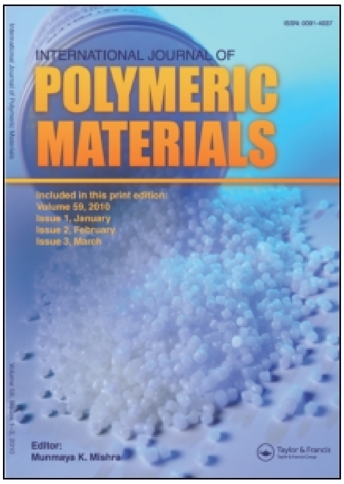

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Cadmium Chloride Catalyzed Degradation of PVC – Effect of Temperature and Concentration

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Conductometric and UV-visible spectroscopic techniques were used to study the effect of temperature and concentration on cadmium chloride catalyzed degradation of PVC. HCl evolved during degradation was measured for pure PVC and the samples containing 1-2 mol% of $CdCl_2$ by conductometric technique. Films of PVC containing $CdCl_2$ were degraded in an oven at different temperatures and UV-visible spectroscopic analyses were carried out. Spectroscopic results indicated that polyene linkages are formed and the formation of $H^+CdCl_3^-$ complex with them show absorption at 485, 430 and 360 nm for the films degraded at 100, 150 and 180 ± 1°C respectively. This was explained due to decrease in the average size of conjugated chain forming complex with increase in the degradation temperature.

Keywords: PVC; thermal degradation; $CdCl_2$; effect of temperature and concentration; DHCl and UV-visible analyses

1. INTRODUCTION

Intrinsically poly(vinylchloride) (PVC) is thermally unstable polymer and its applications are rather limited due to this problem. Intensive academic and industrial research has been carried out to understand degradation and stabilization processes of PVC [1-5]. Among the thermal degradation processes, dehydrochlorination (DHCl) of PVC

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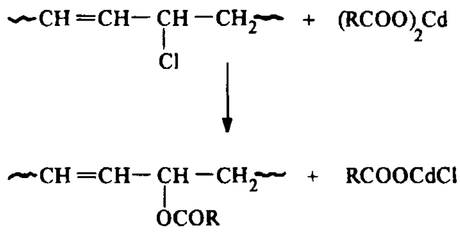
is predominant starting just above the glass transition temperature [6]. The mechanisms of DHCl have been studied [7, 8] in detail. It is well known that the primary process of PVC degradation is composed of three steps. (i) Initiation of HCl loss at labile chlorine atom [9, 10] (*e.g.*, at tertiary and allylic chlorine). (ii) DHCl proceeds adjacent to the unsaturation by a 'zipper' reaction catalyzed by the HCl formed, resulting in conjugated double bonds (polyenes) in the polymer backbone [11]. (iii) Termination of the zip-elimination process [10]. All these steps lead to discoloration of the PVC sample, even at very low concentration of polyenes.

Various techniques [12–14] have been used to characterize the small amount of polyenes present in the initial stage of the degradation process [15]. Conductometry and UV-visible spectroscopy are frequently used. The absorption energy of the polyenes depends on their lengths. This makes it possible to study the formation of polyenes by UV-visible spectroscopy [16].

Among the stabilizers, metal stearates/salts (especially of lead, zinc, barium and cadmium), organic compounds and organotin compounds have been extensively studied. These metal carboxylates are considered to be effective stabilizers of PVC. However, in case of zinc and cadmium carboxylates, the metal chlorides produced as a result of stabilizing action have been found to increase the degradation process [17–21] *i.e.*,



$$\sim CH{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{C}}H{-}CH_2\sim \; + \; (RCOO)_2Cd \;\longrightarrow\; \sim CH{=}CH{-}\underset{\displaystyle OCOR}{\underset{|}{C}}H{-}CH_2\sim \; + \; RCOOCdCl$$

$$RCOOCdCl \; + \; HCl \longrightarrow RCOOH \; + \; CdCl_2$$

Ahmad and coworkers have studied [12–15, 22, 23] the effect of Zn and Cd chlorides on thermal degradation of PVC using various techniques and have reported the kinetic parameters of the DHCl process in the presence of Zn and Cd chlorides.

In the present work, UV-visible spectroscopic technique has been used to study the effect of cadmium ion and the mechanisms of this catalyst on PVC degradation at different temperatures (100, 150 and 180 ± 1°C). The shift in the absorption maxima obtained due to the formation of complex at different temperatures has been explained.

2. EXPERIMENTAL

Dehydrochlorination process involved in degradation of pure PVC and samples containing different proportions of $CdCl_2$ at 180 ± 1°C was studied using conductometry. UV-visible spectroscopic analysis of PVC films containing different amounts of $CdCl_2$ degraded for various intervals of times was carried out at different temperatures (100, 150 and 180 ± 1°C).

Chemicals

(a). PVC

Analytical grade PVC obtained from BDH Ltd., with the following specification was used as received.

Molecular weight:	100,000 ± 20
Viscosity number:	[ISO/R 174 to 1961 (E) 87]
Paricle size:	100% passes B.S. 60 mesh
	74% passes B.S. 200 mesh

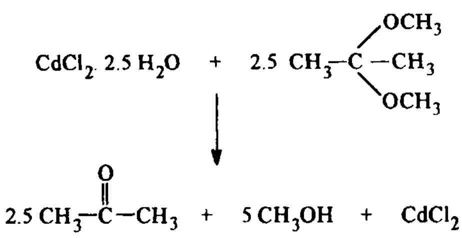
(b). 2,2-Dimethoxy Propane

AR-grade 2,2-dimethoxy propane supplied by E. Merck was used as such.

(c). $CdCl_2$

It was obtained from BDH Ltd. and contained 2.5 water molecules. To remove water 2,2-dimethoxy propane was used. $CdCl_2$ $2.5H_2O$ and 2,2-dimethoxy propane were taken in appropriate stoichiometric ratio and the mixture was shaken vigorously for 1 hr. The solution was then allowed to evaporate at 60°C in a vacuum oven. The water reacted with dimethoxy propane to produce acetone and alcohol.

The $CdCl_2$ was dried further in vacuum to a constant weight. It was



$$CdCl_2 \cdot 2.5\,H_2O + 2.5\,CH_3C(OCH_3)_2CH_3 \longrightarrow 2.5\,CH_3COCH_3 + 5\,CH_3OH + CdCl_2$$

kept under anhydrous conditions in a vacuum desiccator.

(d). Tetrahydrofuran (THF)

Peroxide free analytical grade THF (E. Merck) was used.

(e). Nitrogen Gas (N_2)

N_2 was used to provide dry and inert atmosphere during the sample preparation of PVC with $ZnCl_2$ and for conductometric measurements. It was obtained from Pak Oxygen Limited. It was purified to remove the traces of oxygen by passing it through alkaline pyrogallol solution and then dried by passing over NaOH pellets and silica gel. The purified N_2 was then passed at the rate of 20 ml/min through a reactor where PVC degradation was carried out.

(f). Conductivity Water

Doubly distilled water-having conductivity in the range of 1 – 2 μS was prepared in the Lab by redistilling the water in the presence of alkaline $KMnO_4$.

For UV-visible spectroscopic analysis, PVC films of uniform thickness were cast under an inert atmosphere by dissolving PVC containing different amounts of $CdCl_2$ (1 – 2 mol%) in THF and then evaporating the solvent over pure Hg on a smooth leveled glass plate. Films were dried further in a vacuum desiccator for 5 days at 60°C. Thickness of the dried films was in the range of 0.12 ± 0.002 mm. All these films were transparent and were cut and mounted on a metallic strip with a window of 4 × 1 cm for UV-visible spectroscopic analysis. The films were degraded at 100, 150 and 180 ± 1°C for various intervals of time in a furnace and their UV-visible spectra recorded on a 220-S Hitachi Spectrophotometer.

For DHCl, samples of pure PVC and PVC with homogeneously mixed $CdCl_2$ were placed in a reaction vessel and degraded at 180 ± 1°C for various intervals of time under a N_2 flow rate of 20 ml/min. N_2 gas carried away the HCl produced which was absorbed in the conductivity water placed in a thermostat at 25 ± 0.02°C. The conductance was measured using Orion Research Conductivity Meter Model 101 which had a precision of 0.3% in measurement in all ranges from 1 μS to 1 S.

3. RESULTS AND DISCUSSION

The Figure 1 describes UV-visible spectra monitored for PVC films contaiing 1 mol% $CdCl_2$, non-degraded and degraded for 180 min at 100, 150 and 180°C. The absorption for the degraded samples as compared to the virgin PVC was found to increase with the temperature of degradation. The formation of conjugated structure during degradation was more intense when the degradation was carried out at higher temperature. UV-visible spectra of the similar samples degraded for 240 min is described in Figure 2 and the concentration of the polyene linkages formed were found to increase with the higher degradation time.

The appearance of a broad peak with maxima at 485 nm was observed for the films degraded at 100°C (Fig. 1). The absorption peak was found to shift towards shorter wavelength region *i.e.*, 430 nm when the degradation temperature was 150°C and with further rise in the degradation temperature *i.e.*, 180°C, this absorption maxima was observed at 360 nm. The absorption peaks observed at these temperatures for the higher degradation time *i.e.*, 240 min (Fig. 2) were in the same range as observed in Figure 1.

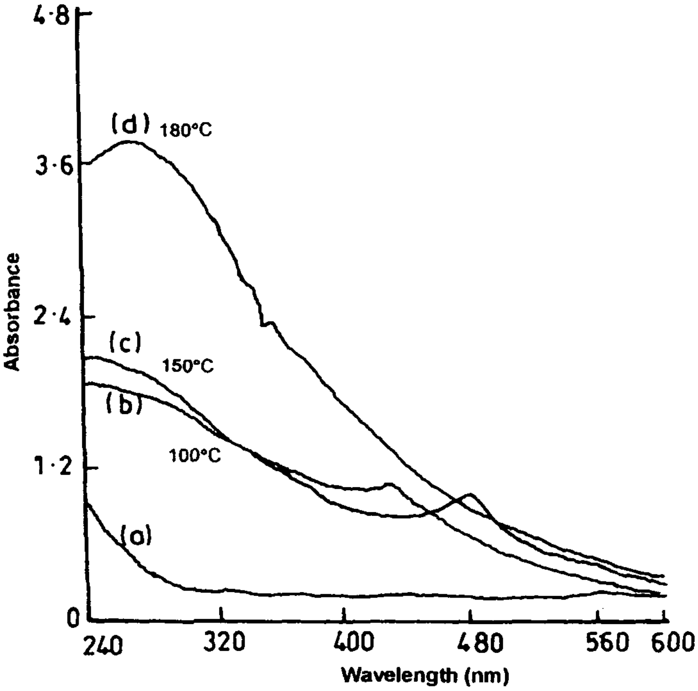


FIGURE 1 UV-visible absorption spectra of PVC film containing 1 mole% $CdCl_2$ (a) virgin, (b–d) degraded at different temperatures for 180 min.

The absorption spectra of PVC containing 2 mol% $CdCl_2$ degraded for 180 min at different temperatures are shown in Figure 3. A comparison of the data with Figure 1 shows that higher proportion of $CdCl_2$ in PVC slightly shifts maxima towards shorter wavelength region. Also the absorbance was more intense as compared to the samples of PVC mixed with 1 mol% $CdCl_2$ meaning that larger amounts of metal chloride in PVC enhances the degradation rate. The Figure 4 depicts the UV-visible spectra for the PVC samples containing 2 mol% $CdCl_2$ degraded for 240 min. Its comparison with Figure 3 shows higher absorbance but the position of the maxima at different temperatures was the same as that for the sampels degraded for 180 min. However, Figure 4 also shows that higher amount of $CdCl_2$ (2 mol%) shifts the maxima slightly towards shorter wavelength

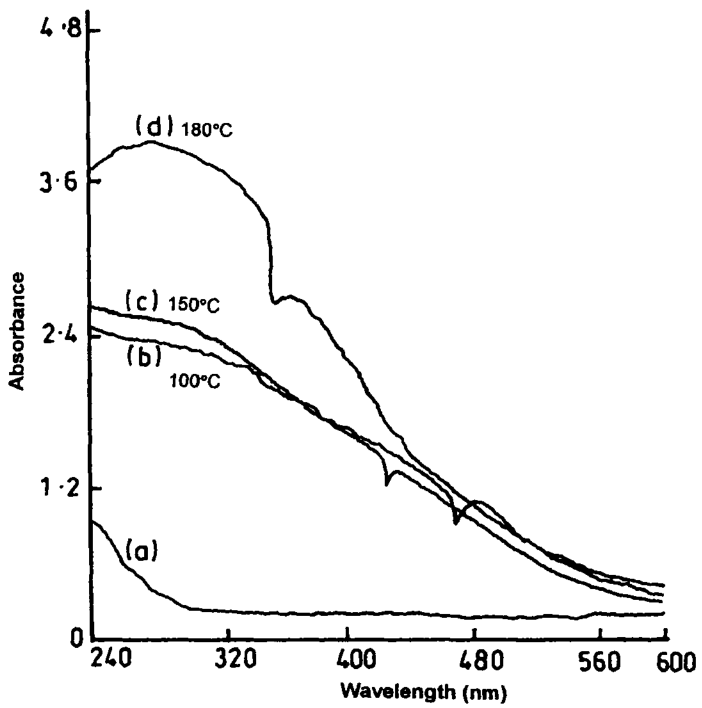


FIGURE 2 UV-visible absorption spectra of PVC film containing 1 mole% $CdCl_2$ (a) virgin, (b–d) degraded at different temperatures for 240 min.

as compared to Figure 2 where the amount of $CdCl_2$ is 1 mol% for the same degradation time.

The addition of $CdCl_2$ into the PVC matrix catalyzes the degradation process. $CdCl_2$ may associate with the HCl produced or abstract allylic chlorine from the PVC chain forming a colored complex with the conjugated chain that can absorb in the visible region. The interaction of similar metal chlorides, *i.e.*, $ZnCl_2$ with various conjugated molecules has been referred [24, 25] due to the formation of a σ complex giving absorption in the visible region.

We have reported the experimental evidences indicating the interaction of $CdCl_2$ with various polyene sequences formed during PVC degradation, responsible for broad absorption [23] in the visible region. $CdCl_2$ may also react with the PVC chain and abstract Cl and

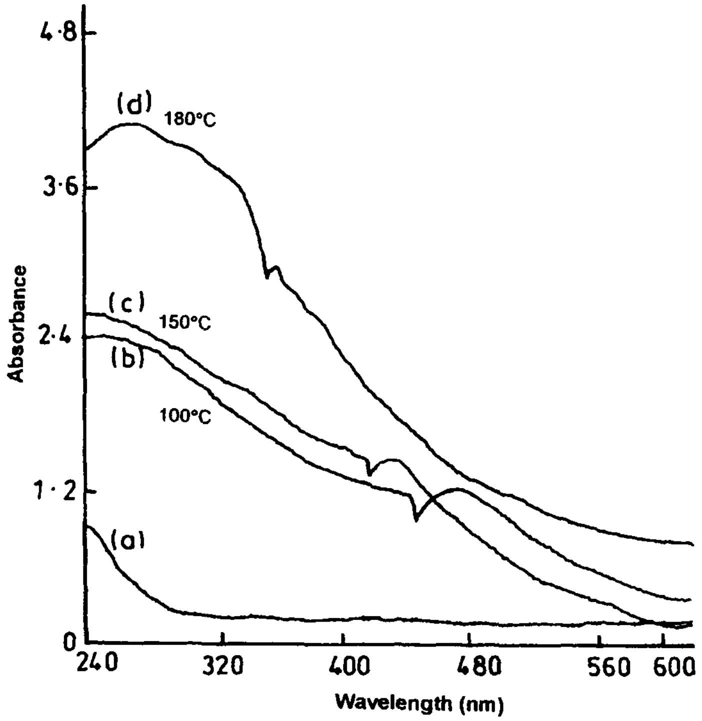
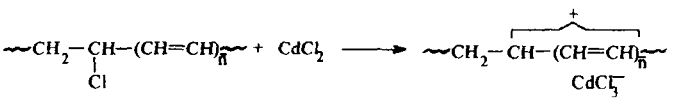


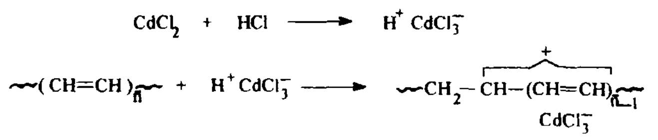
FIGURE 3 UV-visible absorption spectra of PVC film containing 2 mole% $CdCl_2$ (a) virgin, (b–d) degraded at different temperatures for 180 min.

the distribution of polyene sequences that occur as a result of degradation can be described by the process;



$$\sim CH_2-\underset{\large Cl}{CH}-(CH=CH)_n\sim + CdCl_2 \longrightarrow \sim CH_2-\overbrace{CH-(CH=CH)_n}^{+}\sim \atop CdCl_3^-$$

Another mechanistic pathway can be when $CdCl_2$ react with available HCl to form $H^+CdCl_3^-$. This may lead to colored species as



$$CdCl_2 + HCl \longrightarrow H^+CdCl_3^-$$

$$\sim(CH=CH)_n\sim + H^+CdCl_3^- \longrightarrow \sim CH_2-\overbrace{CH-(CH=CH)_{n-1}}^{+}\sim \atop CdCl_3^-$$

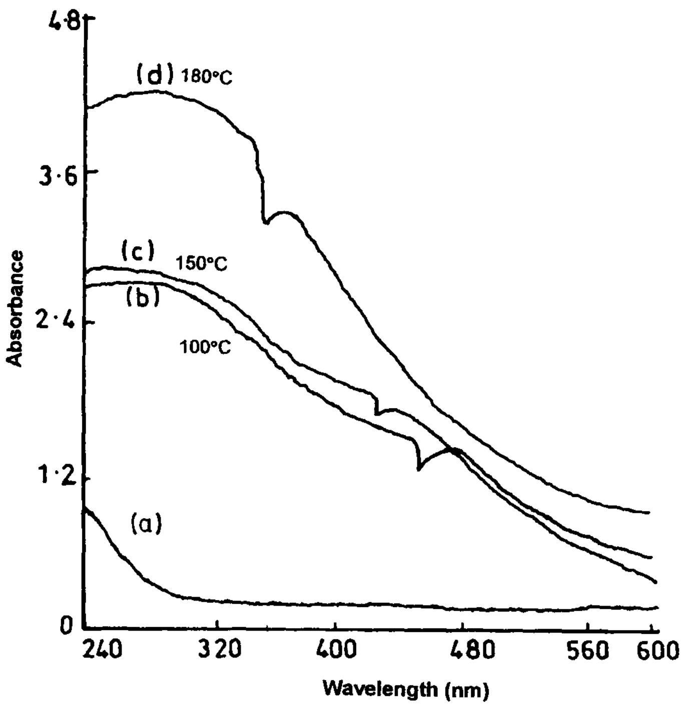


FIGURE 4 UV-visible absorption spectra of PVC film containing 2 mole% $CdCl_2$ (a) virgin, (b–d) degraded at different temperatures for 240 min.

In our previous work [15, 23], a broad absorption peak around 370 nm was observed for the films which were degraded at 180°C which was explained due to the interaction of $H^+CdCl_3^-$ with PVC chains. In the present work absorption maxima for same compositions of $CdCl_2$ in PVC degraded at higher temperatures showed absorption at shorter wavelengths (485, 430 and 360 nm at 100, 150 and 180°C respectively). At low temperature, the number of polyene linkages formed are less, however, the size (value of $\bar{n}$) of polyene linkages forming complex may be relatively large. Thus they give absorption at a lower wavelength. Increase in temperature may cause breakage of chain consequently decreasing the size of conjugation ($\bar{n}$) giving absorption at higher frequency region as observed in the present work.

Our studies [12] on thermal-nonoxidative degradation of PVC using mass spectrometry have shown that polyene sequences with 4–10 conjugated double bonds were formed. When the temperatue was increased, the longer polyene linkages break down in to smaller polyene linkages and the concentration of C_3 and C_4 polyene increases while the concentration of C_6, C_7 and C_8 decreases sharply when the temperature is raised from 230 to 250°C. This has been confirmed in the present studies as the absorption maxima shifted from 485 to 360 nm with rise in temperature from 100 to 180°C.

The comparison of the UV-visible spectra obtained in the present work (Figs. 1 and 2 or 3 and 4), however, do not show any shift in the absorption maxima when the polymer samples are degraded for longer time. This means that the average size of the polyene linkages $\bar{n}$ remains constant with increase in degradation time as studied in the present work. Ahmad and coworkers [23] have reported recently UV-visible spectra of thermally degraded PVC containing $CdCl_2$ with time at 180°C. Polyene sequences with 4–10 conjugated double bonds have been observed for degradation time up to 4 hrs. The average number of conjugated double bonds, $\bar{n}$, in stable polyene sequences with degradation time were calculated. They observed that the average size of the polyene linkages remain constant (Fig. 5) during degradation and does not change with time and there is a regular distribution of

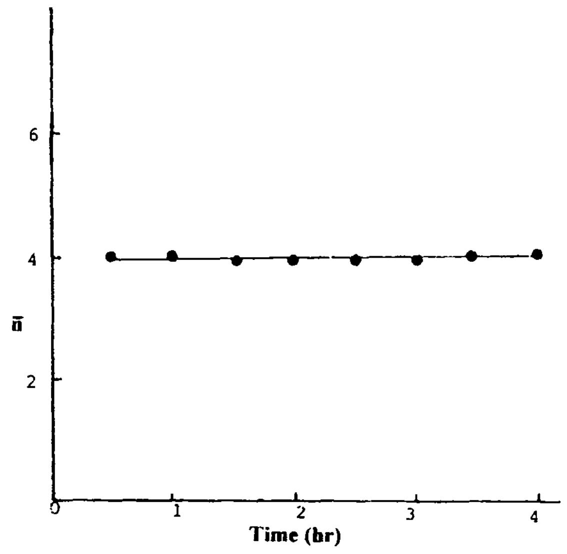


FIGURE 5 Change in the average length of conjugated double bond ($\bar{n}$) with degradation time for PVC film degraded at 180°C.

polyene sequences. Similar results have been reported by Xu Ruijian and Li Dean [26, 27]. In present work, we have also observed that the absorption maxima for the same $CdCl_2$ concentration and temperature appeared at the same wavelength irrespective of the degradation time. This means that the $\bar{n}$ remains almost the same for 180 min or 240 min degradation. A small increase in degradation time may not shift the peak as it increases the concentration of polyene linkages but not the size; however, increase in temperature of degradation reduces the average size of the polyene linkages thereby, shifting the maxima.

Thermal dehydrochlorination of pure PVC and samples containing different compositions (1–2 mol%) of $CdCl_2$ at 180 ± 1°C were studied by conductometric measurements. HCl loss % was found to be higher in case of PVC containing 1 mol% $CdCl_2$ than pure PVC (Fig. 6). When the amount of $CdCl_2$ is increased to 2 mol%, HCl loss

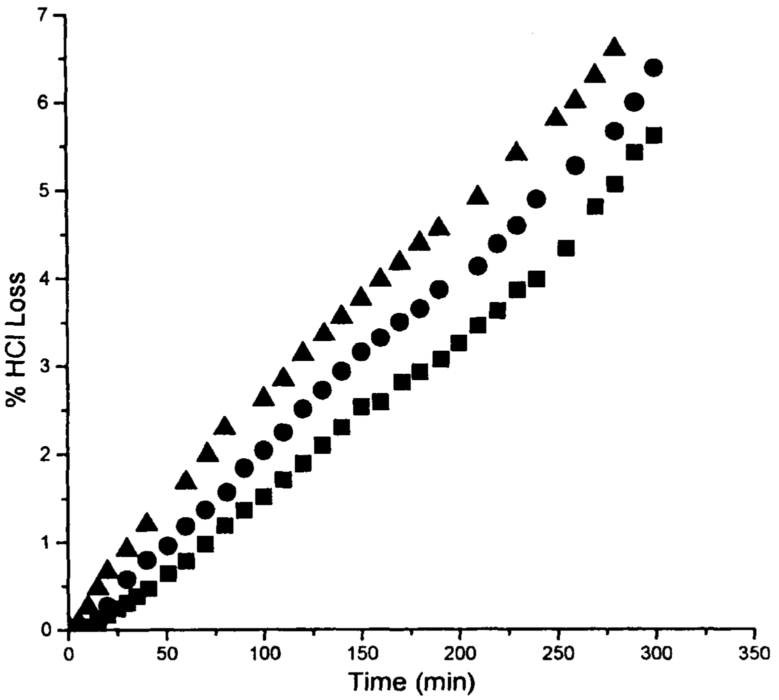


FIGURE 6 Dehydrochlorination of (■) pure PVC, (●) PVC + 1 mole% $CdCl_2$, (▲) PVC + 2 mole% $CdCl_2$ degraded at 180 ± 1°C.

is found to be higher which confirms the degrading effect of $CdCl_2$. The increased amount of $CdCl_2$ increases the proportion of catalyzed degradation process in comparison to uncatalyzed one, as formation of $H^+CdCl_3^-$ complex is favored by the strong interaction between Cd and Cl, which is due to the formation of $3p\pi$, $4d\pi$ overlapping. Such an overlap produces π-bond character thus giving extra stability to the complex. So the degradation rate increases as $CdCl_2$ proportion increases. As a result, the number of polyene linkages formed in case of PVC mixed with $CdCl_2$ are more than pure PVC and the concentration of small size polyene linkages increases with the increase in the amount of $CdCl_2$ in PVC film thus increase in UV-visible absorption and DHCl is observed with increase in concentration of $CdCl_2$.

$CdCl_2$, therefore, acts as degrading catalyst for PVC forming a stable complex by interacting with the polyene linkage produced. The absorption maxima occur at shorter frequency range at lower degradation temperature due to increase in the average size of polyenes produced. For a particular temperature, different times of degradation studied in the present work did not change the position of the maxima as the average size of the polyenes remained constant and this confirms the findings of Ahmad and coworkers [23].

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