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Green-stabilized PVDC copolymer films using Precocene I

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ABSTRACT

Precocene I; 7-methoxy-2, 2- dimethyl chromene extracted from the plant Ageratum conyzoides (Ifiora, 2019), was incorporated into extrudable vinylidene chloride – methyl acrylate copolymer by heating the copolymer under reflux in methanol solvent in a three necked Quick fit flask under dry nitrogen gas until the weighed copolymer dissolved in the solvent. The weighed precocene I was then added drop wise to the resulting copolymer solution with continuous stirring and heating under nitrogen atmosphere to exclude oxygen as well as moisture. The product recovered on cooling the solution and evaporating the solvent methanol was weighed and later subjected to thermogravimetric analysis to determine weight loss data. A comparison of the infra-red (Ir) spectrum of the product of incorporation with that of the copolymer without incorporation did not show any new prominent absorption bands in the product obtained after incorporation but cannot be conclusive evidence in the absence of scale expansion facilities which may have provided further evidence. Plots of thermogravic data against time were linear at each of the three temperatures of 170 °C, 180 °C, and 190 °C both for initiation and for propagation processes, and lend support for the statement that dehydrochlorination of the vinylidene chloride – methyl acrylate copolymer followed first – order kinetics at these three experimental temperatures with the incorporation of precocene I as additive. Rate constants for initiation of degradation under experimental isothermal conditions were obtained as 1.16 x 10^{-5} s^{-1}, 2.50 x 10^{-5} s^{-1}, and 5.58 x 10^{-5} s^{-1} at the constant temperatures of 170 °C, 180 °C, and 190 °C, respectively, while values for rate constants of propagation were 2.32 x 10^{-5} s^{-1}, 4.41 x 10^{-5} s^{-1} and 7.60 x 10^{-5} s^{-1} for the respective constant temperatures. These values show a steady decrease in the rate of degradation under the conditions of the experiment when compared with known literature values without additives as well as with nitrogen bases. Thermodynamic quantities derived from plots of these experimental quantities are as follows: Enthalpy of activation, $\Delta H^{\#}$, 98 kJ mol^{-1}, Arrhenius parameter, ΔE_a, 133 kJ mol^{-1}, and Entropy of Activation, $\Delta S^{\#}$, -128 J mol^{-1} K^{-1}, as against corresponding values without any additive, namely 116 kJ mol^{-1}, 125 kJ mol^{-1}, and –32 J mol^{-1} K^{-1}. The relative lowering of the energy requirements in the presence of precocene I additive indicates a more stable arrangement with lower degradation spontaneity. A reversal of such spontaneity is clearly supported by the negative value of the Entropy of Activation, $\Delta S^{\#}$. Precocene I additive was extracted from the plant Ageratum conyzoides using $CHCl_3$ as extracting solvent. Separation from other co-components was effected using Gas chromatography (GC) and isolation was by trapping in liquid N_2. Identification was by Mass Spectrometry (MS) using the fragmentation pattern: molecular ion mass M^+, m/z 190 (EIMS), base peak m/z 175 (EIMS), molecular formula $C_{12}H_{14}O_2$. These as well as IR spectrum subsequently obtained from the isolated compound were compared with those stored on the NIST database which also confirmed identification by supplying ^1H and ^{13}C NMR spectral characteristics.

INTRODUCTION

Vinylidine chloride, also referred to as 1,1-dichloroethylene (1,1-DCE) is a colourless liquid (b.p. 32.2°C), produced by dehydrochlorination of 1,1,2 – trichloroethane [$Cl_2CH.CH_2Cl$], a relatively unwanted by-product formed in the production of 1,1,1–trichloroethane and 1,2–dichloroethane. Conversion to 1,1–DCE involves a base – catalyzed reaction as shown in figure 1.

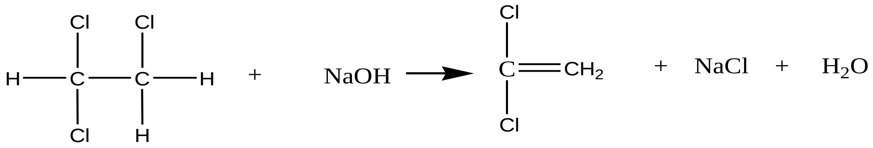

Fig. 1 1, 1, 2-trichloroethane 1, 1-dichloroethylene (Rossberg *et al*., 2006)

1,1–DCE is thus an important chemical substance which serves as a solvent as well as a monomer (Rossberg *et al*., 2006). 1,1–DCE is considered a potential occupational carcinogen by the US National Institute for Occupational Safety and Health (NIOSH Pocket Guide #0661). As with several other alkenes, 1,1–DCE can be polymerized to form the homopolymer poly(vinylidene chloride), PVDC, a form that is not commercially important because experimental data have been generated which demonstrated unequivocally that it undergoes what has been described as catastrophic decomposition at its melt temperature (above 125°C), producing HCl (Piringer and Baner, 2008). 1,1 – DCE as monomer forms copolymers with other monomers such as vinyl chloride and these copolymers are commercially viable (Paisley, 2007). Polyvinylidene chloride resins and coatings have reportedly been a part of flexible packaging for sometime. They are presented as possessing a unique combination of functional characteristics which have made them find numerous applications. According to Paisley, (2007) PVDC products are available in a variety of forms, such as aqueous dispersions or latex, for coating on a number of different film and paper substrates, extrudable powders for production of multilayer films and sheets, and soluble powders for solvent – based coatings. Unique properties possessed by PVDC copolymers enable their use for protection from moisture loss or gain, protection against oxidation of ingredients, prevention of oil and grease permeation, and excellent printing characteristics. Paisley, (2007) is also on record as asserting that PVDC – coated biaxially-oriented polypropylene (BOPP) films held, as at 2005, a 53% share of barrier film use in the USA. Such a figure does indicate the extensive use of PVDC products and therefore of their importance.

Again according to Paisley, (2007), during production of PVDC, other comonomers/additives are usually introduced, depending on the quality of copolymer desired. Thus, one comonomer/additive may be introduced to improve heat processability by decreasing melt temperature or to enable suitability of the polymer for film production, while another is introduced to provide some desired properties that would enhance polymer aesthetics, such as printability, adhesion, and / or thermoforming shrink flexibility. Thus several of these comonomers/additives may be added depending on desired effects. Additives are common in general polymer use. For instance, plasticizers are used to make PVC more flexible and therefore more easily processed. On the other hand, terpolymers are increasingly in use, and include the acrylonitrile - butadiene - styrene (ABS) system which is generally formulated as an unbranched, head - to - tail terpolymer in which the individual comonomers are statistically distributed (Lewis, 1993).

Copolymerization generally results in regular structure, namely, head-to-tail, unbranched and highly crystalline. This structure has been reported to be present in the ABS system (http://www.bing.com). Both PVDC and Poly (vinyl chloride) (PVC) have also been reported to have regular (linear) structure, the monomers being arranged mainly head-to-tail, which means that the single chloride atoms in vinyl chloride are on alternating carbon centres. The relative stereochemistry of these chloride centres in PVC is however random and therefore atactic but with some degree of syndiotacticity of the chloride which reportedly gives some degree of crystallinity to the PVC (Handbook of Plastics, 2002). Details of the microstructure of PVDC copolymers on the other hand are not yet available but it is reasonable to speculate that the two bulky chlorine atoms on one carbon atom joined to neighbouring carbon by a double bond in the monomer 1,1- DCE would provide sufficient steric hindrance to free rotation such that the relative stereochemistry in the resulting PVDC copolymer would not be random but would be predominantly syndiotactic leading to crystallinity to a greater degree. Thus PVDC copolymers are generally high density and high crystallinity with relatively few defect sites. High vinylidene chloride (VDC) content copolymers do however undergo thermally-induced degradative dehydrochlorination at process temperatures, and these degradations have been of interest ever since such copolymers came into use (Matheson and Boyer, 1952). The dehydrochlorination process has more recently come under close scrutiny, and has been studied using largely thermogravimetric techniques (Howell *et al.*, 2000).

Data generated in these thermogravimetric studies have been used to propose that only HCl is lost during degradation, and that weight loss of a PVDC copolymer sample directly indicates the extent of degradation which is usually represented in figure 2:

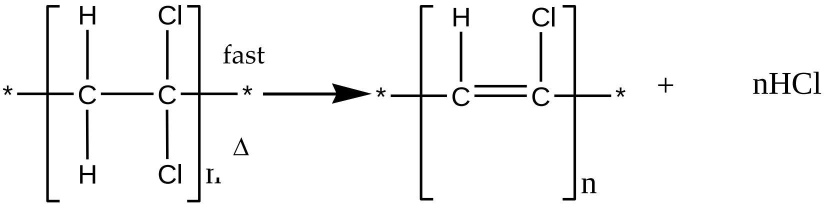

Figure 2

This is the primary degradation process which accompanies the processing of the polymer. The early stage of dehydrohalogenation is uncomplicated by interfering processes, and the only product observed by evolved gas analysis is hydrogen chloride (Howell and Rajaram, 1993).

Thermally-induced degradation of vinylidene chloride copolymers has resulted in considerable losses of polymer material during the production process. It has been proposed (Howell, 1987) as resulting from a process of heat absorption which homolyses an allylic carbon–chlorine bond, generating in the process a carbon-chlorine radical pair. The resulting hot chlorine atom subsequently abstracts an adjacent hydrogen atom to extend the unsaturation in the copolymer chain by one unit, thus propagating the dehydrochlorination down the copolymer chain. The mechanism is presented in Figure 3:

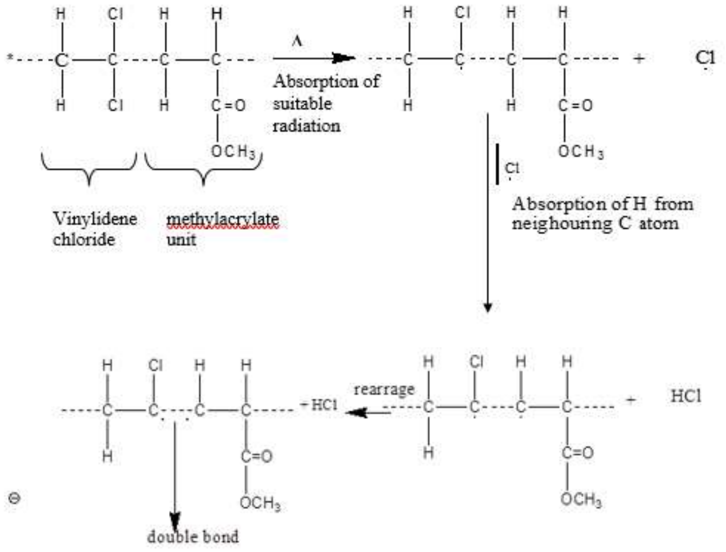

Figure 3: Mechanism for the thermal degradation of vinylidene chloride polymers, illustrating hydrogen chloride (HCl) elimination, double-bond formation, and subsequent molecular rearrangement processes (adapted from Howell & Liu, 1994).

Thus homolysis of the C – Cl bond sets up a conjugated polyene sequence, which resulted in the coloration of the copolymers, thereby making them unsuitable for use as films or inhibiting their use as barrier films in packaging applications for food and pharmaceuticals (The Dow Chemical Company, 2005). A second and more serious consequence of the degradation is the evolution of hydrogen chloride which reacts with the walls of process equipment, commonly stainless steel, at process temperatures, to form iron (III) chloride, a strong Lewis acid catalyst which can enhance the dehydrohalogenation process. A major research effort has thus been directed towards obviating this corrosion effect of evolved HCl (Howell and Liu, 1992), as well as avoidance of the regeneration of allylic dichloromethylene (= CCl_2) units in the copolymer main-chain which serve as initiation sites for the degradation and subsequent propagation of the dehydrochlorination reaction (Howell, 1987). Open literature on this research effort indicates that additives have continued to be introduced into the production mix which would remove hydrogen chloride as it is formed, to prevent the reaction with the walls of process equipment. Such additives have included basic substances, whether passive (for example, magnesium oxide) (Howell and Sastry, 1993) which negatively impact clarity of finished items, particularly for film production, or organic (pyridine derivatives) (Howell and Liu, 1992), which are reportedly too basic to absorb evolved hydrogen chloride. Some of these introduced additives have however reportedly also raised compatibility issues (passive bases), or have proved too basic (hindered amines) to function satisfactorily as stabilizing additives in the copolymers (Howell and Uhl, 2000; Howell and Rajaram, 1993). The search for a solution to the dehydrohalogenation process would appear to be a continuing one.

Thus these two problems, namely, thermal dehydrochlorination of PVDC copolymers at process temperatures (a production problem) and the degradation of production equipment by the resulting product of dehydrochlorination would need to be solved, using suitable comonomers and / or appropriate additives. A fundamental aim of further research in PVDC production is therefore to minimize this loss by formulating a product in such a way as to reduce to its barest minimum or eliminate completely this loss of material by dehydrochlorination. Recourse has been made in this direction to the formulation of copolymers with other monomers, such as acrylates and simple vinyl monomers, thus progressively reducing the amount of vinylidene chloride monomer and consequently making the resulting copolymers commercially viable (Wessling, 1977). A major research area in the dehydrochlorination process has been concerned with the effective scavenging of evolved HCl. Howell and Smith, (1988) have explained that these degradations stem from defect structures arising from internal unsaturation (allylic dichloromethylene groups) which serve as initiation sites, and efforts have been made to proffer solutions by seeking to prevent such polyene sequences from arising or building up. While passive bases such as magnesium oxide and tetrasodium pyrophosphate have been suggested and introduced into the polymer melt during processing to absorb evolved HCl and partially overcome this problem, (Howell and Rajaram, 1993), the suggestion has been made that the presence of inorganic bases would negatively impact clarity of finished items, particularly for film applications. Subsequently, organic bases have been sought which would be compatible with the polymer and also be capable of absorbing evolved HCl. Recent reports indicate that present practice involves the use of some hindered organic bases some of which are still considered too basic for the purpose and may aid in the production of vinylidene chloride – like entities (Howell and Uhl, 2000).

The challenge thus, still remains how best to obviate the degradation of PVDC copolymers without collateral damage to production equipment. A fact that has been established since the beginning of the systematic study of polymers is that to form part of a chain, an atom must clearly have a minimum valency of two. The oxygen atom in an oxygen heterocyclic organic substance satisfies this condition. The ability of an oxygen atom bound in this way to take part in interparticle interactions (H–bond formation is one of such interaction) also stands it in good stead in providing an extra point of attachment for possible adventitious chemical groups occurring along the chain when conditions for interaction exist and collision probabilities are appropriate. The possibility of incorporating the heterocycle into a copolymer chain, such as would be afforded by the presence of a double bond in the heterocycle, would also make polyene sequences that would occur from dehydrochlorination highly unlikely, as it would tend to separate the units that would favour such conjugation along the polymer chain. There is also a third possibility: a compound with easily detachable H-containing group(s) from which H-abstraction can occur.

The chromenes offer a typical example of the oxygen heterocycle proposed for study in this research. The double bond in the 3 : 4 position in these chromenes offers an extra point of attachment for any adventitious group or even for attachment to the main polymer chain. Also, H-abstraction from a chromene molecule would be quite competitive from any of its several H-atoms from the copolymer chain. Lastly, chromene derivatives, which include their chromene – 2 – one counter parts, have been associated with hypothermal characteristics (Soine, 1991) and may well play roles in mixtures or in combination that would affect heat absorption by components of the combination or mixtures. Bicyclic oxygen heterocycles that result from the fusion of benzene ring with 5, 6 – positions of either 2H– or 4H– pyran ring systems are designated as 2H - chromenes (2H - 1 - benzopyrans), and 4H – chromenes (4H – 1 – benzopyrans) (Ellis, 1977). The structures of these isomeric substances are shown in Figure 4.

I II

2H – Chromene 4H – Chromene

(2H – 1 – benzopyran) (4H – 1 – benzopyran)

Figure 4 Chromene Isomers

The pyran moiety in a 2H - benzopyran molecule has an active double bond in the 3 : 4 position which is retained in several of its derivatives, but which has been shown in recent microbial studies of the biotransformation of precocene II to lead to identifiable metabolites through the opening up of this 3:4 double bond (Sariaslani *et al*., 2014). Pratap and Ram, (2014) have reviewed the natural and synthetic chromenes with emphasis on their versatility in Organic Synthesis. The 3 : 4 double bond of several chromenes, both synthetic and natural, tend to be stable with respect to chemical reaction. 2H-Chromene derivatives have been described as natural products known to be widely distributed in nature and specifically present in the plant genus *Ageratum*, a precocious flowering plant (Burkill, 1985). Isolations of chromenes from this plant genus have been done from the species *Ageratum houstonianum* (Dike *et al*.,1991), from *Ageratum fastigiatum* (Del-Vechio *et al*., 2008), as well as from *Ageratum conyzoides* (Gonzalez *et al*., 1991). One of the most studied of the genus *Ageratum*, namely, *Ageratum conyzoides* (AC), has been known to contain several chromene derivatives in its phytochemistry and these derivatives include coumarins, as well as precocenes I, II and III. Both coumarins and precocenes are chromene derivatives with the difference that precocenes have dimethyl groups in the C – 2 position in place of a carbonyl group (ChEBI, 2016).

Aim and objectives of study:

The aim of this study is to assemble kinetic data on the effect of introducing an oxygen heterocycle into vinylidene chloride copolymer.

The Specific objectives are;

i to incorporate an appropriate oxygen heterocycle into vinylidene chloride copolymer with methyl acrylate comonomer and thereafter examine any compatibility issues visually or otherwise;

ii to obtain kinetic data after the incorporation of the oxygen heterocycle with a view to determining any changes in the rate of dehydrochlorination of the product of incorporation;

iii to seek to explain the rate data in terms of any derived thermodynamic parameters, relate these parameters to the dehydrohalogenation process, and propose a mechanism for the process, if possible.

Significance of Study

The result of this work will hopefully help:

to solve PVDC production problems arising from degradation of PVDC copolymers under production temperatures, namely, eliminate the corrosion effect of evolved HCl by preventing such degradation and / or eliminating the degradation altogether;

Provide an avenue for improved preservation of materials coated with PVDC copolymers whether paper food or pharmaceuticals, and this includes materials of construction.

METHOD

Incorporation of the additive, 7- methoxy - 2, 2-dimethyl -1-benzopyran (precocene 1), into a vinylidene chloride–methyl acrylate copolymer; Scanning of the resulting PVDC copolymer – plus – additive product using a Thermogravimetric Analyzer (TGA) for data on thermal dehydrochlorination following incorporation; Analyzing TGA data for relevant thermodynamic parameters and inferring possible action of the additive on the dehydrochlorination process.

Thermogravimetry (TG)

Thermogravimetry (TG) is the branch of thermal analysis which examines the mass change of a sample as a function of temperature (in the scanning mode) or as a function of time (in the isothermal mode) (Hatakeyama and Quinn, 1999). In this method of analysis, changes in the mass of sample are studied while the sample is subjected to a program in which changes in temperature affect the sample. Thermal changes which bring about changes in mass of a sample include desorption, absorption and decomposition. Thus volatile products or gaseous products lost during the reaction in thermoplastics, thermosets, composites, films and similar materials can be collected and analysed (Handbook of plastics, 2002). A thermogravimetric analyzer was used to record data on the kinetics of the dehydrochlorination of the vinylidene chloride – methylacrylate – additive copolymer after incorporation of the additive Much of the recent research on 1,1–DCE has been carried out in private (company) research laboratories, the most prominent of which is The Dow Chemical Company (2005). Only towards the end of the twentieth century have publications begun to appear in the open chemical literature on 1,1–DCE polymers, much of it published by Howell and his group.

Dow researchers made polyvinylidene chloride into a dark green film which acquired the name *Saran*^{TM} (Cole *et al.*, 2003). The uses of *Saran*^{TM} to include habitually and successfully spraying it on U.S. military fighter planes to guard against salty sea spray and thereby preventing degradation due to the rusting process. Car makers have also been reported as using some formulation of *Saran*^{TM} for upholstery. Another formulation was devised by Dow that was free of unpleasant odour and green colour, both characteristics arising from the thermally–induced degradation of PVDC. A very important specialty use of *Saran*^{TM} is as *Saran Wrap*, a plastic food wrap introduced in the nineteen fifties, and regarded as the most well-known household use of polyvinylidene chloride (Paisley, 2007).

Desirable properties of *Saran Wrap* include good thermal stability in use under ambient conditions, a superior chemical resistance to attack by alkalis and acids, insolubility in oil and most organic solvents, very low moisture regain, and imperviousness to mould, bacteria and insects. It is also used to produce a variety of fibre, both monofilament and multifilament (Cole *et al*., 2003). *Saran^{TM}* is however soluble in polar solvents such as methanol, acetone and ethylacetate. *Saran Wrap* has continued to be in use as food wrap, and such other persistent use as well as variety of use of PVDC has aroused interest in both the kinetics and mechanism of degradation of PVDC polymers to enable amelioration of loss at production temperatures (Strandburg *et al*., 1991).

Polyvinylidene chloride is currently being applied as water – based coating to other plastic films such as biaxially-oriented polypropylene (BOPP) and polyethylene terephthalate (PET) to increase the barrier properties of these films (Paisley, 2007) in their various applications. Some observations regarding the material reviewed in the literature is to that, no information in the literature regarding any published studies already carried out on the effect of any oxygen heterocycle on either polyvinylidene chloride (PVDC) copolymers or on any other polymeric material. The second observation which follows from the first is that the chemistry of the chromenes is yet to be fully explored.

Not much of the chemical reactions involving precocene I and II is available in the chemical literature. Pratap and Ram, (2014) suggested that the several chromenes and coumarins extracted from their natural sources and reviewed by them are resources for funtionalization and further exploitation. Thirdly the establishment and use of standards, controls or reference points serves as a useful aid in qualitative and quantitative science. It is so particularly in chemistry.

Thermogravimetric Analysis

The identified benzopyran derivative (precocene I) was incorporated as additive / comonomer into the vinylidene chloride copolymer by first heating the copolymer under reflux in methanol (CH_3OH) in a reaction vessel, (a three–necked Quickfit flask), until the previously weighed copolymer dissolved in the solvent. A Quickfit mercury–in–glass thermometer was inserted into the flask through one of the necks. The previously weighed derivative was then added dropwise through the second neck, while the central (third) neck was fitted with a water–cooled twelve – foot condenser for reflux. The addition lasted for about thirty minutes after which heating was continued for about 60 (sixty) more minutes. The mixture was cooled, the solvent evaporated after the condenser had been removed and the resulting white solid mass thereafter weighed and subjected to thermogravimetric treatment.

Analysis of the vinylidene chloride / methylacrlate / precocene I product by thermogravimetry

A weighed sample of the vinylidene chloride / methylacrlate / precocene I product was subjected to T G A at constant temperatures of 170 °C, 180°C, and 190°C. Analysis of the three curves as well as the T G A printout of masses were further carried out to derive kinetic as well as thermodynamic data using the equations:

$$\boldsymbol{k} = \mathbf{A}\,.\,e^{-Ea\,/RT} \tag{1a}$$

$$\mathrm{Ink} = \mathrm{InA}\ .\ \text{-}\mathrm{Ea}\ /\ \mathrm{RT} \tag{1b}$$

Using the plot Ink versus the reciprocal of T (various temperatures), the value of the slope is equal to –Ea / RT; Equation 1b is in the form $y = mx + b$ where $y = \mathrm{Ink}$; $m = \mathrm{Ea} / \mathrm{RT}$; $x = 1 / T$ and $b = \mathrm{InA}$.

$$\mathrm{Ink} = \Delta H / RT + \Delta S / R \tag{2}$$

where ΔG = change in Gibbs free energy

ΔH = change in enthalpy

ΔS = change in entropy.

RESULT AND DISCUSSION

The TGA trace obtained for the decomposition of the vinylidene chloride / methylacrylate (5 mole %) copolymer in the isothermal mode at a constant temperature of 170°C after incorporation of precocene additive is reproduced in Figure 5. The trace is a plot of mass loss (%) against time (t) in minutes. It thus enables the derivation of kinetic data with which the decomposition process can be studied and characterized.

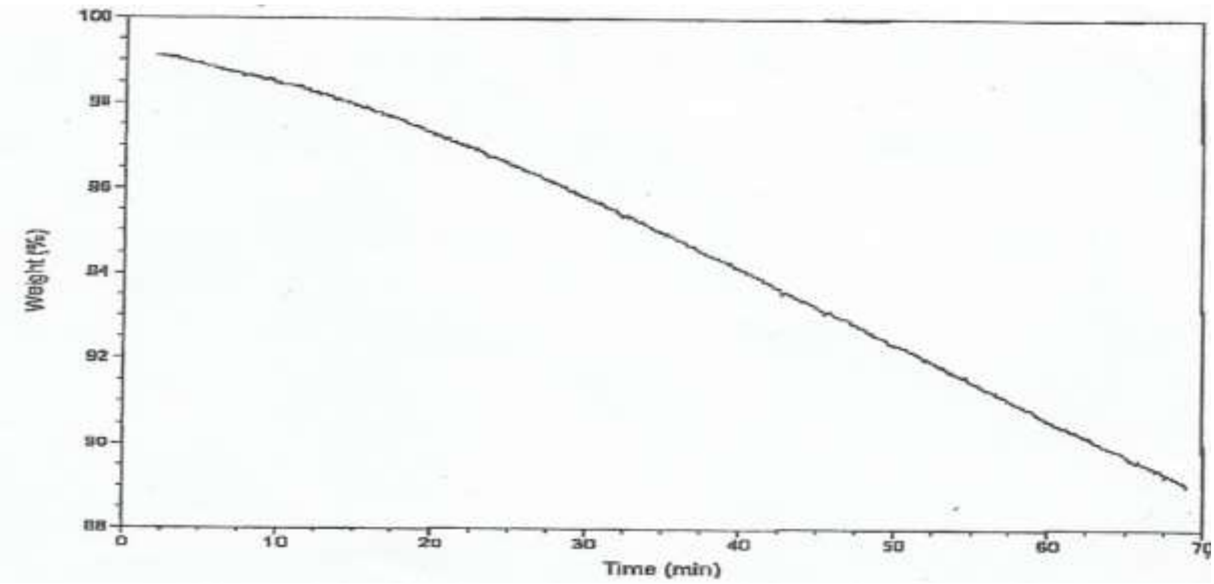

Figure 5 Thermogravimetric trace of the isothermal Degradation of Vinylidene Chloride / Methylacrylate (five mole per cent) / precocene I (0.1 mole %) additive at 170°C

Accordingly, two segments are clearly discernible in the TGA trace. The first segment extends from zero time to about ten (10) minutes and is characterized by a gentler slope. It is recognizable as the initiation segment of the decomposition process during which energy is absorbed to start the process. This first segment gradually progresses into the second segment which ranges from about twenty (20) minutes to about forty (40) minutes and constitutes the propagation stage of the decomposition process. This is the segment in which the energy absorbed in the first segment, during the initiation stage serve to overcome the energy barrier to the decomposition process.

Data from TGA Trace

Data derived from the TGA trace have been assembled in Table 1. They have been obtained as follow: The mass of copolymer / additive remaining undecomposed after time (t) is (Wt) was determined from the TGA trace. These values of Wt and their corresponding times were therefore tabulated in Table I and used to obtain the plot in Figure 6

Table 1 TGA Kinetic Data Extracted from the trace in Figure 6
W_o (mass of copolymer at time zero) = 0.99 W_∞ (mass of copolymer at infinite time) = 0.466

Time (min)	Time (s)	W_t	(W_∞ - W_o / W_∞ - W_t)	ln (W_∞ - W_o / W_∞ - W_t)
2.2	132	0.98	1.0194	0.0192
3.3	198	0.96	1.0607	0.0589
5.5	330	0.949	1.0849	0.0815
6.6	396	0.04	1.1055	0.1003
9.8	588	0.931	1.1269	0.1195
13	784	0.84	1.4010	0.3372
16.4	984	0.768	1.6795	0.5185
19.7	1182	0.706	2.1833	0.7808
23	1380	0.654	3.7872	1.0250
26	1560	0.609	3.6643	1.2986
29.5	1770	0.572	4.9434	1.5980
32.8	1968	0.538	7.2778	1.9848
36	2160	0.51	11.9091	2.4773
39	2340	0.486	26.2	3.2657
43.6	2616	0.466		

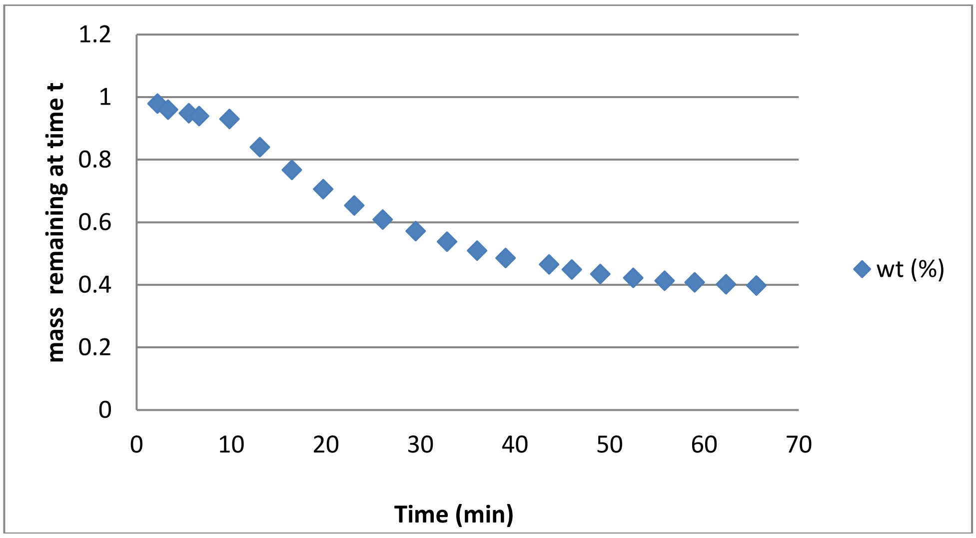

Figure 6 Plot of mass of Terpolymer remaining at time t (min) during degradation at 170°C

In the determination of these Wt values, cognizance was taken of the fact that both initiation and propagation phases of degradation can be deduced from the plot of mass remaining versus time shown in Figure 7. The initiation phase is however more easily recognized in the plot of ln $[(W_\infty - W_o) / (W_\infty - W_t)]$ versus time as shown in Figure 2, where:

W_∞	is mass of sample at infinite time (t_∞), taken as that mass of sample which remained after about one – third of the initial mass of vinylidene chloride component had been lost; this would correspond to the loss of about one mole of hydrogen chloride from each vinylidene chloride repeat unit in the polymer.
W_t	is the sample mass remaining at any time, t, during the experiment.
W_o	is the sample mass at time zero, t_o, taken as the time at which the first point on the graph was obtained.

The linearity of the plot in Figure 8 confirms the first order kinetic of the decomposition process, and results in the derivation of the rate constant for the initiation process. Figure 9 shows the corresponding plot of data obtained at long degradation times for the propagation process and gives the rate constant for the propagation of degradation. The linearity of both plots is in accord with results obtained from earlier studies of this degradation process such as those by Matheson and Boyer, (1952). Plots obtained in Figure 7 and Figure 8 were carried out using SCATTER in Microsoft Excel 2007. The value for the rate constant for the initiation of decomposition of vinylidene chloride / methyl acrylate / precocene I obtained from Figure 8 was 1.16 x 10^{-5} mol s^{-1}, while that for propagation obtained from Figure 9 was 2.32 x 10^{-5} mol s^{-1}.

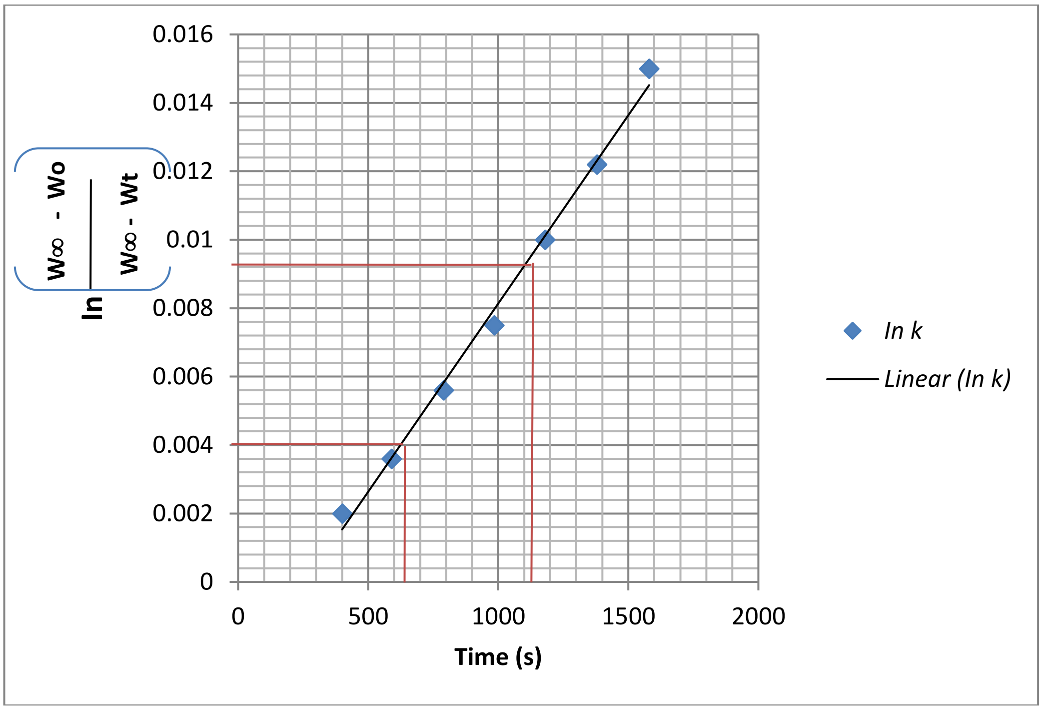

Figure 7 Plot of Data for the initiation of Degradation of PVDC / methyl acrylate copolymer / precocene I (0.1%) at 170°C

Slope = $\Delta y / \Delta x$
= (0.0092 - 0.004) / (1100 – 650)
= 0.0052 / 450
= 1.16 x 10^{-5}
y = mx + c = 1.16 x 10^{-5} x 1580 + c = 0.018328 + c = 0.015
c = 0.015 - 0.018328 = - 0.003328

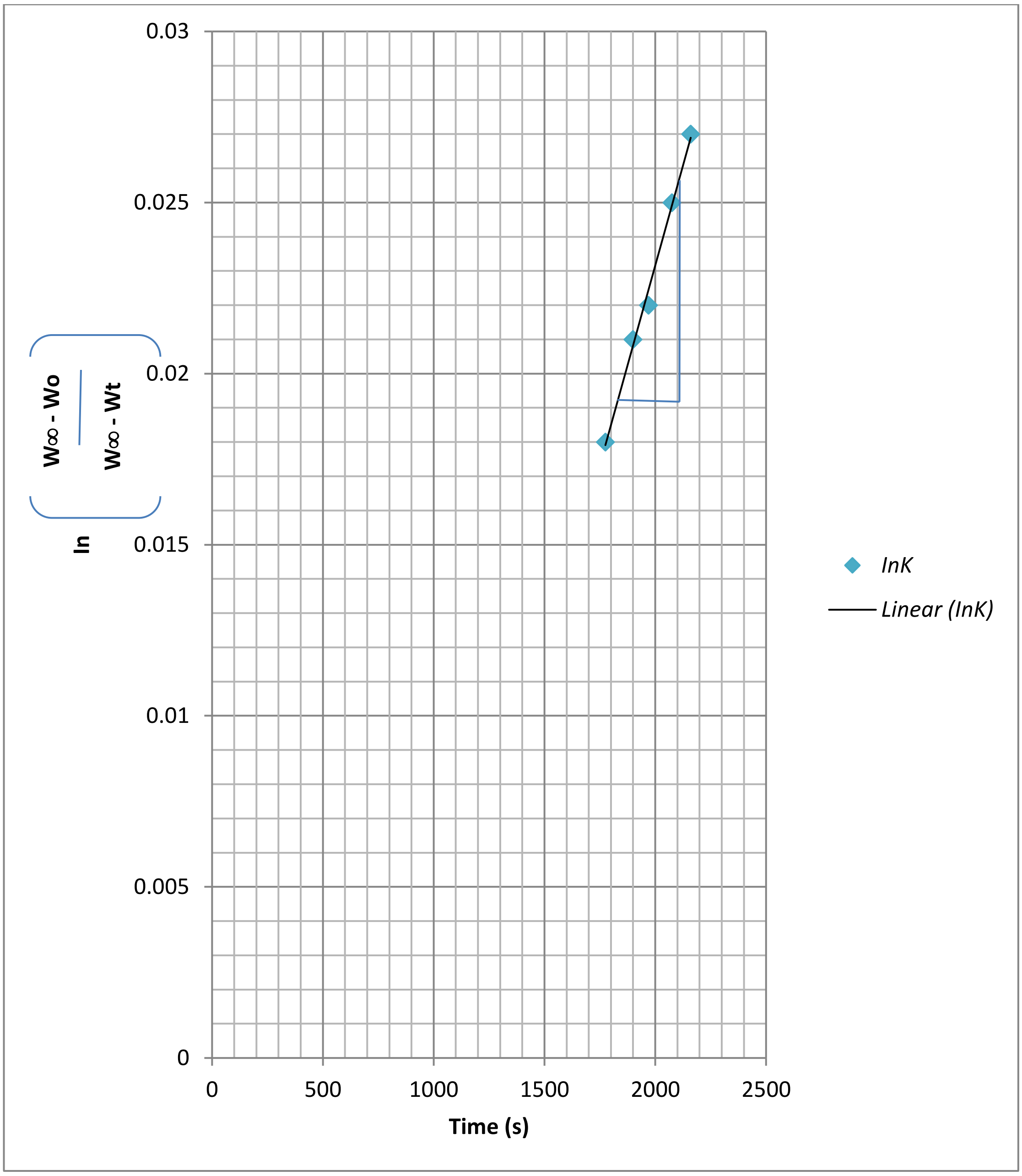

Figure 8 Plot of Data for the propagation of Degradation of PVDC / methyl acrylate copolymer / precocene I (0.1%) at 170°C

Slope = $\Delta y / \Delta x$ = (0.0255 - 0.019) / (2100 – 1820)
= 0.0065 / 280
= 2.32×10^{-5}
$y = mx + c$ = $2.32 \times 10^{-5} \times 2075 + c$ = $0.04814 + c = 0.025$
c = $0.025 - 0.04814 = -0.02314$

Temperature Variation Studies of the Thermal Decomposition

Rate Data were additionally obtained at two other temperatures, namely, 180°C and 190°C. This was to attempt the derivation of the thermodynamic data for the decomposition process. TGA traces obtained at each of three different temperatures, namely 170°C, 180°C and 190°C, were generally similar in form, showing areas of initiation and of propagation at each temperature.

Whereas, however, the initiation regime took relatively longer times with increase in temperature, the propagation sequence showed correspondingly shorter times. Similar treatment of the mass – loss – versus – time data for the three temperatures resulted in corresponding values of rate constants for both initiation and propagation sequences. These values have been assembled in Table 2. Table 2 also includes literature data from Howell *et al*., (2007) for corresponding data using vinylpyridine as additive, for the purpose of comparison.

The data from Howell *et al*. (2007) also presented in Table 2 are for vinylidene chloride / methyl acrylate (five percent) without additive and with 4-vinylpyridine (0.1 mole %) addition. Both sets of data result in higher values for the rate constant both for initiation of degradation and for propagation sequence, while data from the incorporation of precocene I additive give comparatively lower rate values for the initiation sequence, but almost equal values for the propagation sequence at two temperatures, namely, 170°C and 180°C. At 190°C, however, the change of value from 8.97 x 10^{-5} s^{-1} (without additive) and 9.28 x 10^{-5} s^{-1} with 0.1% 4 -vinylpyridine, to 7.6 x 10^{-5} s^{-1} (with precocene I additive) becomes quite considerable. These changes indicate a lowering of the tendency of this natural phenomenon to occur. This means in effect that the spontaneity of the system suffered a reversal at about 190°C and prompted further efforts to obtain thermodynamic parameters for the degradation reaction from these data.

Table 2 Values of Rate constant (k_i) for initiation and rate constant (k_p) for Propagation in the Thermal Degradation of the PVDC / methyl acrylate (5%) copolymer without and with additives (0.1%):

[additive] (mole %)	k_i x 10^5 (s^{-1})	k_p x 10^5 (s^{-1})	temperature (°C)
0	1.54	2.07	170∗
0	3.31	4.27	180∗
0	6.27	8.97	190∗
[4 – vinylpyridine]			
0.1	1.86	2.26	170∗
0.1	3.65	4.76	180∗
0.1	6.62	9.28	190∗
[precocene I]			
0.1	1.16	2.32	170
0.1	2.50	4.41	180
0.1	5.58	7.60	190

∗ Data taken from Howell *et al*., (2007)

Derivation of thermodynamic parameters for the Degradation reaction

Data from the temperature variation of the degradation reaction tabulated in Table 2 have been used to determine various possible parameters for the assessment of the tendency of a reaction such as the degradation reaction under consideration to move in a particular direction. Data obtained for 0.1 mole of additive (precocene I), to the copolymer have been used to prepare appropriate plots to further characterize the nature of the degradation. Accordingly, plots have been obtained of ln k versus [reciprocal of T (K)] for both the initiation, ln k_i, and the propagation, ln k_p, steps. Figure 9 yields the value of the Arrhenius energy E_a of activation for the initiation process. The slope of this plot is given by -16 x 10^3 and is equal to $-E_a/R$, where R is gas constant; E_a, activation energy, has the value 133 kJ mol^{-1} from this plot. The plot of ln k_p/T versus 1/T in Figure 11 yielded a value of

98.27 kJ mol^{-1} for the propagation process. The plot yielded the value of enthalpy of activation for propagation of dehydrochlorination. The slope gives the value of $\Delta H^{\#}$ from the relationship slope = -$\Delta H^{\#}/R$.

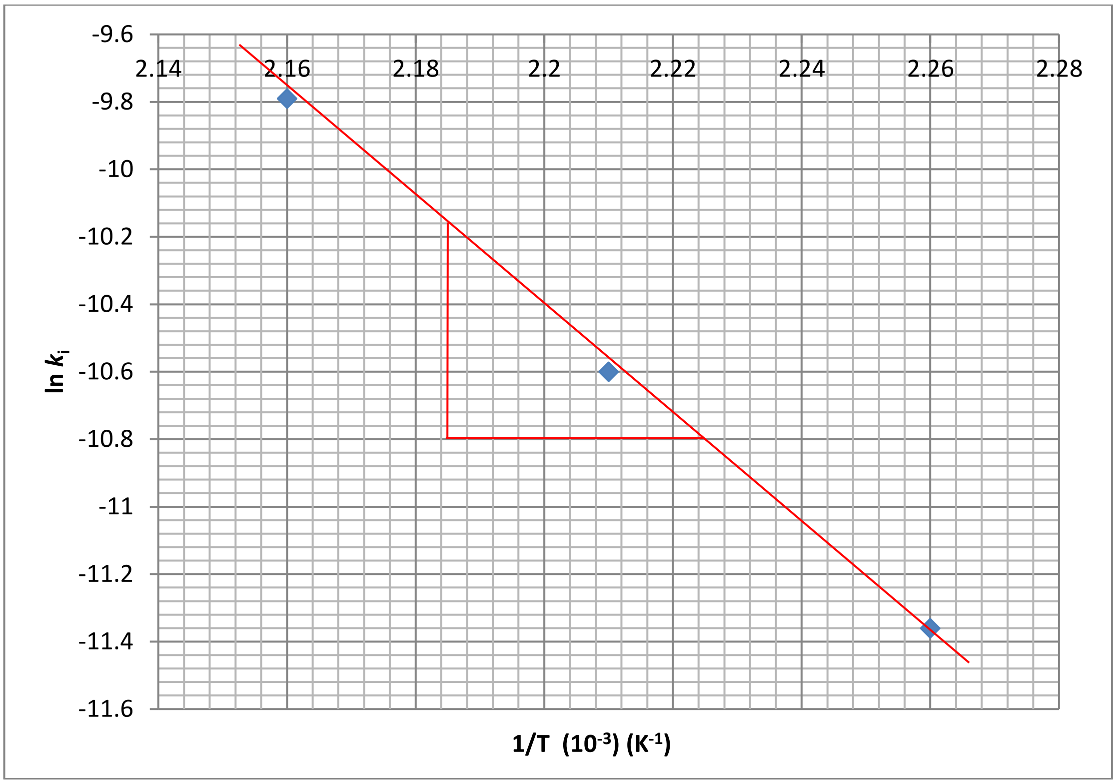

Figure 9Plot of ln k_i versus reciprocal of T for the initiation process.

Slope = $\Delta y / \Delta x$

= -10.16 - (-10.8) / (2.184–2.224) x 10^{-3} = 0.64 / -0.04 x 10^{-3}

= -16 x 10^{3} K

The value of the slope (m) is equal to $-E_a / R$, where R is a constant equal to 8.314 J/mol K^{-1}

-16 x 10^{3} = $-E_a / 8.314$

E_a = 16 x 10^{3} x 8.314 = 133024 J mol^{-1}

= 133 kJ mol^{-1}

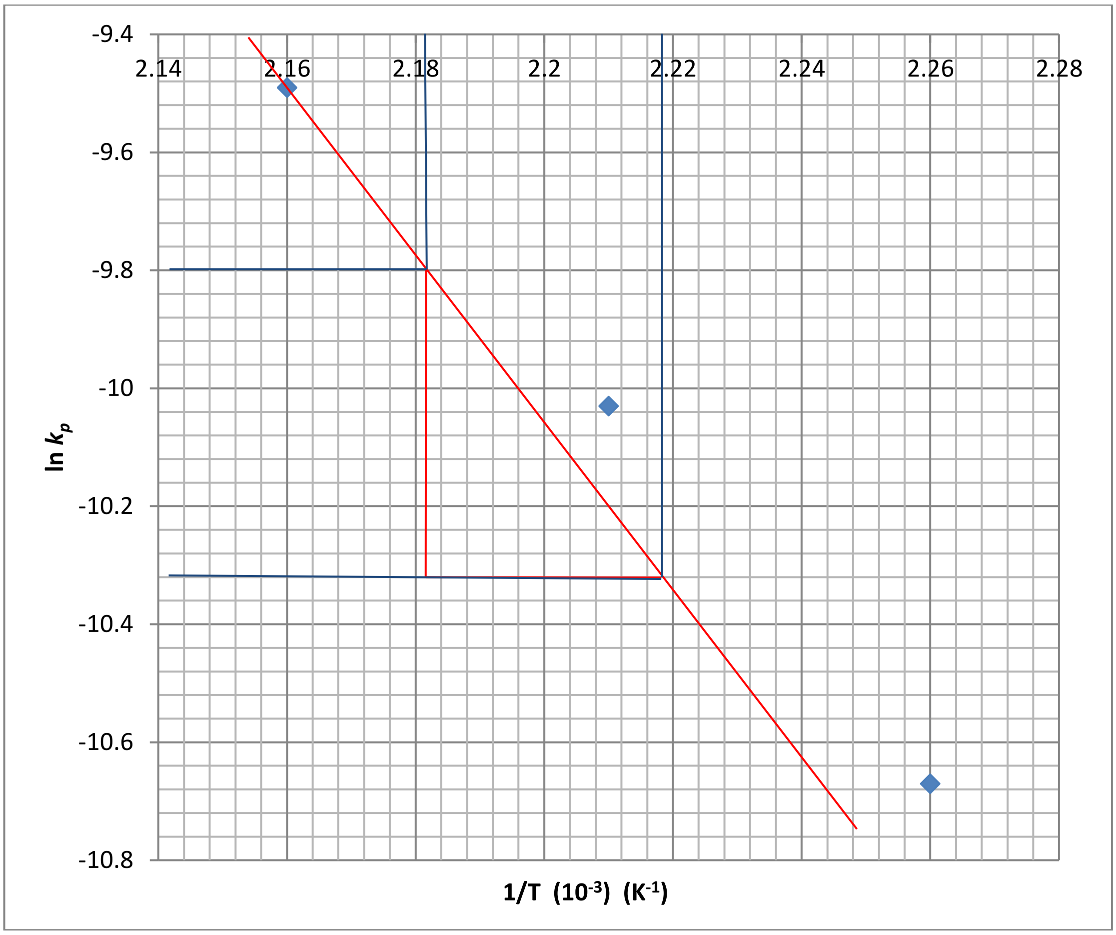

Figure 10 **Plot of ln k_p versus reciprocal of T for the activation enthalpy for the propagation process.**

Slope = $-9.8 - (-10.32) / (2.188 - 2.232) \times 10^{-3}$ = $0.52 / -0.044 \times 10^{-3}$
= -11818.18 = $-\Delta H^{\#}/R$
$\Delta H^{\#}$ = 11818.18×8.314 = 98256.36 J mol^{-1}
$\Delta H^{\#}$ = 98.26 kJ mol^{-1}

The theory of absolute rates, (Fried *et al.*, 1977; Isaacs, 1977) based on transition state concepts, gives an expression for the rate of a chemical reaction for constant pressure conditions, in terms of three fundamental constant, h (plank's constant), k (Boltzman constant) and R (gas constant):

$$k_{rate} = kT/h \ . \ e^{\Delta S\# / R} \ . \ e^{-\Delta H\# / RT}$$

This is a fundamental equation of activated complex theory, which can be written in the form:

$$\Delta S^{\#}/R = \ln k_{rate} + \Delta H^{\#}/R \ . \ 1/T + \text{constant}$$

This form enables the evaluation of the activation entropy ($\Delta S^{\#}$) from the experimental rate of propagation. It has been used to determine the value of $\Delta S^{\#}$ by plotting In (k_p/T) versus 1/T in Figure 12, and substituting appropriate values for the fundamental constants in the expression:

k, Boltzmann constant,	1.380×10^{-23} J K^{-1}
h, Planck constant,	6.626×10^{-34} J s

$\Delta H^{\#}$ (enthalpy of activation) is assumed to be temperature – invariant in the temperature range 170°C - 190°C. The plot in Figure 11 gives the value of the entropy of activation for the propagation of dehydrochlorination in the presence of precocene I at 190°C as -128 J $K^{-1}mol^{-1}$. Experimental values of Activation parameters for degradation have been assembled in Table 2 for comparison.

Table 3 Comparison of values of Activation parameters for the propagation step for the Thermal Degradation of Vinylidene Chloride / methyl acrylate copolymer at 190°C with and without additive.

Additive (mol%)	Enthalpy of Activation $\Delta H^{\#}$ (kJ mol^{-1})	Arrhenius Parameter E_a (kJ mol^{-1})	Entropy of Activation $\Delta S^{\#}$ (J K^{-1} mol^{-1})
None	121	125 (Source: Howell *et al.*, 2007)	-32
4 – Vinylpyridine (0.1)	116	120 (Source: Howell *et al.*, 2007)	-37
Precocene I (0.1)	94	133	-128
	(Source:	this work)	

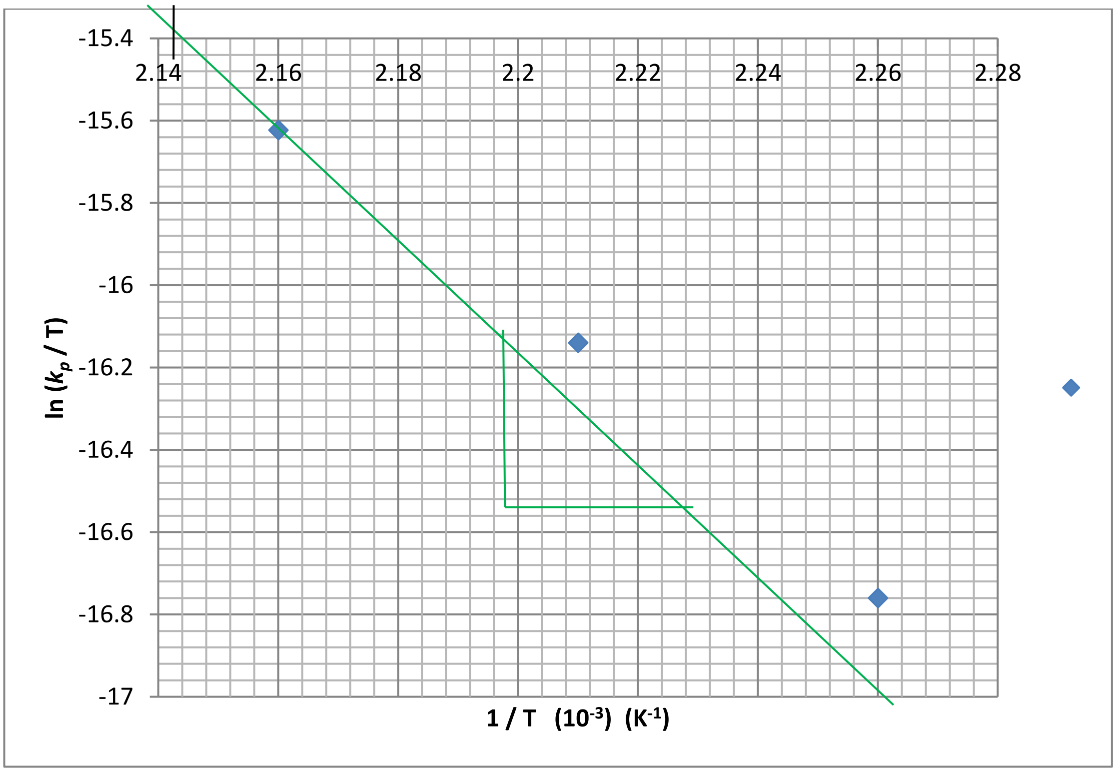

Figure 11 Plot of ln k_p / T versus reciprocal of T for the propagation process.

Slope = -16 – (- 16.36) / (2.196 – 2.228) X 10^{-3}
= 0.36 / -0.032 x 10^{-3}
= -11250

Slope = $-\Delta H^{\#} / R$
$\Delta H^{\#}$ = 8.314×11250 = 93532.5 J mol^{-1}
= 93.53 kJ mol^{-1}
$\Delta S^{\#}$ = Intercept x R = -15.38×8.314 = -127.87 J mol^{-1} K^{-1}
≈ -128 J mol^{-1} K^{-1}

The thermodynamic activation data in Table 2 may be used to analyse and evaluate the molecular configuration in the system. For instance, the value of the enthalpy of activation shows a steady decrease, from 121 kJ mol^{-1} with no additive to the copolymer to the lower value of 116 kJ mol^{-1} in the presence of 0.1 mole % 4 - vinylpyridine additive. The still much lower value of 94 kJ mol^{-1} in the presence of 0.1 mole % precocene I additive is indicative of a considerable change in the sum total of the energy required for breaking old bonds and forming new bonds in the system. This is reflected in the expression (1):

$$\Delta H = \Delta U + P\Delta V \quad (1)$$

Where U represents the internal energy of the system, and V represents the volume which, for a solid substance or even for some liquid systems at moderate pressures, is assumed constant. The $P\Delta V$ term thus vanishes, leaving only changes in internal energy. In the absence of additive, the bonds to be broken are the C – Cl bond of the vinylidene chloride entity (one bond), as well as the C – H bond of an sp^3 carbon in the copolymer chain. The bond to be formed is the product H – Cl bond. Approximate estimates of the values involved can be made using data from the Tables such as those compiled by Pauling, (1960). The bond energies of the C–Cl bond and of the C – H bond are given therein as 416 kJ mol^{-1}, and 328 kJ mol^{-1}, respectively. It would thus require at least a total of 744 kJ mol^{-1} to break both bonds. Formation of HCl by combination of H· radical and Cl· radical would result in the net introduction of the bond energy of HCl, namely, 432 kJ mol^{-1} to the system, resulting in net energy requirement of 312 kJ mol^{-1}. Thus ΔH is -312 kJ mol^{-1}. Approximately this latter value would also be the value of the enthalpy of activation with added 4 – vinylpyridine. This additive has been characterized as sufficiently basic to actively strip hydrogen chloride from vinylidene chloride units thereby generating initiation sites for the propagation of thermal degradation (Howell *et al.*, 2007).

Precocene I is neither acidic nor basic, and cannot therefore contribute to the promotion of H – abstraction which both acidic and basic substances contribute to. The situation with precocene I additive may thus be rationalized using bond energies and postulating that chromenes, especially precocene I, release the methyl radical (CH_3·) with relative ease into the system. The subsequent formation of CH_3Cl from the hot methyl radical (CH_3·) released with relative ease from precocene I and the equally hot chloride radical (Cl·) available form the vinylidene chloride unit of the copolymer chain would release at least the bond energy of the gaseous methyl chloride product into the system, giving a net value of the entropy of activation, $\Delta S^{\#}$. This value, - 128 J K^{-1} mol^{-1} in the presence of precocene I additive, is the highest of the three values quoted in the Table. The entropy is a parameter that comes into reckoning when stable states of molecular aggregations are considered. Thus the most stable state of any assemblage of molecules is said to be that which has the lowest accessible Gibbs free energy, G, which has the composite nature as in expression (2):

$$\Delta G = \Delta U + P\Delta V - T\Delta S \quad (2)$$

Expression (1) $\Delta U + P\Delta V = \Delta H$ has been shown here to result in the estimated value of –662 kJ mol^{-1}. The value estimated for $T\Delta S$ is about 60kJ mol^{-1} at T = 463 K.

Thus ΔG has the estimated value of –600 kJ mol^{-1}. This negative value predicts a reversal of the direction of reaction, and therefore the nondehydrochlorination direction.

It is therefore postulated that precocene I additive offers a more facile alternative to H – abstraction from the copolymer chain. This postulation is supported by the thermodynamic parameters obtained in these experiments and presented in Table 2. It is important here to observe that all the chromene derivatives identified in the GC–MS experiment had one characteristic in common. Their respective fragmentation patterns in the MS exhibited a relatively strong (M – 15) peak, an indication of the facile breaking of the CH_3 bond at the C-2 position in the chromene molecule. The energy requirement for the breaking of their C–CH_3 bond may be estimated at about 45 kJ mol^{-1} at 190 °C which is relatively low compared with other energy values already considered. The chromene derivatives, in which the carbonyl (C=O) group has replaced the C-2 methyl groups present in the chromenes, do not exhibit the (M – 15) ion peak.

CONCLUSION

A neutral oxygen heterocycle, precocene I, extracted from *Ageratum conyzoides* using Choroform as the extractant, was separated from other co-components using gas chromatography (GC). Isolation was by trapping in liquid nitrogen while identification was by mass spectrometry (MS) using the fragmentation pattern. The compound was incorporated into VDC methyl acrylate copolymer. The kinetic data obtained from the TGA analysis of the product of incorporation were analyzed graphically, and derived thermodynamic parameters indicated a more stable arrangement in the product of incorporation with lower degradation spontaneity when compared with known literature values without additives as well as with nitrogen bases. The chromatographic separation and isolation (GC) and structural elucidation (MS) indicated that AC contained terpenoids (chromenes and its derivatives). Precocene I an oxygen heterocyclic compound was extracted as a pure compound by the method of extraction used. The incorporated product which was examined visually had no compatibility issue. There was a reduction in the rate of dehydrochlorination of the product of incorporation. At 190°C, however, the change of value from 8.97 x 10^{-5} s^{-1} (without additive) and 9.28 x 10^{-5} s^{-1} with 0.1% 4 -vinylpyridine, to 7.6 x 10^{-5} s^{-1} (with precocene I additive) is quite considerable. These changes indicate a lowering of the tendency of this natural phenomenon to occur and the spontaneity of the system suffered a reversal at about 190°C

The natural tendency for the copolymer formed by vinylidene chloride / methylacrylate (5 mole per cent) towards dehydrochlorination has been reversed in the presence of 0.1 mole percent precocene I. The values of rate constants obtained in the kinetic experiment indicate this reversal. The negative value of the Gibbs energy for the dehydrochlorination process in the presence of precocene I additive is supportive of this reversal. The work reported here has introduced for the first time the use of a chromene to seek for the solution of the problem of degradation of polyvinylidene chloride copolymers or any other polymer. Data obtained from initial kinetic studies after the incorporation of precocene I into the polyvinylidene chloride / methyl acrylate copolymer have been shown to indicate appreciable reduction of degradation compared with results obtained other named additives. Both the rate constants of degradation as well as thermodynamic derived data support this view. In particular, the thermodynamic activation parameters point to a more ordered system in the presence of precocene I additive

Recommendation for Further Work

It is recommended that the dehydrochlorination process be further studied using the dynamic method in Thermogravimetry.

- Degradation processes may be studied in two ways, namely, degradation as a function of temperature (dynamic degradation), and degradation at constant temperature as a function of time (isothermal degradation).

- The dynamic method should hopefully yield complementary data on the stability of vinylidene chloride / methyl acrylate (5 mole percent) / precocene I (variable mole %), including the temperature of maximum dehydrochlorination. This would enable comparison of data obtained therefrom on the relative stabilities of the copolymer with respect to E2 elimination (H – abstraction) in vinylidene chloride / methyl acrylate copolymers as these eliminations concern the generation of initiation sites for the onset of further degradation. Therefore it is necessary to examine this dynamic method using an optimal temperature.
- It is further recommended that experimental data should be generated to determine the nature of the aggregation of the vinylidene chloride / methyl acrylate (5 mole %) copolymer in the presence of precocene I additive. This will enable the assessment of the preferred role played by the additive and therefore the extent of its involvement in bond formation.
- A corollary to the second recommendation above is that appropriate data ought to be generated on the relative presence of HCl and or CH_3Cl in mixtures of the copolymer and varied quantities of precocene I additive so as to determine the favoured product of dehydrochlorination.

REFERENCES

Burkill, H.M. (1985). The Useful Plants of West Tropical Africa, Kew: Royal Botanic Gardens. vol. I.

ChEBI (Chemical Entities of Biological Interest) @ www. obi.ac.uk/chebi/ last visited Jan. 21, 2016.

Cole, D. J., Browning, E., and Schroeder, F. E. H. (2003). Encyclopedia of Modern Everyday Inventions. Greenwood Publishing Group. pp 129 – 132.

Del – Vechio – Vierral, G., Orlando, V. S., Celia, H., and Marin, A. C. K. (2008). Antimicrobial activity of Essential oils of Ageratum fastigiatum by agar - diffusion method and minimal inhibitory concentration measurements. Rec. Nat. Prod. 3, 52.

Dike, S. Y., Merchant, J. R. and Sapre, N. Y. (1991). Precocene I and II: Isolation from Ageratum houstonianum and antihormonal activity in Sensitive insects. Tetrahedron, 47, 4775.

Ellis, G. P. (Editor). (1977). Chemistry of Heterocyclic Compounds. Vol. 31 Chromenes, Chromanones and Chromones. Wiley, New York. pp 10 – 120.

Gonzalez, A. G., Aguiar, Z. E., Grillo, T. A., Luis, J. G., Riviera, A., and Calle, J. (1991). Phytochemistry, Methoxy Flavones from Ageratum conyzoide. 30, 1269.

Handbook of Plastics, Elastomers and Composites (2002). 4th Ed. McGraw – Hill. Charles A. Harper (Editor - in - Chief) pp 205 – 208.

Hatakeyama, T. and Quinn, F. X. (1999). Thermal Analysis Fundamentals and Applications to Polymer Science: Thermogravimetry, 2nd Ed. John Wiley & Sons. pp 45 – 71.

Howell, B.A., (1987) Thermally – induced Degradation of Vinylidene Chloride Copolymers: Effect and Defect Structures. J. Polym. Sc., Polym. Chem. Ed., 25, 1681.

Howell, B.A. and Smith, P. B. (1988). Studies of the effects of internal unsaturation and the incidence of Defect Structures on the Dehydrochlorination of Polyvinylidene chloride copolymers. J. Polym. Sc., Polym. Chem. Ed. 26, 1287.

Howell, B.A., and Liu, H. (1992) Degradation of Vinylidene chloride / methyl Acrylate copolymer in the presence of organic nitrogen basesThermochim. Acta, 212, 1

Howell, B.A., and Sastry, B.B.S. (1993). Degradation of Vinylidene Chloride / Methyl Acrylate Copolymers in the presence of phosphine", PROCEEDINGS, 22nd North American Thermal Analysis Society Meeting, pp 122 – 127.

Howell, B.A. and Rajaram, C.V. (1993). Evolved Gas Analysis in the Thermal Degradation of Vinylidene Chloride Copolymer system, J. Therm. Anal., 40, 575.

Howell, B.A., and Liu, M. (1994). Thermogravimetric analysis of the Dehydrochlorination of Vinylidene Chloride Copolymers. Thermochim. Acta, 214, 169.

Howell, B.A., and Uhl, F. M. (2000). Degradation of Vinylidene Chloride / methyl Acrylate Copolymers: Deleterious Effects of Hindered amines. Thermochim. Acta, 357, 113.

Howell, B.A., Ahmed, Z. and Ahmed, S.I. (2000). Thermal Degradation of Vinylidene Chloride Copolymers studied under Thermal analysis. Thermochim. Acta, 357/8,10

http://www.bing.com (last visited 18/4/2014)

Ifiora U. F., 2019. Doctoral dissertation, Nnamdi Azikiwe University, Awka, Nigeria. Accessed at http://phd-dissertations.unizik.edu.ng 81231835800_126721663848.pdf on 13 May 2024.

Isaac, N. S. (1977). Liquid Phase High Pressure Chemistry, John Wiley & Sons. Chap. 4, pp 181 – 198.

Lewis R. S., (1993) Hawley's Condensed Chemical Dictionary Van Nostrand Reinhold, New York, 10th Ed. pp 70 – 75.

Matheson, L.A., and Boyer, B.F. (1952). The Thermal Stability of Vinylidene Chloride Copolymers at modest temperatures (120□ - 200□C). Ind. Eng. Chem., 44, 867

National Institute for Occupational Safety and Health (NIOSH). Pocket Guide to Chemical Hazards No.0661. Available at http://www.cdc.gov/niosh/npgd0661.html.

NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Linstrom, P. J. and Mallard W. G., (Eds.), available at http://webbook.nist.gov.

Paisley, Kirk (2007). PVDC: New Developments, New Opportunities PLACE Conference St. Louis Missouri, USA.

Piringer, O. G. and Baner, A. L. (2008) Plastic packaging: Interactions with Food and Pharmaceuticals. John Wiley □ Sons pp 40 – 45.

Pratap, R. and Ram, V. J.(2014). Natural and Synthetic Chromenes, Fused Chromenes, and Versatility of Chromenes in Organic Synthesis. Chem. Rev. 114, 10476.

Rossberg, M., Lendle, W., Pfeiderer, G., Togel, A., Dreher, E–L., Langer, E., Rassaerts, H., Kleinschmidt, P., Strack, H., Cook, R., Beck, U., Lipper, K–A., Torkelson, T. R., Loser, E., Beutel, K. K., and Mann, T. (2006). "Chlorinated Hydrocarbons" in Ullman's Encyclopedia of Industrial Chemistry, Wiley – VCH, Weinheim, Germany. pp 230 – 272.

Sariaslani, F. S., McGee, L. R., and Ovenall, D. W. (2014). Applied and Environmental Biology Microbial Transformation of Precocene II: Oidation Reaction by Streptomyces griseus. 53, 1780.

Soine, T. O. (1991). The Phytochemical and Pharmaceutical profile of 2H-pyran-2-one in isolated and fused ring derivatives. J. Pharm. Sci. 53, 231.

Strandburg, G., Delassus, P. T., and Howell, B. A. (1991) in S. J. Rich and J. H. Hotkiss (Eds.). Food and Packaging Interactions II. ACS Symposium Series, No. 473, Washington DC. Chap. 12, pp 195 – 227.

The Dow Chemical Company. (March, 2005) SARANTM: PVDC Resins and Films and the Environment. Form No. 190 – 0050 – 0305 SMG.

Wessling , R.A., (1977) "Polyvinylidene Chloride" Gordon and Breach, New York. pp 21 – 27.