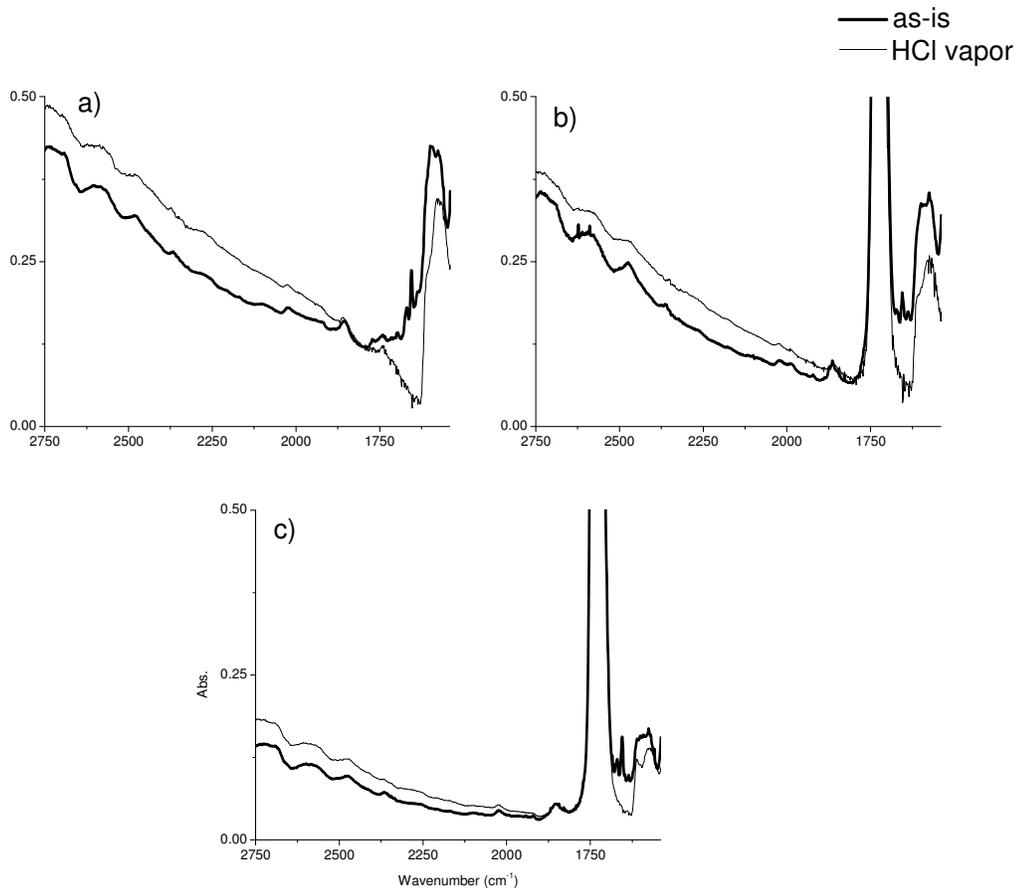


Figure 34: FTIR spectra of PANI and HQ blended polymers before and after doping with HCl vapor (10 h), PVC (a), Blend (PVC/PVAc) (b), copolymer (c).

ii-) UV Exposed Polymers

The extensive protonation of PANI in chloride containing polymers, which are blended with HQ, are shown in Figure 35. It can be stated without any doubt that the doping level in these samples is comparable with the acid vapor exposed ones (Figure 34).

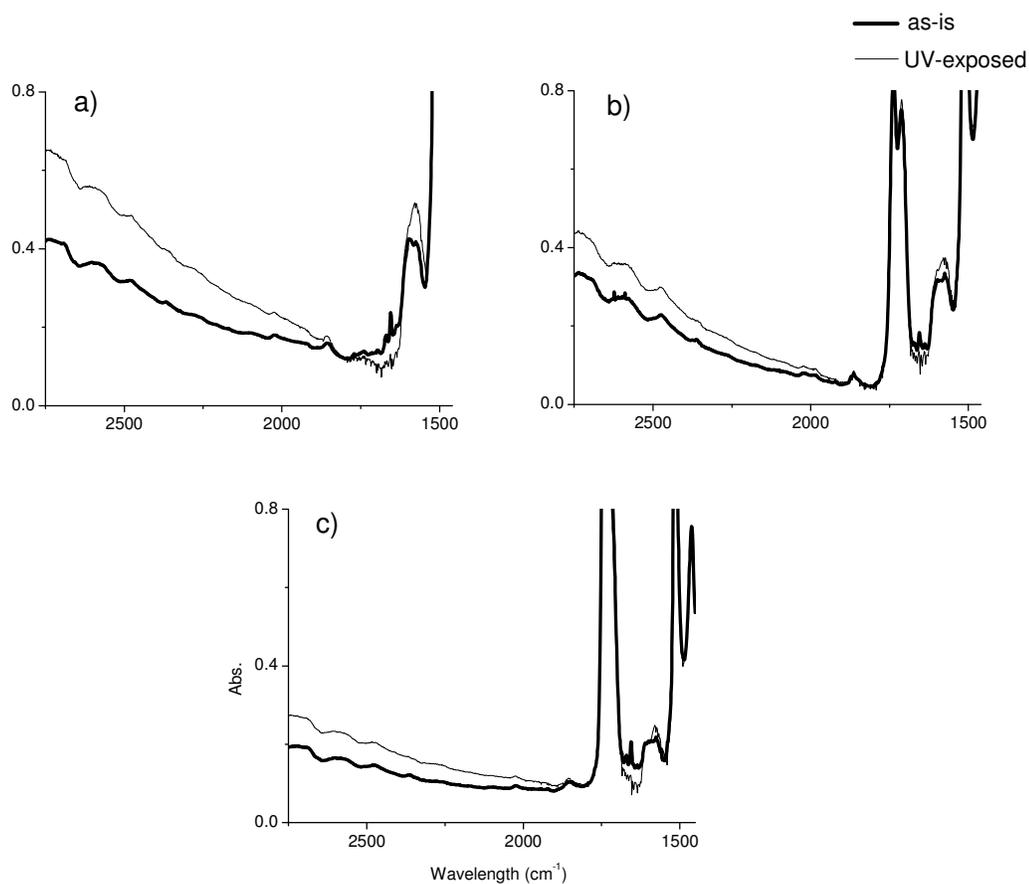


Figure 35: FTIR spectra of PANI and HQ blended polymers; PVC (a), Blend (PVC/PVAc) (b), copolymer (c) before and after UV-exposure (312 nm) for 10 h.

4. CONCLUSIONS

In this thesis, the effects of photodehydrochlorination on thermal and material properties of PVC are investigated using DPMS and TGA in addition to UV-Vis-NIR and FTIR techniques. DPMS and TGA are two complementary methods used in order to specify more precisely the details of the variation in pyrolysis behaviour of light induced samples with temperature. Pyrolysis behavior of species change as depending on structural variations. Therefore, these are valuable techniques to obtain information about the structure of photodegraded polymers. These techniques are destructive as different from others. In DPMS study, HCl evolution behavior of UV-induced PVC exhibits a characteristic property different from unirradiated ones. Assessment of the temperature at which the onset of degradation detected is a valuable clue to distinguish irradiated and unirradiated polymers.

In the first part of the thesis, the effect of HQ assisted PVC photodehydrochlorination at 312 nm is assessed. Sensitization by hydroquinone (HQ) was already investigated using UV-Vis-NIR, FTIR and XPS spectroscopic methods. DPMS and TGA results also confirmed the previous findings.

In addition to the PVC, photodegradation of PVC/PVAc blend, copolymer (PVC-co-PVAc) and PVAc are investigated. UV-induced copolymer exhibits a different behavior from others that its temperature onset is the lowest (140 °C). However, HQ assistance upon 312 nm UV exposure is not significantly observed in the copolymer. Utilization of dehydrochlorination of the polymers blending with basic form of PANI is also investigated since it is known that electrical conductivity increases upon UV radiation.

The low temperature onset of UV-induced copolymer is a promising result to produce longer polyene chains. Polymer backbone starts to decompose after ca. 220 °C. Hopefully, using copolymer we may be able to produce longer polyene chains as an alternative to PVC. However, the real assessment requires further studies with more sophisticated analytical systems and techniques.

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