

# **RESULTS AND DISCUSSION**

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### 3. RESULTS AND DISCUSSION

The choice of the inhibitors (paints, coats and corrosion inhibitors) against metal corrosion in many environments is based on two considerations: first it could be synthesized conveniently from relatively cheap raw materials; secondly, it contains the electron cloud on the aromatic ring or, the electronegative atoms such as nitrogen and oxygen in the relatively long chain compounds. Due to the presence of the –C=N group in the Schiff base molecules, they should be good corrosion inhibitors.

Compounds containing functional groups with heteroatoms, which can donate lone pair electrons, are found to be very efficient as inhibitors against metal corrosion in many environments. Many N-heterocyclic compounds with polar groups and/or  $\pi$  electrons are efficient corrosion inhibitors in acidic solutions. Organic molecules of this type can adsorb on the metal surface and form a bond between the N-electron pair and / or the  $\pi$  electron cloud and the metal, thereby reducing the corrosion in acidic solutions [200,201].

Schiff base inhibitors have been previously reported as effective corrosion inhibitors for steel, copper and aluminum [202,205]. These substances generally become effective by adsorption on the metal surface. The adsorbed species protect the metal from the aggressive medium, which causes decomposition of the metal. Adsorption depends on not only

the nature and charge of the metal but on the chemical structure of the inhibitor.

From the above reasons, this study aims to synthesize Schiff bases and their polymeric derivatives to modify their structures to epoxy resins to use them as organic coatings for steel.

### **3-1. SYNTHESIS OF POLYSCHIFF'S BASES EPOXY RESINS**

#### **3-1-1 Synthesis of Schiff's Base Polymer**

In the present investigation, some of Schiff's bases derived from condensation of hydroxyl aromatic aldehyde with aromatic diamine were prepared in the hope that some of these derivatives might show enhanced thermal stabilities. In this respect, we have prepared Schiff's bases monomers from condensation products of o- hydroxy, m- hydroxy and p- hydroxy benzaldehyde with both o- phenylenediamine and p- phenylenediamine as shown in formula I-VI. The chemical structures of the prepared Schiff's base monomers were represented in *Figure (3.1)*. In this series all derivatives were prepared and purified as illustrated in experimental section. The purity of the prepared Schiff's base monomers is very important because they act as start monomers for epoxy formation. Elemental analysis, reaction yield and physical properties such as melting points and color of the products were measured and listed in *Table (3.1)*. The good agreement

between the experimental and theoretical values of the C, H, N and O reveals that the method of synthesis and the purification of the products were performed successfully.

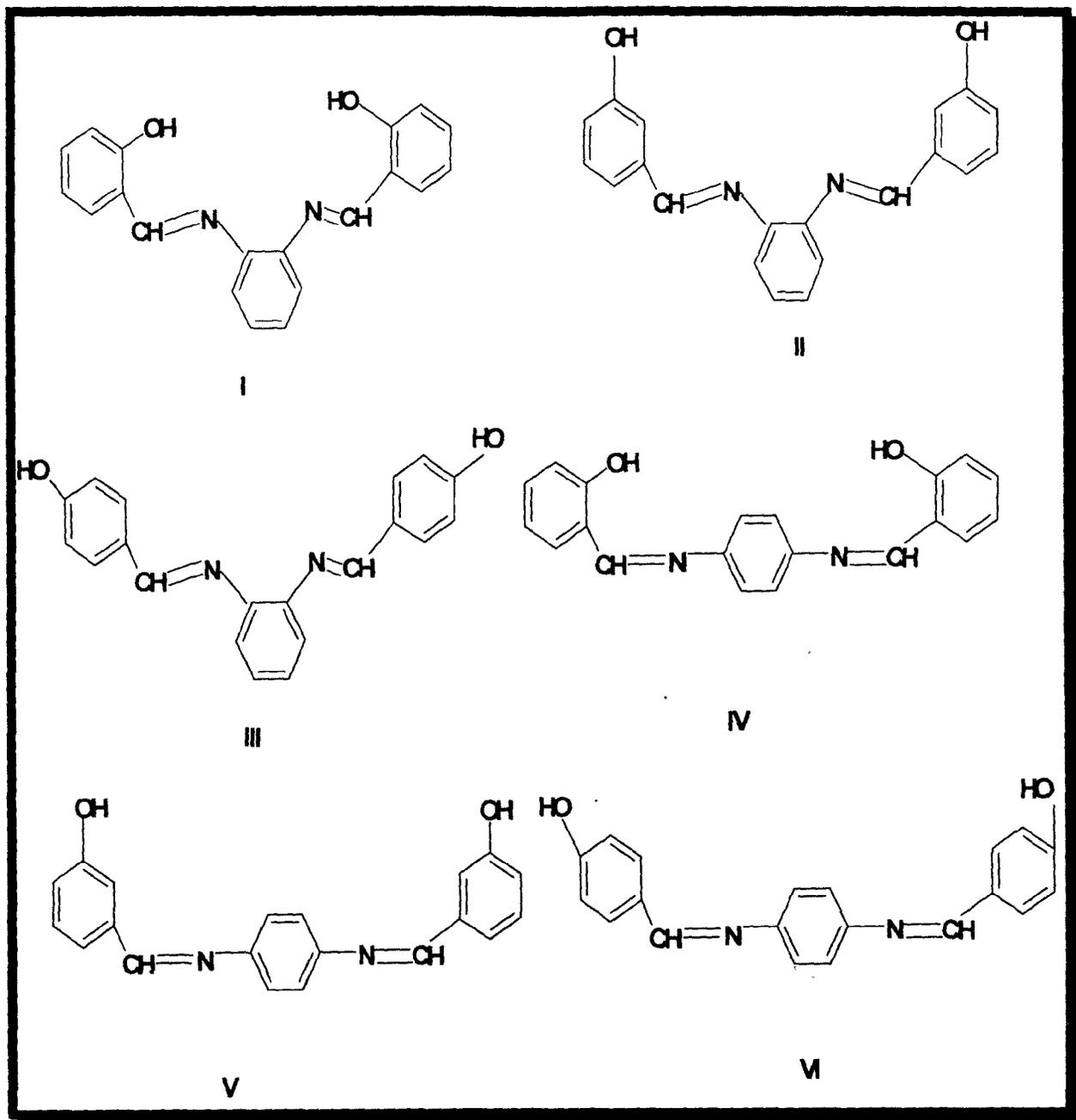
The structure of Schiff's base monomers was verified from their FTIR and  $^1\text{H}$ NMR spectroscopy. In this respect, IR spectra of the products derived from o-phenylenediamine were represented in *Figures (3.2 a-c)*. While IR spectra of compounds based on p-phenylenediamine were illustrated in *Figures (3.3 a-c)*. The  $^1\text{H}$ NMR spectra of some products were not represented here for brevity. The formation of azomethine nitrogen in all compounds was concluded due to the appearance of strong band at  $1600\text{ cm}^{-1}$ . This band indicates the formation of condensed products between aromatic aldehyde and diamine derivatives. The IR spectra of all derivatives show a strong broad band in the region  $3420 - 3200\text{ cm}^{-1}$  assigned to inter and intramolecular hydrogen bond phenolic OH stretching vibrations. The bands at  $1580$  and  $1555\text{ cm}^{-1}$  correspond to aromatic  $\gamma\text{ C}=\text{C}$  stretching vibrations. The medium intense band at  $1257\text{ cm}^{-1}$  may be assigned to  $\gamma\text{ C}-\text{O}$  phenolic stretching. The disappearance of strong bands of aldehyde groups at  $2750$  and  $1700\text{ cm}^{-1}$  which assigned for CH and C=O stretching of aldehyde groups indicates the formation Schiff's base monomer with high purity grade.

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The  $^1\text{H}$ NMR spectra of Schiff's base monomers show a complicated aromatic proton multiplet (7.8 - 6 ppm) and an imino proton singlet at 8.3 ppm downfield from the usual aromatic proton region. The strong band of chemical shift ( $\delta$ ) 10.5 ppm is assigned to OH aromatic of Schiff bases. The spectral data for all derivatives are illustrated in brief *Table*

(3.2). Polymeric Schiff's base is derived from reaction of 5, 5'-methylene -bis-salicylaldehyde and o- phenylene diamine.

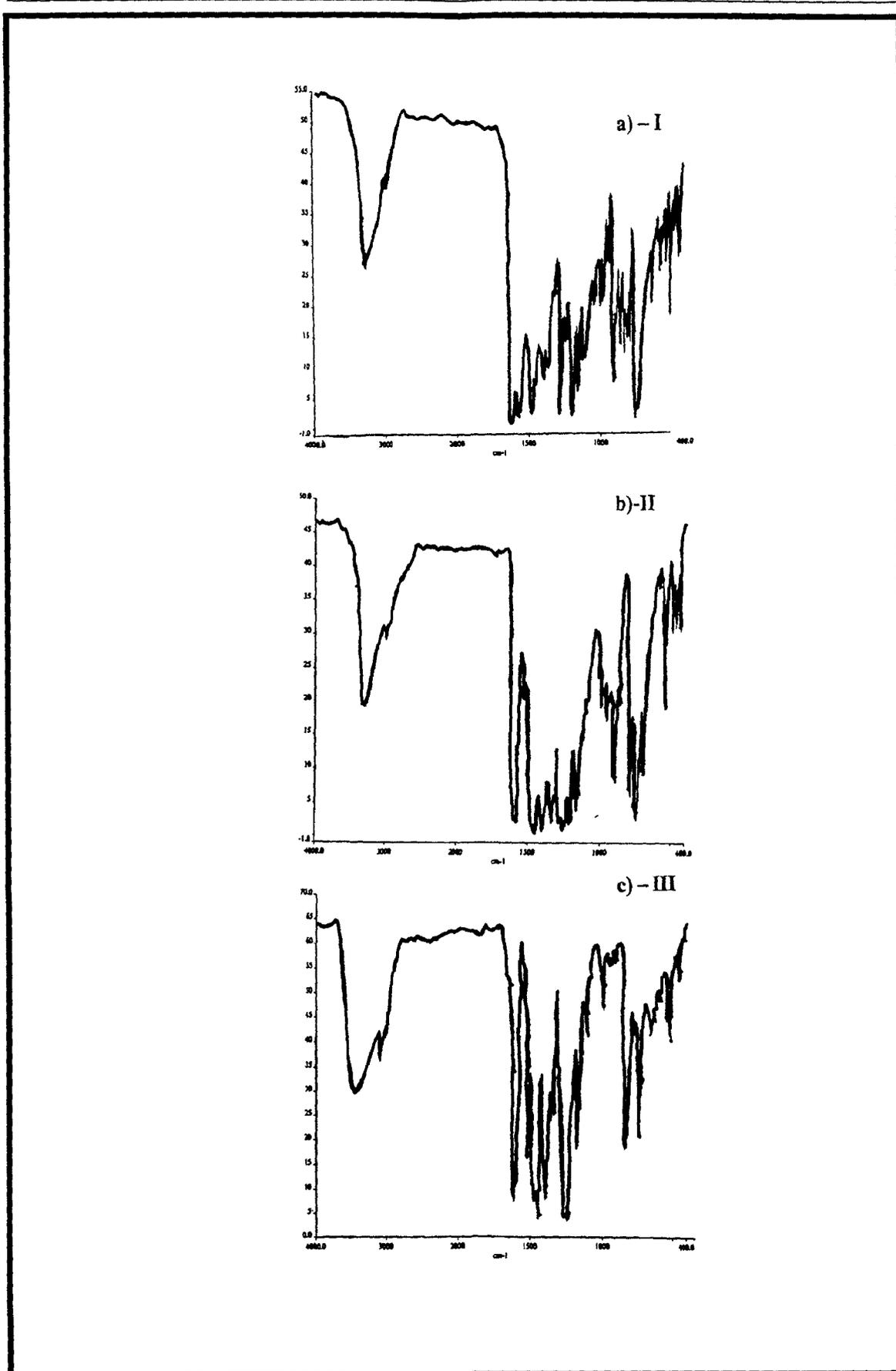
The monomeric dialdehyde, 5, 5'-methylene -bis-salicylaldehyde was obtained in 48 % yield by treating salicylaldehyde with trioxane and sulphuric acid in acetic acid solution, a procedure that is analogous to that used by Marvel [206]. The yield of 5, 5'-methylene -bis-salicylaldehyde is related to the amount of sulphuric acid catalyst used and this relationship can be rationalized on the assumption that the salicylaldehyde to formaldehyde ratio must be very high in order that dialdehyde be formed rather than a polymeric product. It has been shown that the rate of acid catalyzed depolymerization of trioxane to formaldehyde bears a close correlation to the acid concentration of the reaction medium [207]. This low acid concentration helps keep the ratio of salicylaldehyde to formaldehyde favorable for the preparation of dialdehyde.



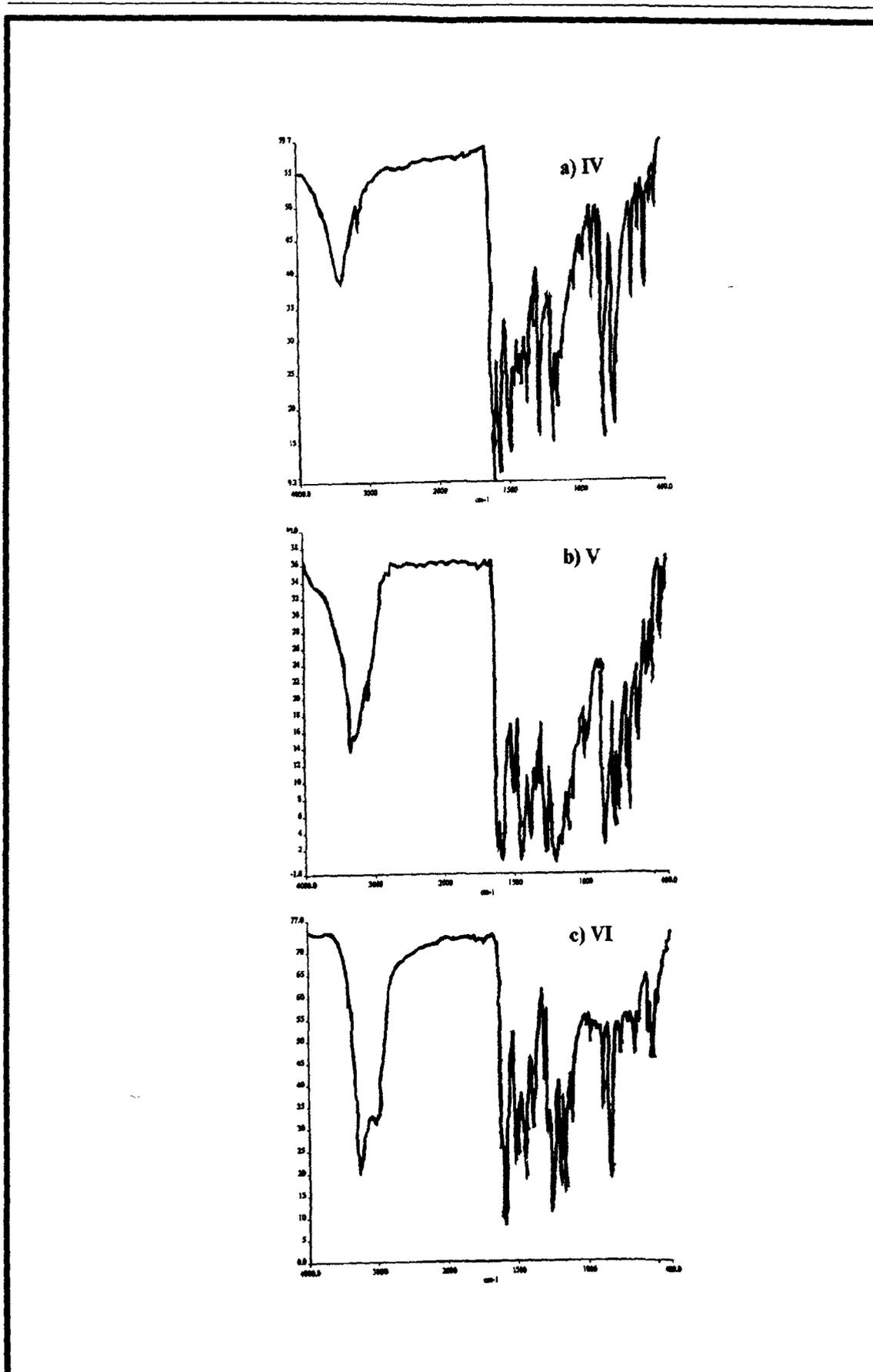
**Figure (3.1): Chemical Structure of the Prepared Schiff's Base Monomers.**

**Table (3.1): Physico-Chemical Properties of Schiff base monomers.**

Characteristics		I	II	III	IV	V	VI
Melting point (°C)		163.5	143.3	189.5	175.2	159.4	183.1
Yield (%)		61	56	63	95	89	87
<b>Elemental analysis</b>							
C %	(calc.)	75.95	75.95	75.95	75.95	75.95	75.95
	(found)	75.84	75.98	75.94	75.96	75.92	75.95
H %	(calc.)	5.06	5.06	5.06	5.06	5.06	5.06
	(found)	4.98	5.04	5.07	5.06	5.09	5.06
N %	(calc.)	8.86	8.86	8.86	8.86	8.86	8.86
	(found)	8.91	8.84	8.86	8.84	8.84	8.87
O %	(calc.)	10.13	10.13	10.13	10.13	10.13	10.13
	(found)	10.27	10.14	10.13	10.13	10.15	10.12
Color		Pale Yellow	Light Grey	Grey	Orange	Green	Dark Yellow
Hydroxyl values mg KOH/g		355.06	354.81	355.10	356.12	354.93	355.11



**Figures (3.2): IR Spectra of Schiff's Base a) I, b)II and c) III Monomers.**



**Figures (3.3): IR Spectra of Schiff's Base a) IV, b) V and c) VI Monomers.**

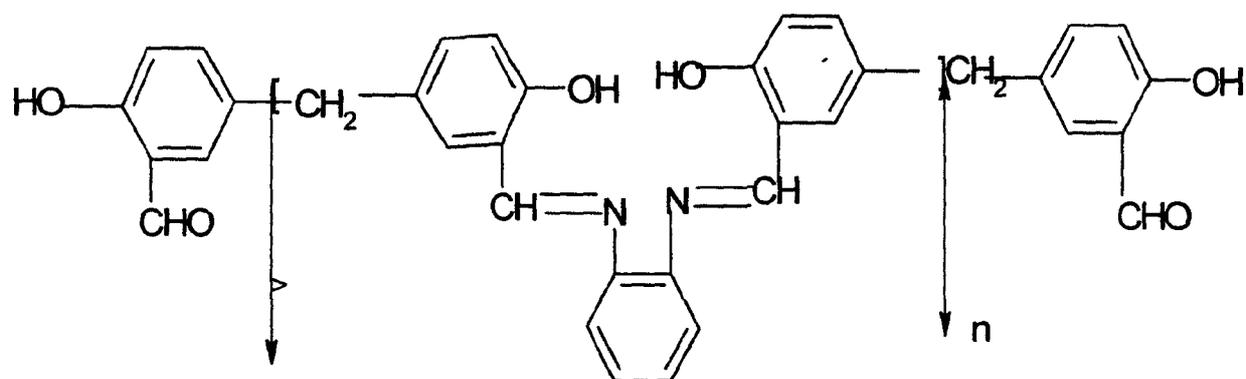
**Table (3.2): Spectral Data of Schiff Base Monomers.**

Assignment	I	II	III	IV	V	VI
<b>Infrared Data (cm<sup>-1</sup>)</b>						
<b>O-H</b>	3350	3400	3350	3400	3450	3350
<b>C=N</b>	1610	1600	1615	1605	1610	1615
<b>Ph-O</b>	1275	1320	1250	1270	1250	1280
<b><sup>1</sup>HNMR Chemical Shift (ppm)</b>						
<b>O-H</b>	10.9	10.8	10.3	10.2	10.3	10.1
<b>H-C=N</b>	8.3	8.1	8.5	8.1	8.0	8.2
<b>Aromatic H</b>	7.8- 7.2 <sup>a</sup>					
	7.1- 6.5 <sup>b</sup>					

<sup>a</sup> Aromatic protons downfield shifted due to the hydroxyl groups

<sup>b</sup> Aromatic protons upfield shifted

The dialdehyde was converted to a polymeric Schiff base by heating it with *o*-phenylenediamine in acetic acid solution. This gave a 88% yield of a yellow product (VII). The molecular weight of the produced polymer, determined by GPC technique, is determined as  $14,860 \text{ g mol}^{-1}$ . The molecular weight of the polymers indicates that approximately 45 monomer units were linked together. The calculated elemental percentages of C, H, N and O as  $(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2)_{45}$  are 76.85, 4.88, 8.55 and 9.72, respectively. The good agreement between the experimental and theoretical values of the C, H, N and O reveals that 45 monomer units are linked to form Schiff base polymer VII.



VII

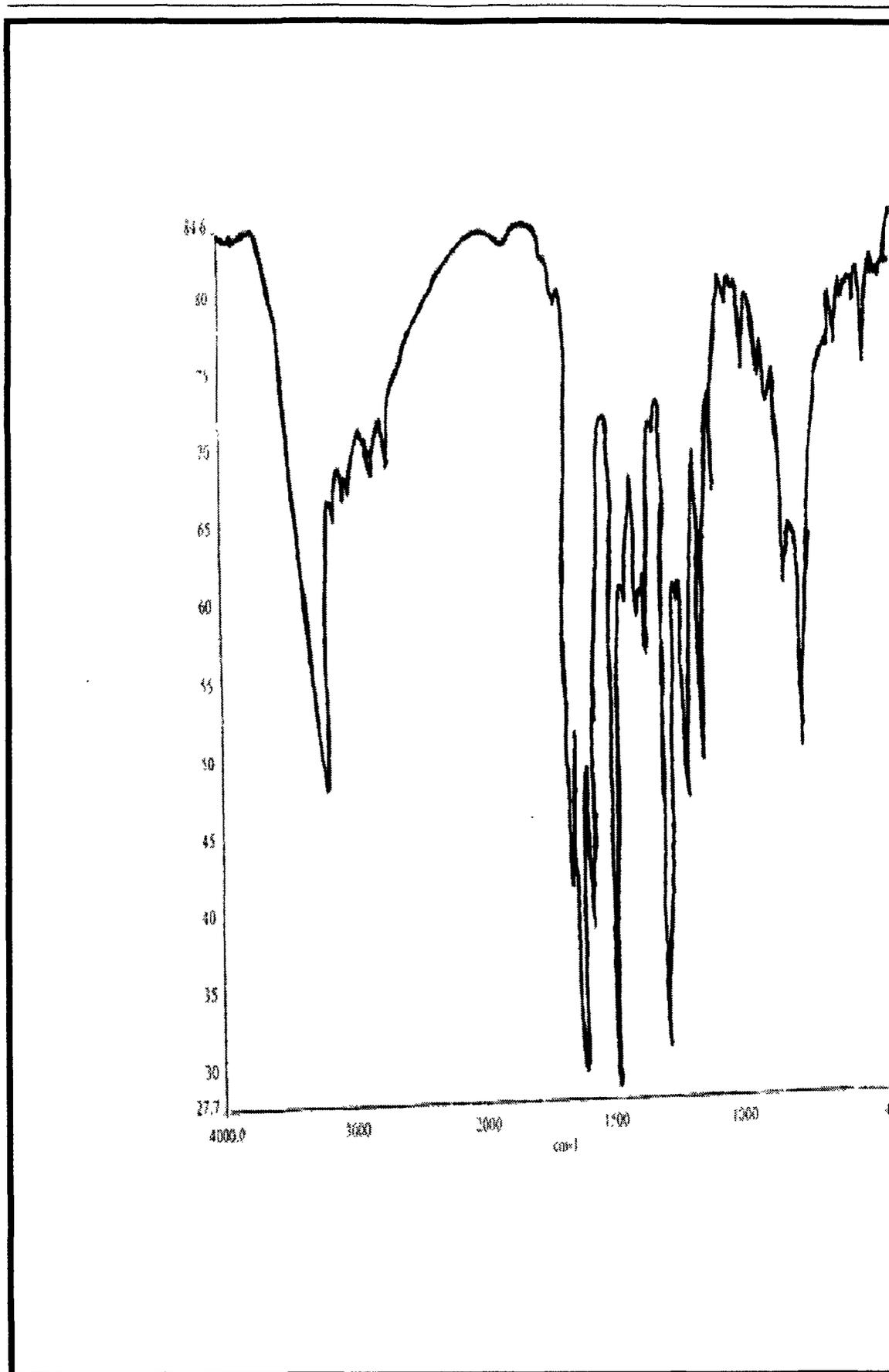
The prepared polymer was characterized by IR and  $^1\text{H}$ NMR for the sake of confirming its structure. The IR spectrum, **Figure (3.4)** shows a strong broad band in the region 3420-3200  $\text{cm}^{-1}$  assigned to ph-o stretching vibrations. The strong

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band at  $1615\text{ cm}^{-1}$  is assigned for  $\gamma\text{ C=N}$  stretching vibrations.

The two strong bands at  $850$  and  $805\text{ cm}^{-1}$  may be attributed to out of plan bending of aromatic rings and indicates the formation of 1,2,4- trisubstituted rings. The appearance of the bands at  $2950$  and  $2875\text{ cm}^{-1}$ , characteristic for  $\gamma\text{ C-H}$  aliphatic, confirms the formation of  $\text{CH}_2$  aliphatic groups as represented in the structure VII. The appearance of band at  $2650$  and  $1700\text{ cm}^{-1}$  indicates the formation of aldehyde end group units as represented in structure VII.

The  $^1\text{H}$ NMR spectrum of VII is not represented for brevity. The chemical structure of Schiff's base polymer VII is resemble to structure I but the appearance of new singlet strong band at  $2.1\text{ ppm}$  indicates the formation of  $\text{CH}_2$  links between monomer units. On the other hand the appearance of band at  $9.5\text{ ppm}$  indicates the formation of aldehyde end group as represented in structure VII.



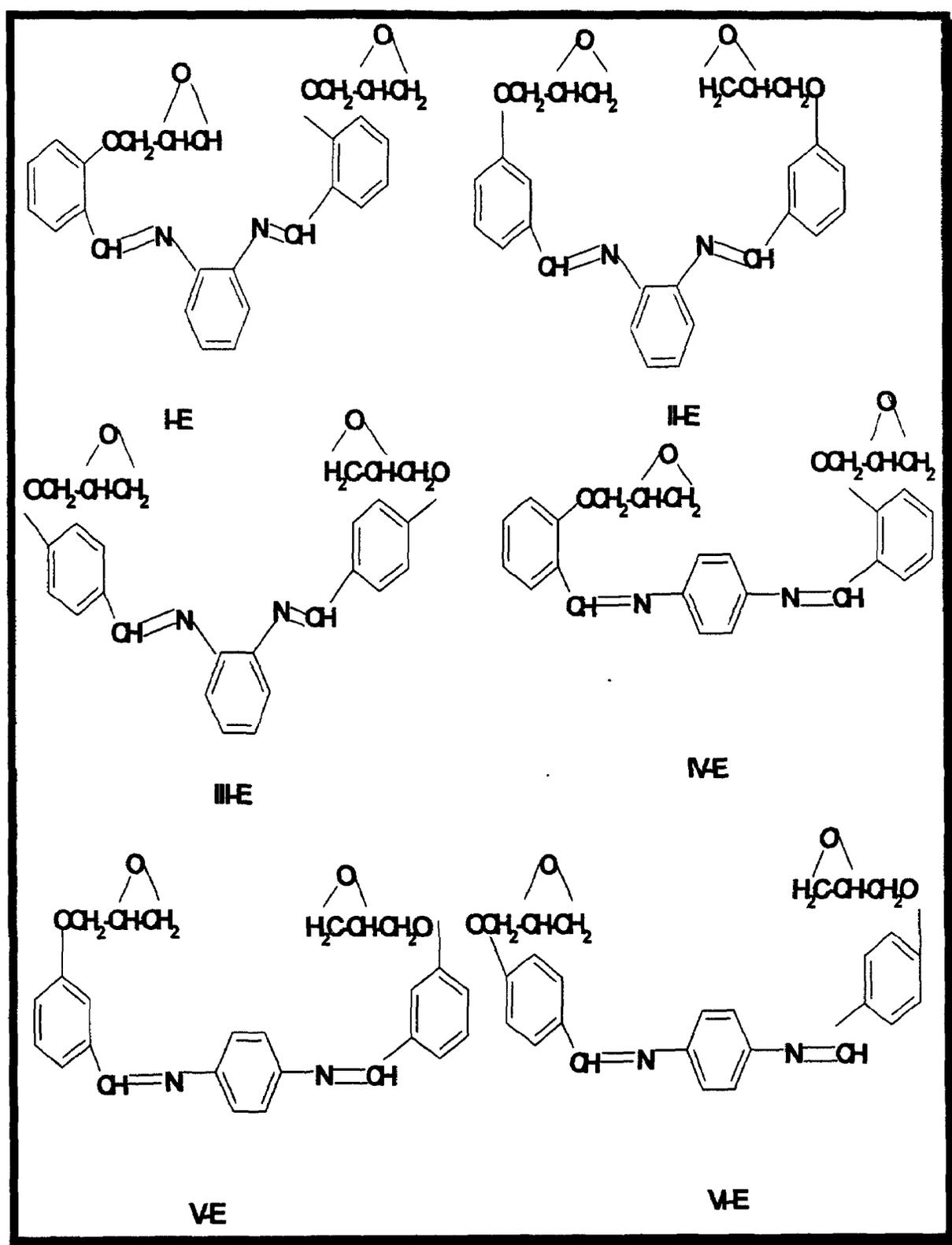
**Figures (3.4): IR Spectrum of Schiff's Base Polymer VII.**

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### 3-1-2. Synthesis of Schiff's Base Epoxy Resins

Epoxy binders are prepared by the reaction of compounds containing an active hydrogen group with epichlorohydrin (EC) followed by dehydrohalogenation in presence of NaOH as a catalyst. From the previous section, it was proved that the chemical structures of Schiff base monomers I –VI have free two hydroxyl groups that can be reacted with EC. It was also noted that multifunctional hydroxyl derivatives of Schiff base polymer VII can be obtained. In the present sections the ability to prepare epoxy resins from the prepared Schiff base derivatives will be discussed.

Glycidyl ether of Schiff base derivatives were prepared through reaction of their hydroxyl group with EC in presence (50 % by weight) NaOH as catalyst. The produced glycidylethers with Schiff base monomers have designated here as E-I to E-VI. The chemical structure of Schiff base epoxy derivatives is illustrated in *Figure (3.5)*. The properties of the produced liquid epoxy binders were listed in *Table (3.3)*. The liquid epoxy resins were mainly characterized by epoxy equivalent weight (EEW), epoxy content (EC), density and molecular weight. It was noted that the epoxide functionality of E-I to E-VI epoxy is 1.8 (which determined from values of MWT and EEW).



**Figure (3.5): Chemical Structure of the Prepared Schiff's Base Epoxy Resins**

**Table (3.3): Characteristics of Epoxy Resins Produced from Schiff base monomers.**

Characteristics	E-I	E-II	E-III	E-IV	E-V	E-IV	
Boiling point (°C)	250	180	220	180	160	220	
Yield (%)	75.2	67.3	84.5	63.4	68.5	89.2	
Color	13	14	11	17	18	16	
<b>Elemental analysis</b>							
C %	(calc.)	72.90	72.90	72.90	72.90	72.90	72.90
	(found)	72.8	73.00	72.7	72.8	72.7	72.8
H %	(calc.)	5.61	5.61	5.61	5.61	5.61	5.61
	(found)	5.2	5.5	5.8	5.4	5.6	5.5
N %	(calc.)	6.54	6.54	6.54	6.54	6.54	6.54
	(found)	6.5	6.4	6.6	6.5	6.6	6.6
O %	(calc.)	14.95	14.95	14.95	14.95	14.95	14.95
	(found)	15.5	15.1	14.9	15.3	15.1	15.1
Mn *	435	428	432	435	433	428	
Density (g/cm <sup>3</sup> )	1.18	1.07	1.02	1.11	1.05	1.14	
Epoxy equivalent weight	237.78	237.13	237.96	237.45	238.05	239.34	
Epoxy functionalities	1.8	1.8	1.8	1.8	1.8	1.8	

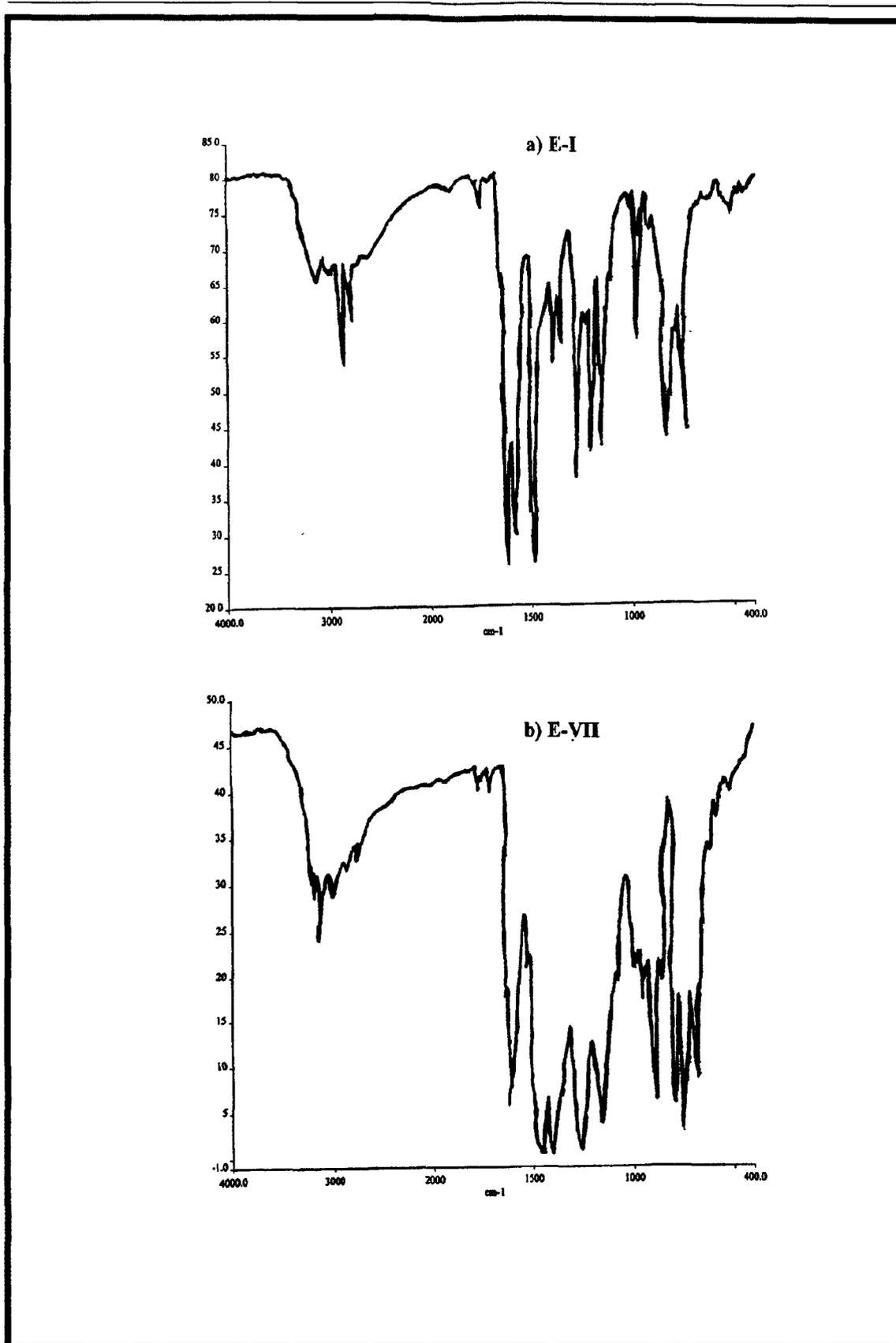
Mn\* is the molecular weight Determined by GPC techniques

This indicates that difunctional hydroxyl groups were reacted with EC. The lower values of MWT for the prepared epoxy indicate that side reaction can be occurred [208]. This side reaction is based on the formation of terminal glycol groups due to hydrolysis of epoxy end groups. The presence of terminal glycol groups can give lower viscosity resin [209].

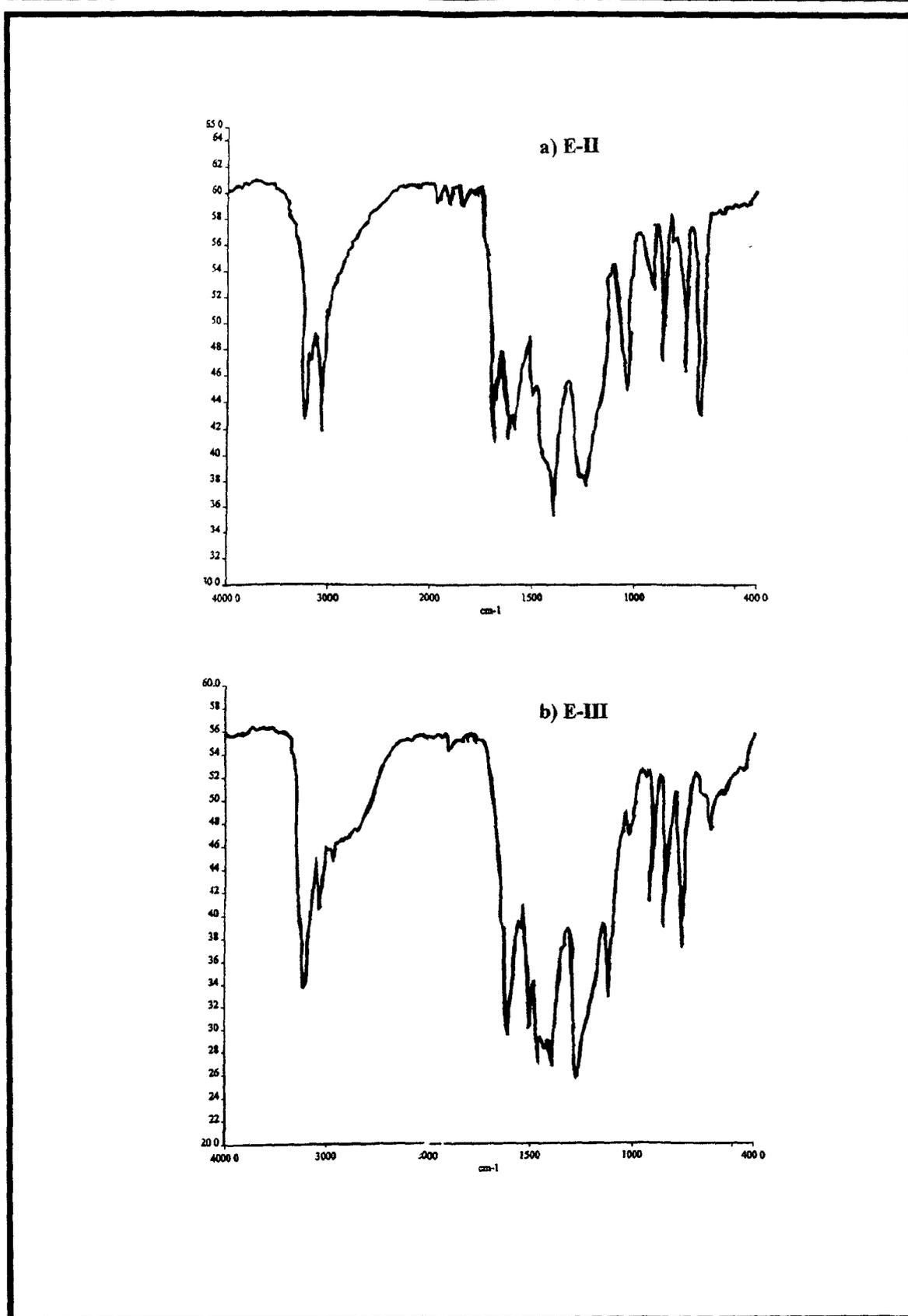
The proposed structures of E-I to E-VI were elucidated by using IR and  $^1\text{H}$ NMR spectroscopy. IR spectra of E-I, E-II –E-III and E-IV –E-VI were represented in *Figures 3.6a, 3.7 a-b and 3.8 a-c*, respectively. While  $^1\text{H}$ NMR spectra of these derivatives were recorded in *Figures 3.9a, 3.10 a-b and 3.11 (a-c)*, respectively. IR spectra show appearance of new strong bands which can be assigned to the symmetrical and asymmetrical stretching modes of epoxy group are found at 840 and 950  $\text{Cm}^{-1}$ , respectively, in all spectra of these epoxides which indicate the presence of epoxid rings in structures of E-I to E-VI[210]. The formation of glycidyl ether was also proved by  $^1\text{H}$ NMR spectra. Absorptions due to the  $\text{OCH}_2$  groups can be found at 2.9 ppm whilst those due to the  $-\text{CH}$ -and- $\text{CH}_2$  – groups of the epoxide ring occur at 4 ppm and 2.7 ppm, respectively. Moreover,  $^1\text{H}$  NMR spectra can be used to determine the epoxy functionality of E-I to E-VI through integration of the characteristic signals. This procedure was applied to determine the chemical composition for graft or block copolymers [211-213]. Accordingly, the same procedure

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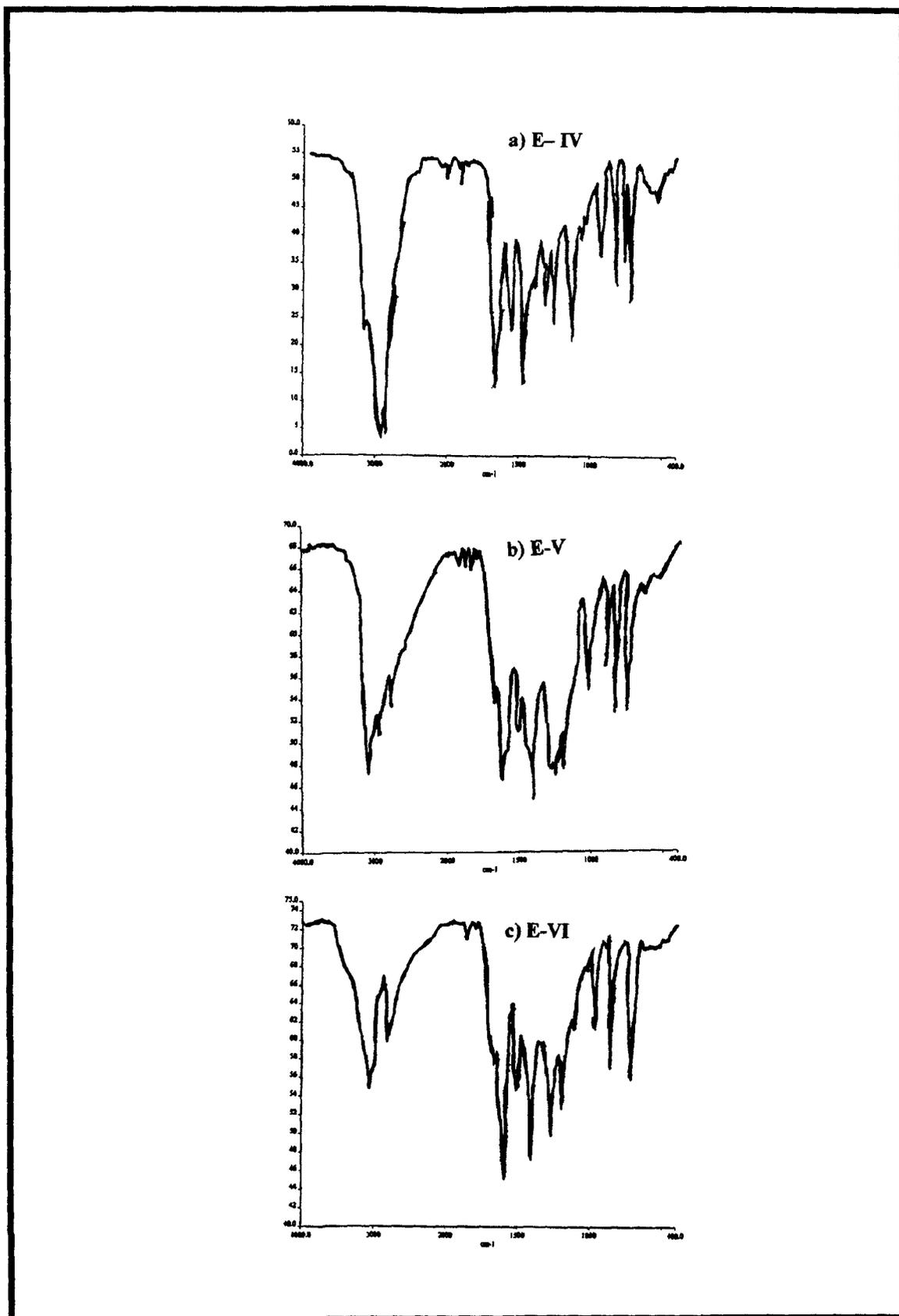
was applied through hereinafter for determining the epoxy functionality of glycidyl ethers. In this respect, the analysis is based on the integration of two signals, namely, at 4 ppm (assigned for- CH- proton of oxirane ring ), and at 10.6 ppm (assigned for unreacted OH- protons of hydroxymethyl group). The ratio of the integrals of these two signals E-I to E-VI, *Figures 3.9 and 3-11*, indicates that two hydroxyphenyl groups were reacted with EC to form glycidyl derivatives the epoxy functionality is very important parameter in modification of epoxy resins. The preparation of multifunctional epoxy is based on the glycidylation of polyhydroxyl derivatives: like as phenol formaldehyde condensates, polyfunctional resin based on phenol and glyoxal derivatives of amino phenol [214-217].



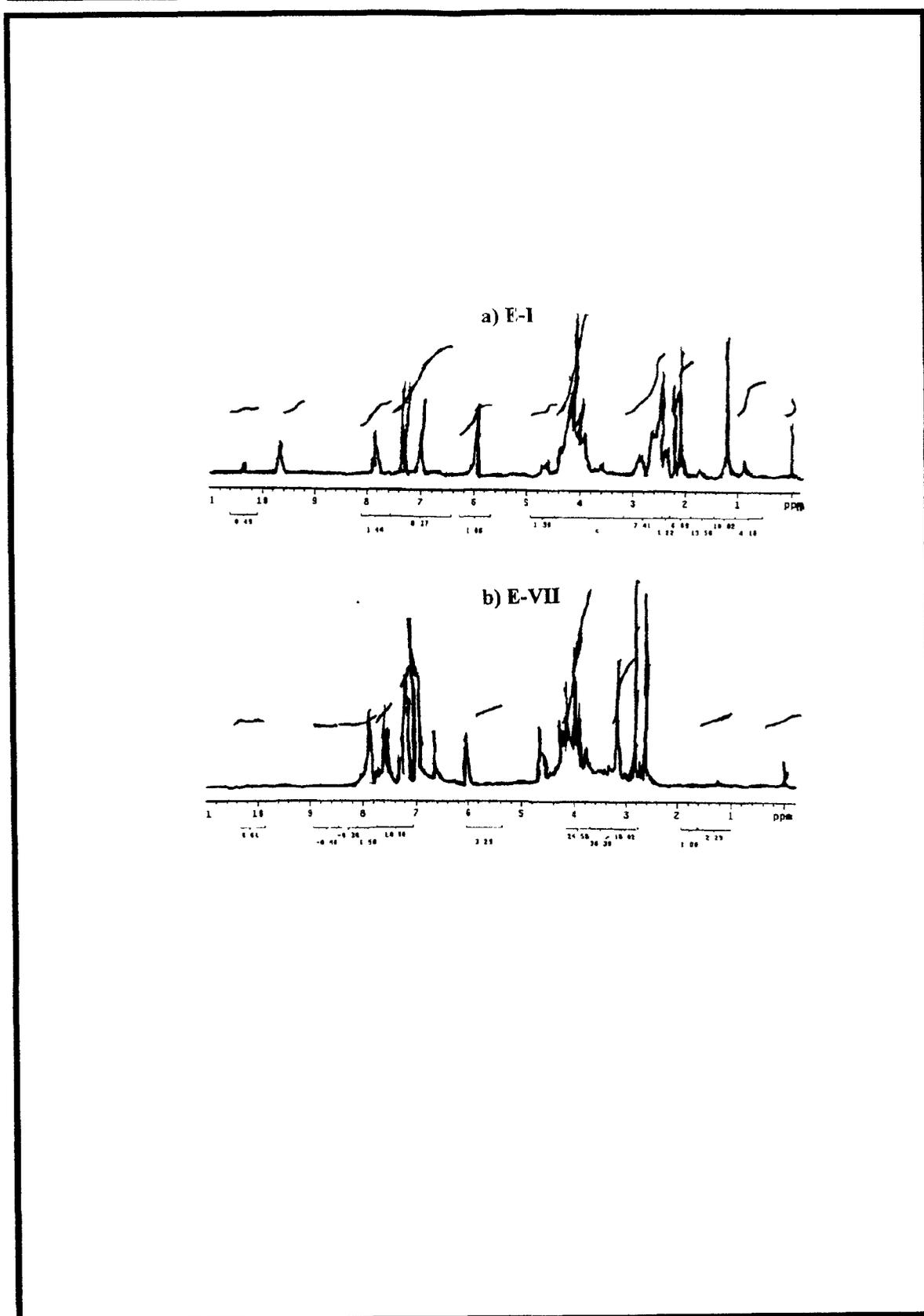
**Figures (3.6): IR Spectra of Schiff's Base Epoxy a) E-I and b) E-VII Resins.**



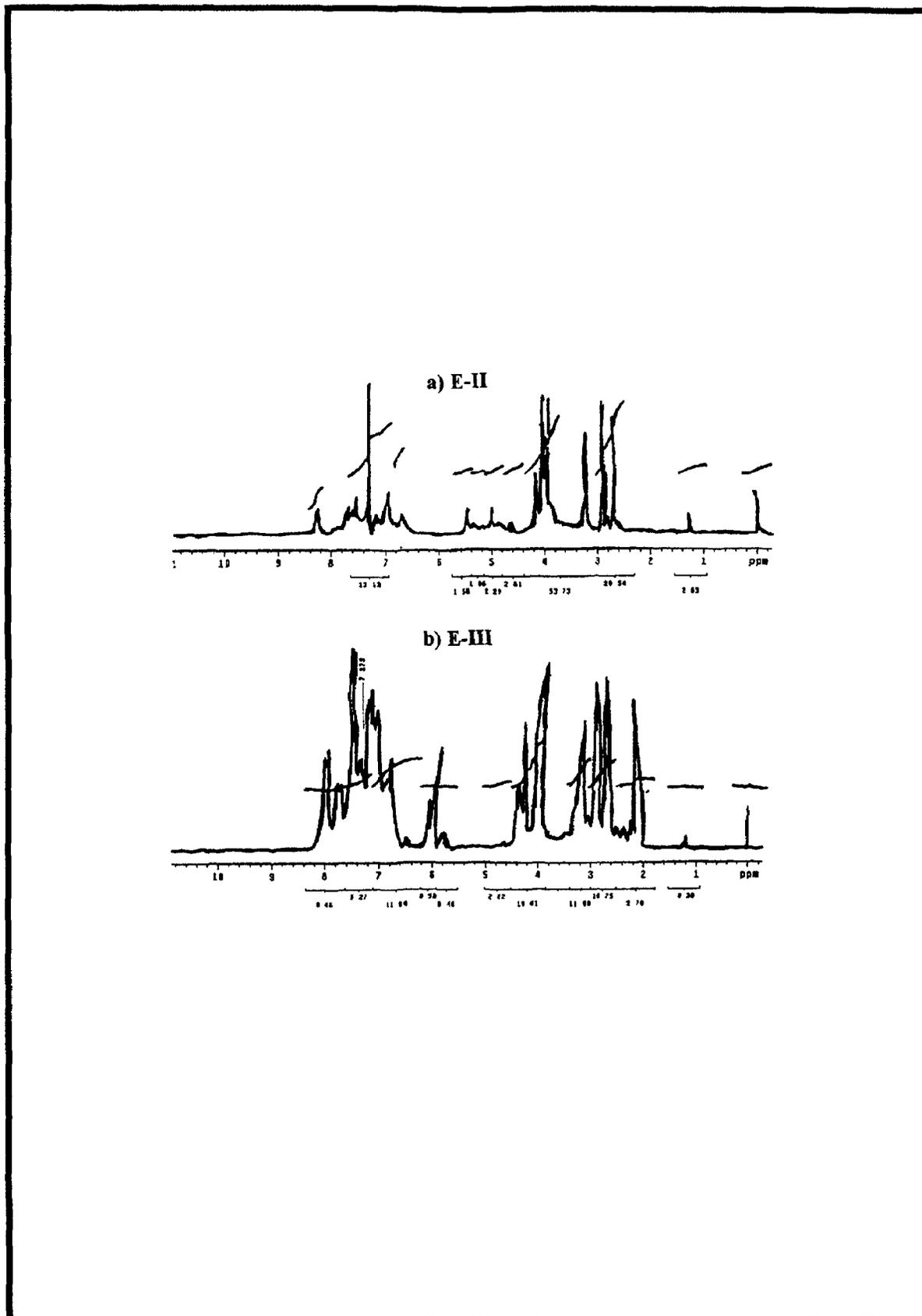
**Figures (3.7): IR Spectra of Schiff's Base Epoxy a) E-II and b) E-III Resins.**



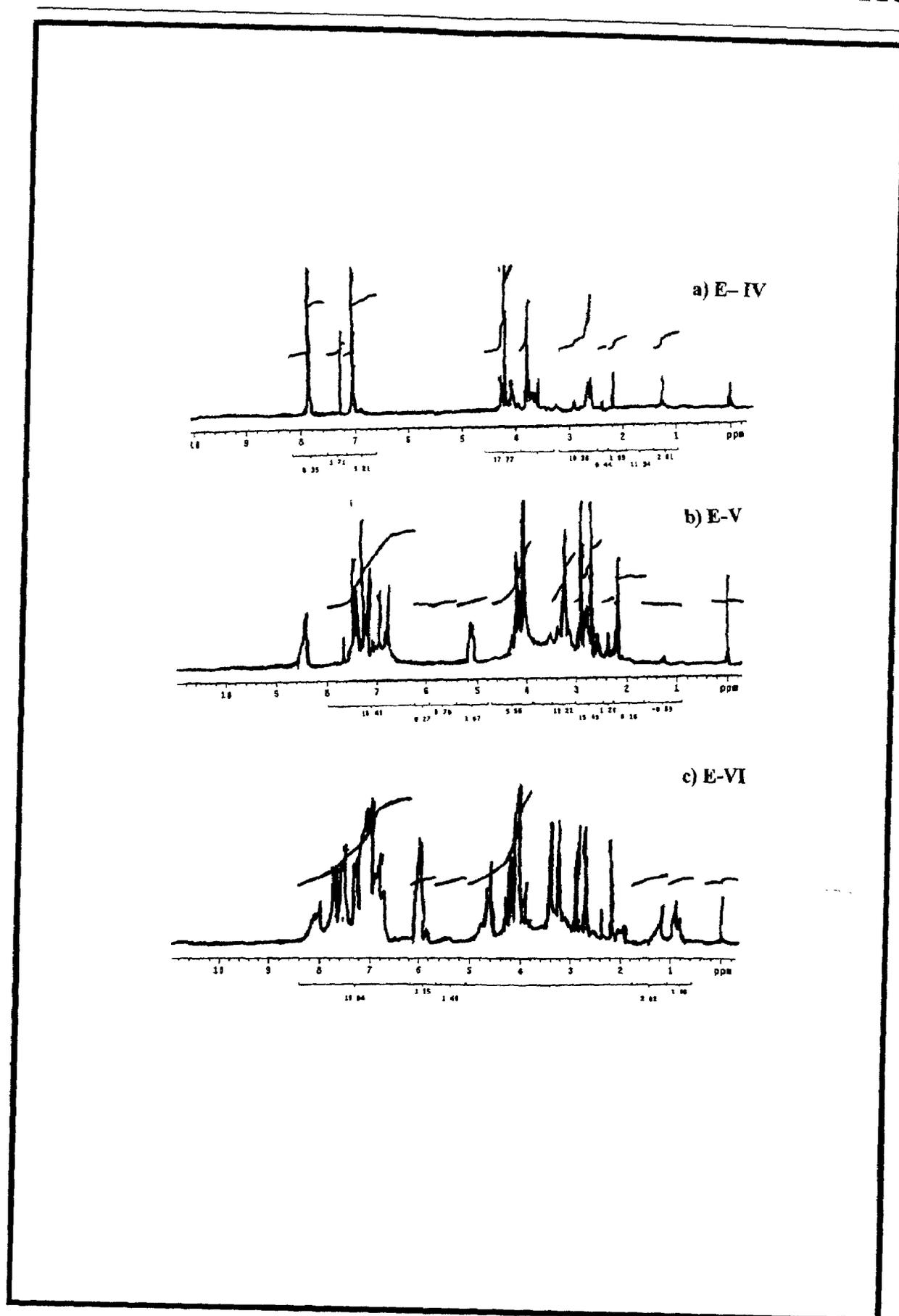
**Figures (3.8): IR Spectra of Schiff's Base Epoxy a) E-IV  
b) E-V and c) E-VI Resins.**



**Figures (3.9):  $^1\text{H}$ NMR Spectra of Schiff's Base Epoxy  
a) E-I and b) E-VII Resins.**



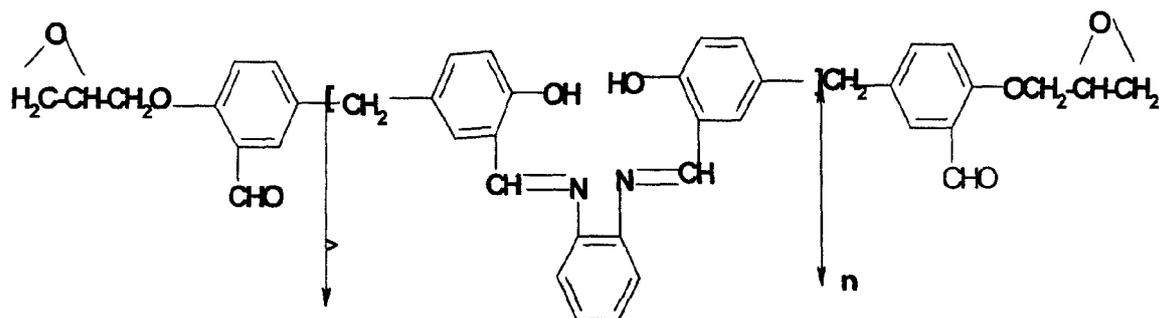
**Figures (3.10):  $^1\text{H}$ NMR Spectra of Schiff's Base Epoxy  
a) E-II and b) E-III Resins.**



Figures (3.11):  $^1\text{H}$ NMR Spectra of Schiff's Base Epoxy

a) E-IV, b) E-V and c) E-VI Resins.

In this respect, the synthesis of multifunctional epoxy resin from Schiff base polymer VII will be discussed in the present section. The Chemical structure of E-VII is represented in the following scheme:



The physic-chemical properties of the prepared resins,  $M_w$  ,EEW and EC, were 15190,3100 and 4.9, respectively. High EEW value indicates that hydroxyl groups were reacted with EC to form multifunctional epoxy resins. The structures of the produced glycidyl ether E-VII was confirmed by IR and  $^1\text{H}$ NMR spectroscopy. IR spectra of glycidyl derivatives were represented in *Figure (3.6 b)*. While their  $^1\text{H}$ NMR spectra were recorded in *Figure (3.9 b)*.

The presence of epoxide groups in IR spectra of glycidyl ether of E-VII was investigated from the presence of strong bands at  $790\text{ cm}^{-1}$  and  $850\text{ cm}^{-1}$  ( $\gamma_{\text{C-O}}$  epoxy). This was also proved from their  $^1\text{H}$ NMR spectra which was indicated from the appearance of bands at 3.8 ppm (CH epoxide) and 2.1 ppm (CH<sub>2</sub> -epoxide). The integrations of peaks between hydroxyl

groups (at  $\delta = 10.5$  ppm) and CH- proton of epoxy (at  $\delta = 3.8$  ppm) can be used for determine the epoxy functionality of resin.

It was noted that hydroxyl protons of glycidyl ether of the prepared epoxy resins have the same ratio of integration as compared to C-H epoxy protons . The lower of integration value of hydroxyl groups at (10.5 ppm) indicates the complete reaction of EC with hydroxyl end groups of VII and its multifunctional hydroxyethyl groups.

### **3-2. THERMAL BEHAVIORS OF SCHIFF'S BASE DERIVATIVES:**

Upon heating the polymer it can undergo various chemical and physical changes accompanied by the formation of gaseous and liquid products. Thermal stability of polymers can be defined as the resistance toward chemical decomposition at elevated temperature. Thermal stability is usually associated by the temperature at which noticeable decomposition of the polymer begins, by the decomposition products formed and by the kinetics of the process. Chemical reactions of polymers at elevated temperatures fall into two main groups: reactions involving rupture of the main chain (proper degradation), and reactions proceeding without rupture of the main chain. When a polymer is heated, the energy of thermal motion at some points of the system, owing to thermal energy fluctuation,

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becomes commensurable with the energy of a chemical bond and causes rupture of the bond. Obviously, a very important factor determining the thermal stability of a polymer is the energy of interatomic bonds in the main chain.

The carbon- carbon bond is one of the most resistant bonds to thermal influences. This bond is especially stable in diamond. The presence of hydrogen atoms in the polymer molecule greatly decreases the energy of C-C bond, and that is why high- molecular weight hydrocarbons and some of their derivatives possess comparatively low stability and are easily degraded by heating.

Rupture of the chemical bonds between carbon atoms may occur by two mechanisms: -

- 1- Intermolecular migration of hydrogen atoms, resulting in two chain fragments; one with saturated end unit, and the other with an unsaturated one. These degradations so- called random ruptures of chemical bonds are characteristic, for instance, for polyethylene.
- 2- Chain rupture does not occur at random points, but at the ends of the macromolecule. This type of degradation is characteristic of polyene compounds.

Substituents greatly affect the thermal stability of macromolecular compounds. The energy of the C-C bond decreases with increasing number of substitution (e.g., methyl groups) in the chain. Substitution of fluorine instead of

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hydrogen atoms increases the thermal stability of a polymer. For instance, polytetrafluoroethylene is a very thermo stable polymer, which does not decompose up to 400°C, but at higher temperatures it degrades to its monomer.

The presence of oxygen in the polymer (especially in the backbone chain) sharply increases the rate of thermal degradation. At an elevated temperature many polymers undergo considerable chemical and physical changes involving no bond rupture in the chain. When such polymers are heated, side substituents are eliminated, forming thermally more stable products. But in some cases, the products lose their stability at thermal treatment.

Thermal stability of polymers can be evaluated by two methods of analysis:

**a) Thermogravimetry (TG):**

TG is a dynamic method in which the weight loss ( $w$ ) of a sample is measured continuously as

- 1- A function of temperature ( $T$ ) at a constant rate;
- 2- A function of time ( $t$ ) at a constant temperature (isothermal or static thermogravimetry).

An experimental plot of weight loss versus temperature is called thermogram and exhibits a thermogravimetric curve, which has been divided into two steps: -

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- 1- A first step which represents a small initial weight loss ( $w_0 - w_t$ ) and which results from adsorption of solvent, if it occur near  $100^\circ\text{C}$ , this may be attributed to loss of water;
  - 2- A second step ( $w_1 - w_2$ ) and sometimes a third step ( $w_2 - w_3$ ), which are results of thermal decomposition of the sample.

### **b) Derivative Thermogravimetry (DTG):**

It is a dynamic method in which the change of mass with respect to time ( $dw/dt$ ) is measured as:

- 1- A function of temperature (T) at constant rate;
- 2- A function of time (t) at constant temperature (isothermal or static derivatives thermogravimetric).

The obtained curve is the first derivative of the mass change curve. A curve contains a series of peaks instead of the stepwise curve. The area under the peaks is proportional to the total change in the mass of the sample.

### **3-2-4. Applications of Thermogravimetry (TG)**

The term 'thermal analysis' comprises a number of analytical procedures for the investigation of physical or chemical changes occurring in materials with heating. Physical phenomena of importance are melting, evaporation, sublimation, desorption and absorption, crystallization, phase transitions of higher order and changes in modification.

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Chemical phenomena include oxidation and decomposition of materials as well as other chemical reactions in the solid or liquid phase (e.g., curing reactions), heterogeneous reactions of materials in the solid or liquid state with the gaseous phase, desolvation and chemisorption. The comparison of polymers on the basis of thermal stability is difficult because of the variety of possible behaviors. It has been shown that epoxy resins decompose in more than one decomposition step. Doyle [218], in a work on estimating thermal stability of experimental polymers by empirical thermogravimetric analysis, put these various behaviors on a common numerical basis by use of an arbitrarily defined 'integral procedural decomposition temperature' (IPDT) which is derived from the weight loss versus temperature plot under rigidly controlled experimental conditions (200 mg pulverized samples heated at a rate of 3 K/min in nitrogen up to 900 °C). The background for the investigations mentioned above with respect to the influence of structure of epoxy resins and curing agents (in terms of their functionality, aromaticity and chemical nature in relation to their effects on controlled thermal degradation, including the char yield) is the examination of materials for application in ablative heat shields for re-entry vehicles.

In connection with the applicability of composite materials in the blast tube of rocket motors a number of materials, including two asbestos epoxy composites, have been

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investigated by dynamic and isothermal TG with respect to their ability to withstand a short-time exposure, e.g., to high temperature by Kershaw et al. [219]. The relevant tests were carried out in nitrogen as a compromise for the gas atmosphere operative in a typical rocket, motor consisting of CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub> and N<sub>2</sub>. The char yield was taken as a measure of assessing the thermal stability of the materials, and the results obtained at 900 °C with dynamic TG correlated well with those obtained at 800 °C with isothermal TG, suggesting that the amount of char residue formed is essentially independent of the heating rate in the range studied. The char yield in excess of 55% was also independent of the specimen surface area if tested under nitrogen. In air, the temperature at which weight loss became measurable was lower for the specimen of higher surface area.

The diglycidyl ether of bisphenol-A (DGEBA) is the most commonly used epoxy resin as it has many attractive properties such as fluidity, low shrinkage during cure and ease of processing. The cured products have good physical strength, excellent moisture, solvent and chemical resistance. Their main problem is relatively poor thermal stability and flame resistance which limits their applications in more demanding areas such as aerospace and electronic industry. The main aim of this work is based on synthesis of new epoxy resins having aromatic moieties to increase its thermal stability. The thermal

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stability of the epoxy resins was assessed with two parameters: initial decomposition temperature (IDT) and integral procedure decomposition temperature (IPDT). IDT indicates the apparent thermal stability of the epoxy resins, i.e., the failure temperatures of the resins in processing and molding. On the other hand, IPDT exhibits the resins' inherent thermal stability, i.e., the decomposition characteristics of the resins' volatile composition. Thermogravimetry (TG) is a technique to determine weight continuously while heating a sample. It can also be run in two different ways. Most frequently the sample is heated at a constant rate under a well-defined atmosphere of nitrogen, air or oxygen. The resulting weight-loss steps can be evaluated kinetically, preferably by the aid of the first derivative of the TG curve. The form and position of the weight-loss steps and, accordingly, the position of the DTG peaks, depend on instrumental and operational factors, as well as on specific properties of the materials under test, namely the thermal stability of the material [220-222].

Thermogravimetry has developed almost independently from differential thermal analysis, although there are a few publications describing a combined application of DTA and TG/DTG by the aid of commercial equipment [223-226] in the field of epoxy resins.

Most of the early work involved inorganic materials and did not involve estimations of kinetic parameters in pyrolysis. One

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of the early attempts to estimate these parameters for the pyrolysis of organic compounds was made by van Krevelen et al [227], and Freeman and Carroll [228] developed a widely used method for the determination of reaction kinetics. The first application of TG in the field of epoxides seems to date back to 1961 when Anderson published a work on the kinetics of pyrolysis of epoxide polymers. So in the initial stages of the application of TG to epoxides, the investigation of kinetic parameters was involved. The application of DTG for the evaluation of kinetics of the pyrolysis of cured epoxide polymers based on the bisphenol-A type was discussed by Anderson [229]. Several degradation schemes are proposed based on the principles of the cleavage of simple ethers and the products obtained from the pyrolysis study. The first step of the degradation is an isomerization of the residual epoxy group into an aldehyde, as proposed by Anderson [229], or an etherification of the residual epoxy groups with the formation of olefinic aromatic derivatives, with a differentiation of decomposition products depending on whether one or two groups attached to ether oxygen are phenyl. Due to the enhanced thermal stability of aromatic residues, it was felt that the ultimate stability of epoxy resin systems might depend upon the degree of crosslink. In order to elucidate the influence of crosslink density of epoxy-aromatic amine systems on the cure and post-cure processes, thermal

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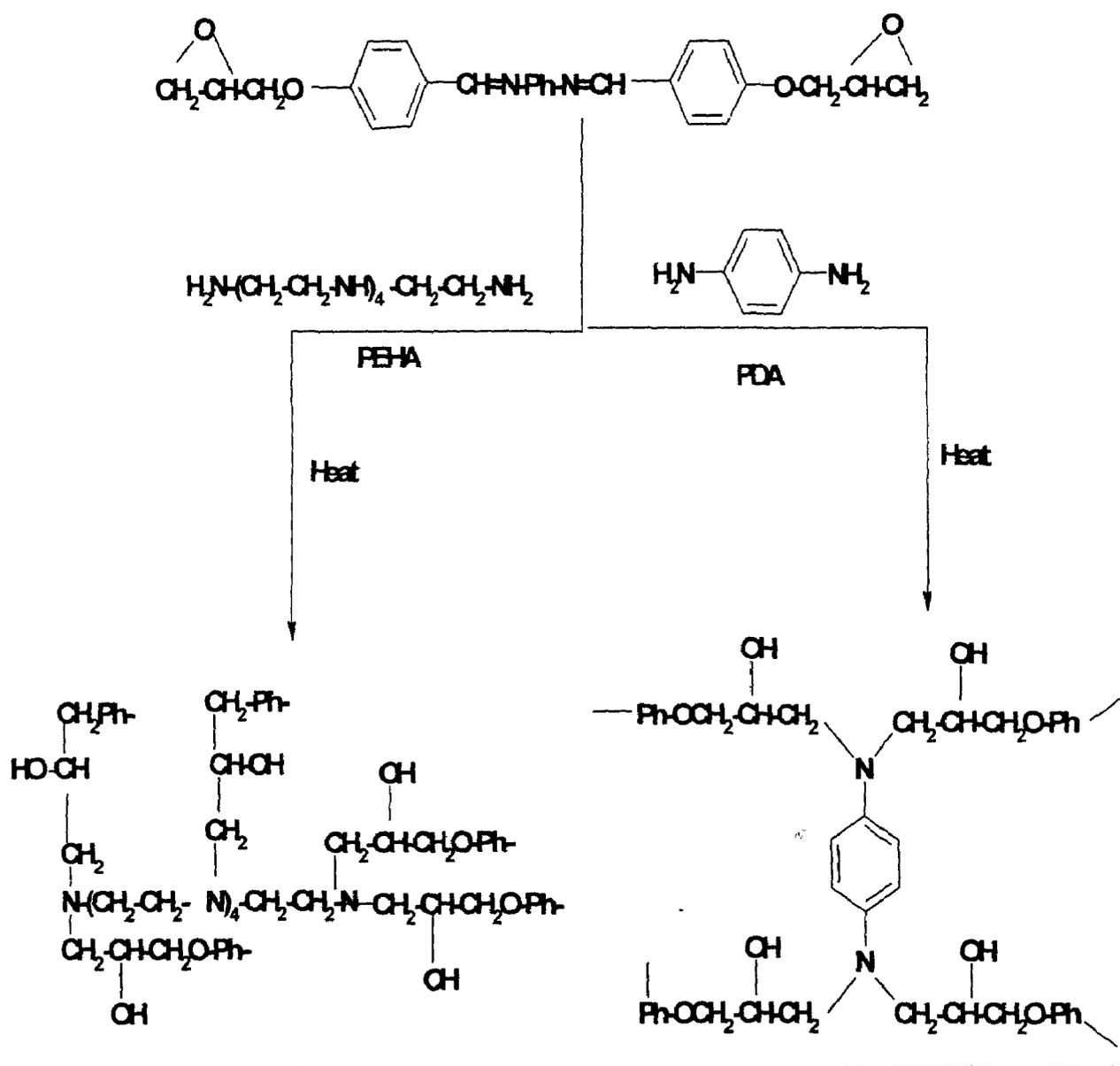
transitions, and (in later parts of this series) thermal stability and degradation reactions, we selected two kinds of amine as curative: PEHA (a polyfunctional amine), which reacts with epoxy resin as a chain extender, and p-phenylenediamine or PDA (a tetrafunctional amine) which reacts with epoxy resins to form a tetrafunctional junction as depicted in *Figure (3.12)*. Other fields of application include the evaluation of thermal stability and the use of TG for analytical purposes or in comparison with other properties.

The effects of the addition of different epoxy resins on the thermal stability of phenolic resoles are reported. Blends of phenolic resins with different compositions of epoxy resins, cured with amine hardeners, were characterized by thermal gravimetric analysis and cone calorimetry to determine their thermal stability and fire resistance. The thermal degradation of phenolic resoles is characterized by a complex mechanism with at least two different processes, which lead to the production of a stable and resistant char structure. While the epoxy resins, either aliphatic or aromatic, degraded in a single step. Phenolic resins are thermosetting polymers with high chemical resistance and thermal stability but low toughness and mechanical resistance. Moreover, phenolic resoles have intrinsic resistance to ignition, low generation of smoke and relatively low cost. On the other hand, a disadvantage is that they are characterized by a complex process of polymerization

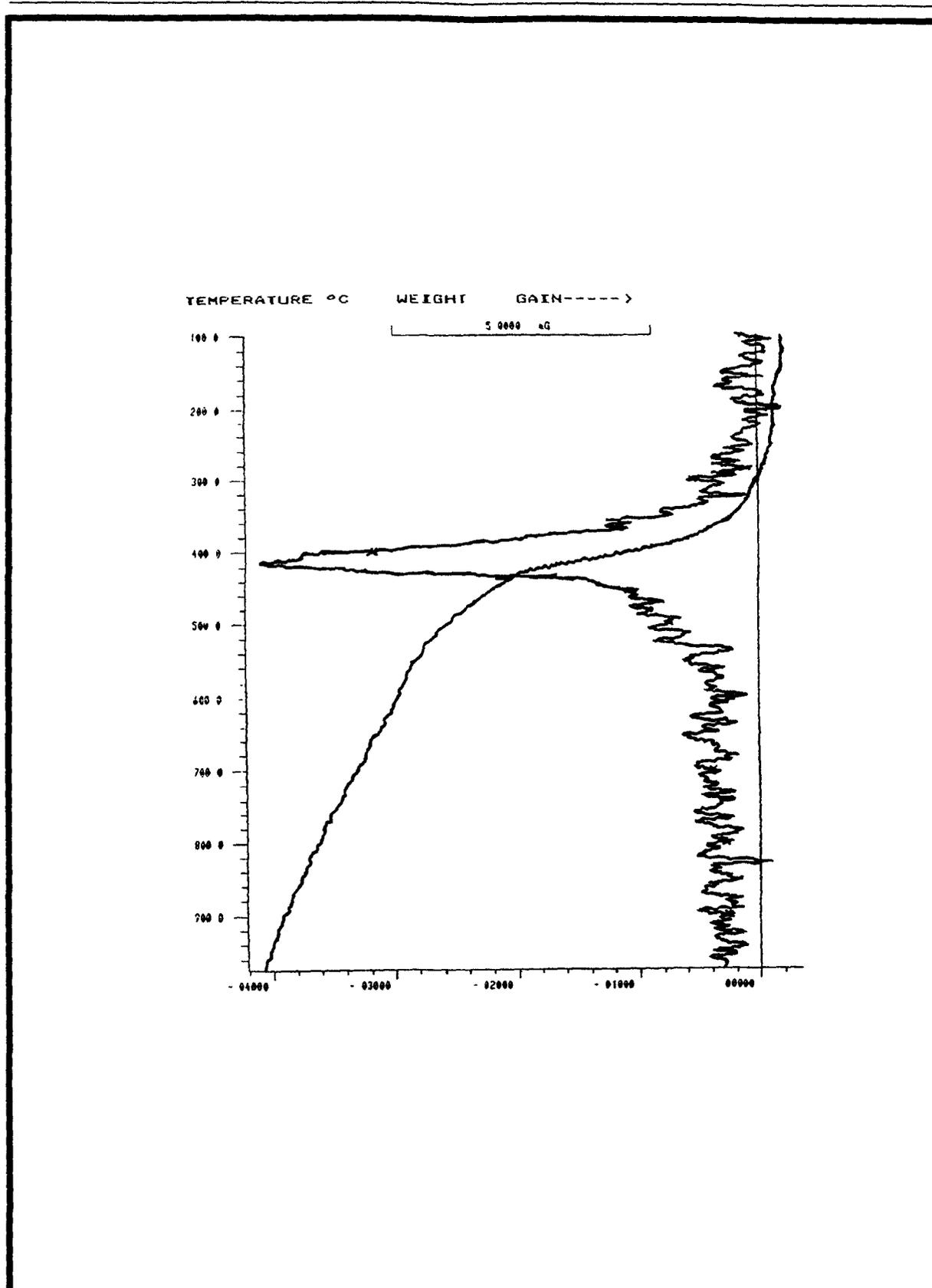
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(cure) with generation of water and formaldehyde, with consequent formation of voids. Therefore, the processing of phenolic materials requires careful temperature control and gradual heating to allow continuous elimination of volatiles and to reduce the number of defects in final components. Normally the time required for these operations is incompatible with common industrial process schedules.

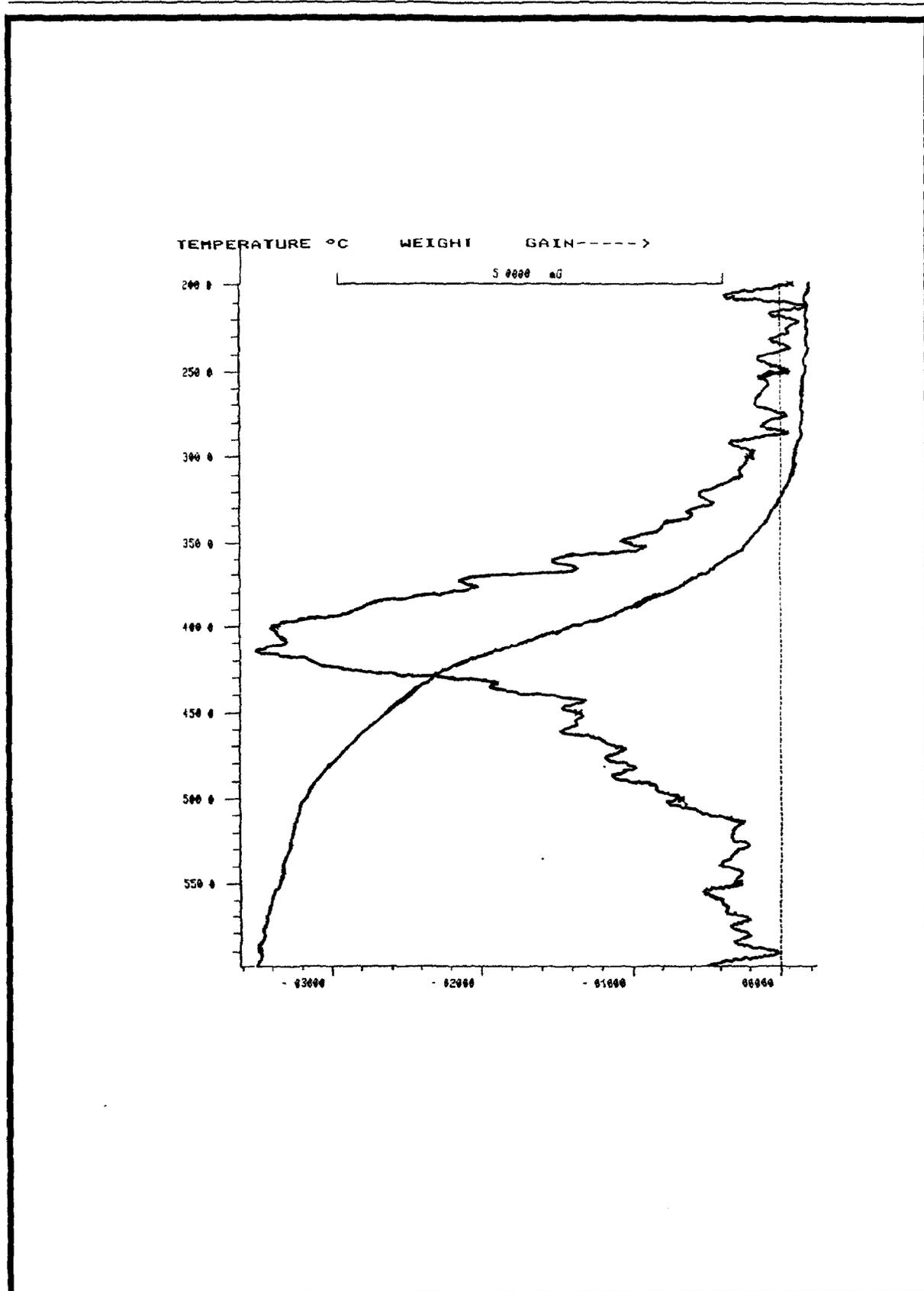
On the other hand, curing of DGEBA with phosphorus containing amines increased the anaerobic char yield at 800 °C. However a decrease in onset temperature of degradation was observed. Incorporation of imide group generally leads to an improvement in thermal stability. In the present work, the phenolic systems will be analyzed for their thermal stability in order to determine how the cured epoxy/amine affects the excellent thermal behavior of phenolic resins. In thermal analysis, thermogravimetric analysis (TGA) is a useful method to determine the thermal stability of materials. In the present study, TGA thermograms are used for evaluating the thermal stability of the prepared Schiff's base derivatives (I – VII) and their epoxy. It is of interest to mention that, the cured epoxy resins are subjected to high temperatures. Accordingly, these resins should be stable at temperature exceeding at least 250°C. In this respect; TGA and DTG thermograms of Schiff's base derivatives (I and VII) are given in *Figures (3.13) and (3.14)*.



**Figure (3.12): Chemical Structures of the Cured Schiff's Epoxy resin VI with both PDA and PEHA**



**Figures (3.13): TGA and DTG Thermogram Schiff's  
Base I Monomer.**



**Figures (3.14): TGA and DTG Thermogram Schiff's  
Base VII Polymer.**

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DTG curve may be obtained from the TGA curve either by manual differentiation method or by electronic differentiation of the TG signal. The DTG curve, whether derived mathematically or recorded directly, contains no more information than does an integral TG curve obtained under the same experimental conditions. Accessory equipment is available for most thermobalances so that the DTG curve can be easily recorded along with the TG curve.

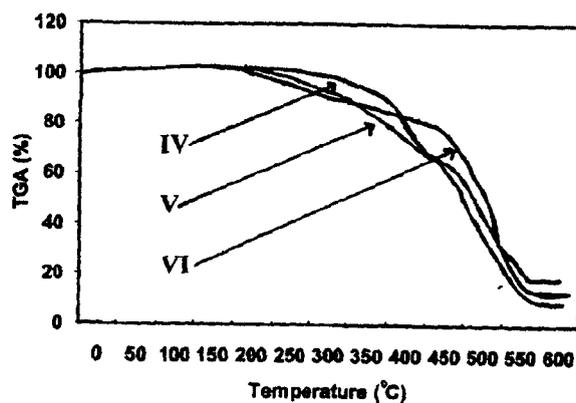
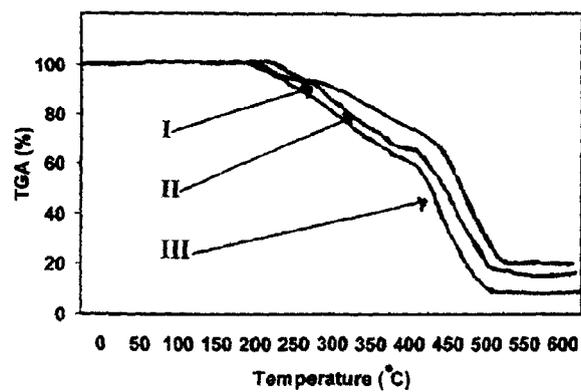
The main application of TGA is in the study of thermal kinetics and thermal stability. In this respect, TGA thermograms of Schiff's base I –VI and their epoxies are plotted in *Figures (3.15 and 3.16)*, while TGA thermograms of cured epoxy resins are given in *Figures (3.17 and 3.18)*.

The thermal data obtained by TGA for Schiff's bases and their epoxy resins were listed in *Tables (3.4) and (3.5)*. The data of TGA include initial degradation temperature (IDT), 10% weight loss temperature (T<sub>10%</sub>), temperature of maximum rate of weight loss (T<sub>max</sub>) and residuum at 600°C (Y<sub>600°C</sub>).

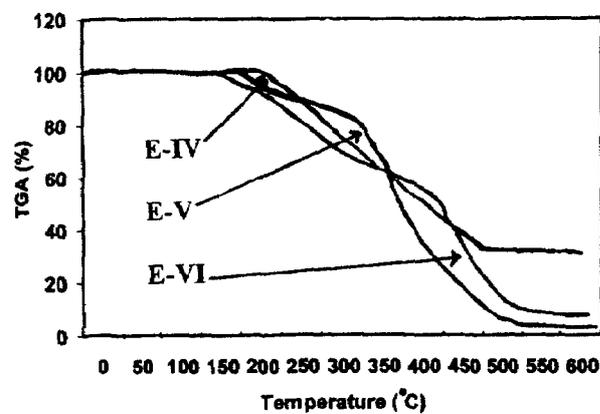
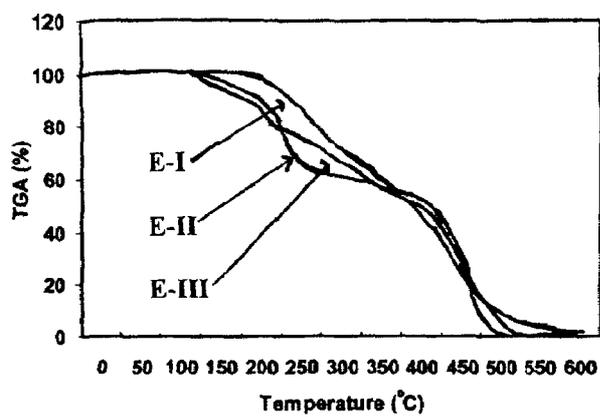
Careful inspection of the thermogram plots of Schiff base derivatives and their epoxy resins show two degradation steps, suggesting the coexistence of more than one degradation process whereas; the cured resins have only one degradation step. On the other hand it was observed that, the thermal stability data of I show that I starts to degrade rapidly and losses 54.4 % of its initial weight between 326 and 453 °C and

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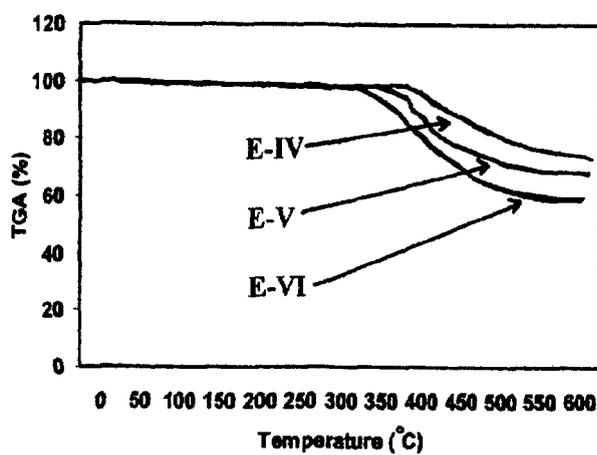
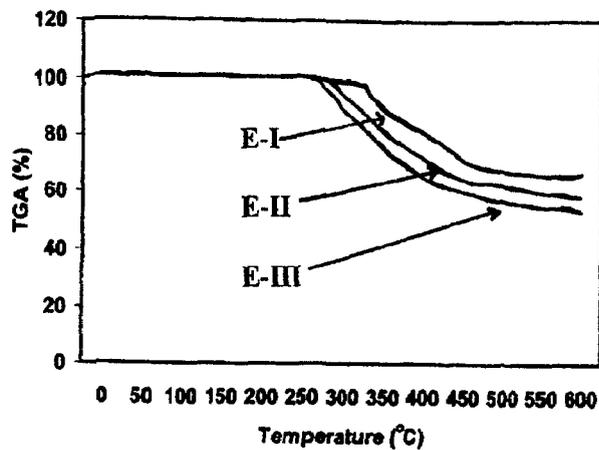
losses 31.8 % of its weight at temperature between 453 and 550 °C. The remaining weight % at 550 °C is 13.8 % of its initial weight. Similarly VII polymer starts degradation at 280 °C which indicates lower thermal stability of VII polymer when compared with its monomer. The decreasing of thermal stability may be attributed to the rupture of CH<sub>2</sub> bond connecting to monomer I. However, Schiff base polymer VII losses about 64.42 % of its initial weight at 445 °C. Comparing the rate of decomposition of I and VII in its temperature range shows a similar rate of decomposition. This may indicates that the polymer degrades to its nonnumeric units.



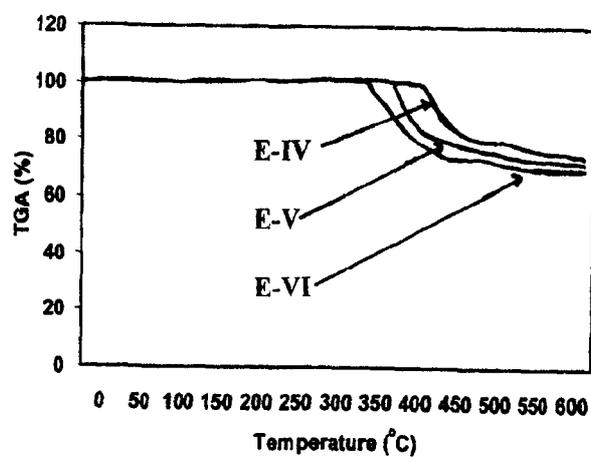
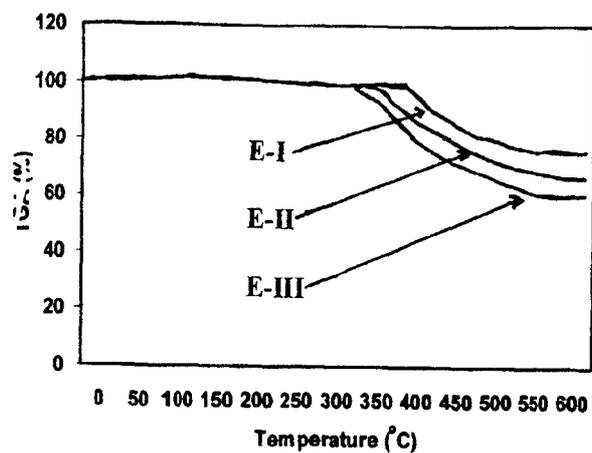
**Figures (3.15): TGA Thermograms Schiff's  
Base I-VI Monomers.**



**Figures (3.16): TGA Thermograms Schiff's Base  
E-I – E-VI Resins.**



**Figures (3.17): TGA Thermograms Cured Schiff's Base E-I – E-VI Resins with PEHA Hardener.**



**Figures (3.18): TGA Thermograms of Cured Schiff's Base E-I – E-VI Resins with PDA Hardener.**

**Table (3.4): Thermal Gravimetric Data of Schiff Bases.**

Monomer	Steps		Weight loss (%)	IDT (°C)	T <sub>10%</sub> (°C)	T <sub>max</sub>	Y <sub>600</sub> (%)
	Start Temp	End Temp					
<b>I</b>	100	250	0	290	350	470	13.8
	250	450	54.4				
	450	600	31.8				
<b>II</b>	100	250	0	250	300	500	15
	250	450	50				
	450	600	35				
<b>III</b>	100	250	10	220	280	480	5
	250	450	30				
	450	600	55				
<b>IV</b>	100	250	0	330	380	500	10
	250	450	35				
	450	600	55				
<b>V</b>	100	250	5	280	320	480	20
	250	450	35				
	450	600	40				
<b>VI</b>	100	250	0	250	300	450	15
	250	450	10				
	450	600	75				
<b>VII</b>	100	250	0	280	320	430	9
	250	450	64.42				
	450	600	26.58				

**Table (3.5): Thermal Gravimetric Data of Schiff Base Epoxy Resins.**

Monomer	Steps		Weight Loss (%)	IDT (°C)	T <sub>10%</sub> (°C)	T <sub>max</sub> (°C)	Y <sub>600</sub> (%)
	Start Temp. (°C)	End Temp. (°C)					
E-I	100	250	10	220	250	350	0
	250	450	60				
	450	600	30				
E-II	100	250	40	150	220	450	0
	250	450	55				
	450	600	5				
E-III	100	250	15	150	200	450	2
	250	450	40				
	450	600	43				
E-IV	100	250	8	220	300	400	30
	250	450	45				
	450	600	17				
E-V	100	250	8	200	280	350	2
	250	450	82				
	450	600	8				
E-VI	100	250	10	180	250	480	5
	250	450	40				
	450	600	45				
E-VII	100	250	14	200	230	330	5
	250	450	65				
	450	600	16				

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It was also observed that all Schiff base - containing epoxy resins showed relatively lower IDTs than did the Schiff base - free resins, since epoxy-groups decompose at low temperatures due to decomposition of ether linkage  $\text{CH}_2\text{-O-CH}_2$  bonds. The thermal behavior of epoxy resins has been extensively studied. Most studies refer to epoxy resins based on the diglycidyl ether of bisphenol A, as such, or cured with amines and anhydrides. In the case of these kinds of resins the decomposition products were identified with the aid of pyrolysis-mass spectrometry experimental technique [230], and the quantitative and qualitative composition of the components having low molecular weight have been established [231]. However, it is observed that the epoxy resin of I shows lower thermal stability than VII epoxy resins. This can be attributed to the fact that the resins having low molecular weight degrade faster than the resins with higher molecular weight. This behavior, which was remarked and reported and for p-nonylphenol formaldehyde novolac resins [232], could be due to the presence of a liquid resinous material (p-nonylphenol glycidyl ether, for instance) in the low molecular weight resins in a quantity larger than in the resins with higher molecular weight. In accordance with other data reported for some epoxy resins with low molecular weight [233] the high molecular weight liquid products suffer a degradation starting with temperatures  $>200$  °C and lead to

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organic and inorganic gases. The presence of epoxy fragments, non-volatile at temperatures up to 300 °C, and their decomposition at temperatures > 200 °C could be the explanation and the line of TG curves recorded for I and VII.

On the other hand, using of p-phenylenediamine (PDA) groups to prepare both Schiff base monomers and their epoxy resins instead o-phenylenediamine (ODA) would significantly increase the IDT. This can be referred to the incorporation of ODA increases steric hindrance of groups more than PDA in both Schiff base monomers and their epoxy resins. This will reflect on their thermal stabilities that decrease with increasing of steric hindrance between groups.

It was also found that the resins' IDT increased with introducing OHB > MHB > PHB for Schiff base monomers. This can be referred to the ease of degradation of OH group between two molecules by dehydration at p- position more than m- and o- positions. This can also be attributed to the ability of Schiff bases based on OHB to form intrahydrogen bond with imine group that reflect on the thermal stability of these derivatives. The same behavior was illustrated for the unusual thermal stability of some polyethylene glycol grafts, which indicates that the hydrogen bonding interactions lead to the formation of a gel-like network structure [234,235].

The cured Schiff base epoxy resins with both PDA and PEHA as curing agents show different thermal behaviors. The thermal

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stabilities of the cured resins with both PEHA and PDA were tabulated in *Tables (3.6) and (3.7)*, respectively. It was observed that, the cured epoxy resins based on PDA possess high thermal stability than that cured with PEHA networks. The initial decomposition of cured resins with PDA begins at 300 °C and the maximum decomposition was observed around 550 °C. While cured Schiff base monomers with PEHA begins at 250 °C and its maximum decomposition was observed around 450 °C. This can be attributed to high aromatic content of cured resins with PDA, which resist the thermal degradation. It was also observed that the cured resins based on polymeric Schiff base epoxy VII and PDA have high thermal resistance up to 800 °C. It was noticed that approximately 75% of its initial weight still resist thermal degradation. This indicates that the cured resins transformed to more stable structure after curing with PDA. On the other hand the cured resins VII with PEHA have 40 % of its initial weight stable at 800 °C. This indicates that the formed char was protected and can be considered as the non-volatile part. Accordingly, the high IDT implies the epoxy resins' potential application in highly anti-thermal coatings and thermal insulating materials.

**Table (3.6): Thermal Gravimetric Data of Cured Schiff Base Epoxy Resins with PEHA.**

Monomer	Steps		Weight loss (%)	IDT (°C)	T <sub>10%</sub> (°C)	T <sub>max</sub> (°C)	Y <sub>600</sub> (%)
	Start Temp. (°C)	End Temp. (°C)					
E-I	100	250	0	350	400	500	65
	250	450	15				
	450	600	20				
E-II	100	250	0	320	370	450	50
	250	450	20				
	450	600	30				
E-III	100	250	0	300	350	430	40
	250	450	25				
	450	600	35				
E-IV	100	250	0	400	430	530	70
	250	450	15				
	450	600	15				
E-V	100	250	0	350	400	480	65
	250	450	15				
	450	600	20				
E-VI	100	250	0	330	380	460	50
	250	450	20				
	450	600	30				
E-VII	100	250	0	480	500	560	67
	250	450	8				
	450	600	25				
<b>(DGEBA)</b> References. 229-231				<b>100-180</b>	<b>200-240</b>	<b>300-400</b>	<b>12-5</b>

**Table (3.7): Thermal Gravimetric Data of Cured Schiff Base Epoxy Resins with PDA.**

Monomer	Steps		Weight loss (%)	IDT (°C)	T <sub>10%</sub> (°C)	T <sub>max</sub> (°C)	Y <sub>600</sub> (%)
	Start Temp. (°C)	End Temp. (°C)					
E-I	100	250	0	400	430	500	70
	250	450	15				
	450	600	15				
E-II	100	250	0	380	400	450	60
	250	450	12				
	450	600	28				
E-III	100	250	0	350	380	430	45
	250	450	20				
	450	600	35				
E-IV	100	250	0	430	470	530	75
	250	450	8				
	450	600	17				
E-V	100	250	0	400	430	480	65
	250	450	12				
	450	600	23				
E-VI	100	250	0	380	410	460	60
	250	450	15				
	450	600	25				
E-VII	100	250	0	520	550	600	80
	250	450	5				
	450	600	15				
<b>(DGEBA)</b> <small>References 229-231</small>				<b>160-250</b>	<b>200-280</b>	<b>350-400</b>	<b>20-8.6</b>

Careful inspection of data listed in **Tables (3.6-3.7)** indicates that the cured epoxy resins (E-I to EVII) have high thermal stabilities than the cured commercial epoxy resins of DGEBA using the same curing agents. This can be attributed to the formation of high crosslinking density networks based on the prepared epoxy resins (E-I to EVII) than that based on DGEBA resins [229-233]. This can be also attributed to the strong interaction between two nitrogens on PEHA and PDA residues and highly conjugated aromatic system of (E-I to EVII) than interaction with benzene ring of DGEBA resins [235]. Accordingly from the above mentioned results we can concluded that the cured epoxy resins based on the Schiff bases with aliphatic and aromatic amines have excellent thermal stabilities towards thermal degradation than the widely commercial epoxy resins based on both DGEBA and phenol formaldehyde epoxy resins [229-223].

### **3-2-2. Thermal Characteristics of Schiff Base Resins by DSC Measurements:**

Thermal effects resulting from physical or chemical changes during heating of materials can be applied for absolute or comparative analytical purposes, i.e., recording the parameters of these changes as a function of temperature (with dynamic test procedures) or with time (with isothermal test procedures) allows conclusions about the composition, structure and

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physicochemical behavior of the products under test to be drawn. The majority of publications deal with differential scanning calorimetry (DSC). Differential scanning calorimetry is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature whilst the substance and the reference material are subjected to a controlled temperature programmer [236]. In reviewing the literature, it is apparent that DSC is the favorite method of investigation, possibly because it was the first method to furnish quantitative thermo-analytical data. The DSC curves demonstrated the earlier beginning of the curing reaction with the cold curing system, and also the fact that for an optimal curing higher temperatures or longer reaction times were necessary.

A comparison of the influence of structural characteristics on the reactivity of epoxy resins and curing agents was undertaken by Batzer et al. [237] by means of DSC measurements of the temperatures of the maximum reaction rate. It is well known that the behavior, the physical and chemical properties of epoxy systems depend, not only on the chemical composition of these systems, but also on the distribution of units along the macromolecular chains (microstructure) and on the relative stereo chemical configuration of the side chains if the main chain has asymmetric carbons. In this sense, it would be of interest to

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analyze the influence of these factors on the thermal behavior of the prepared Schiff base epoxy resins.

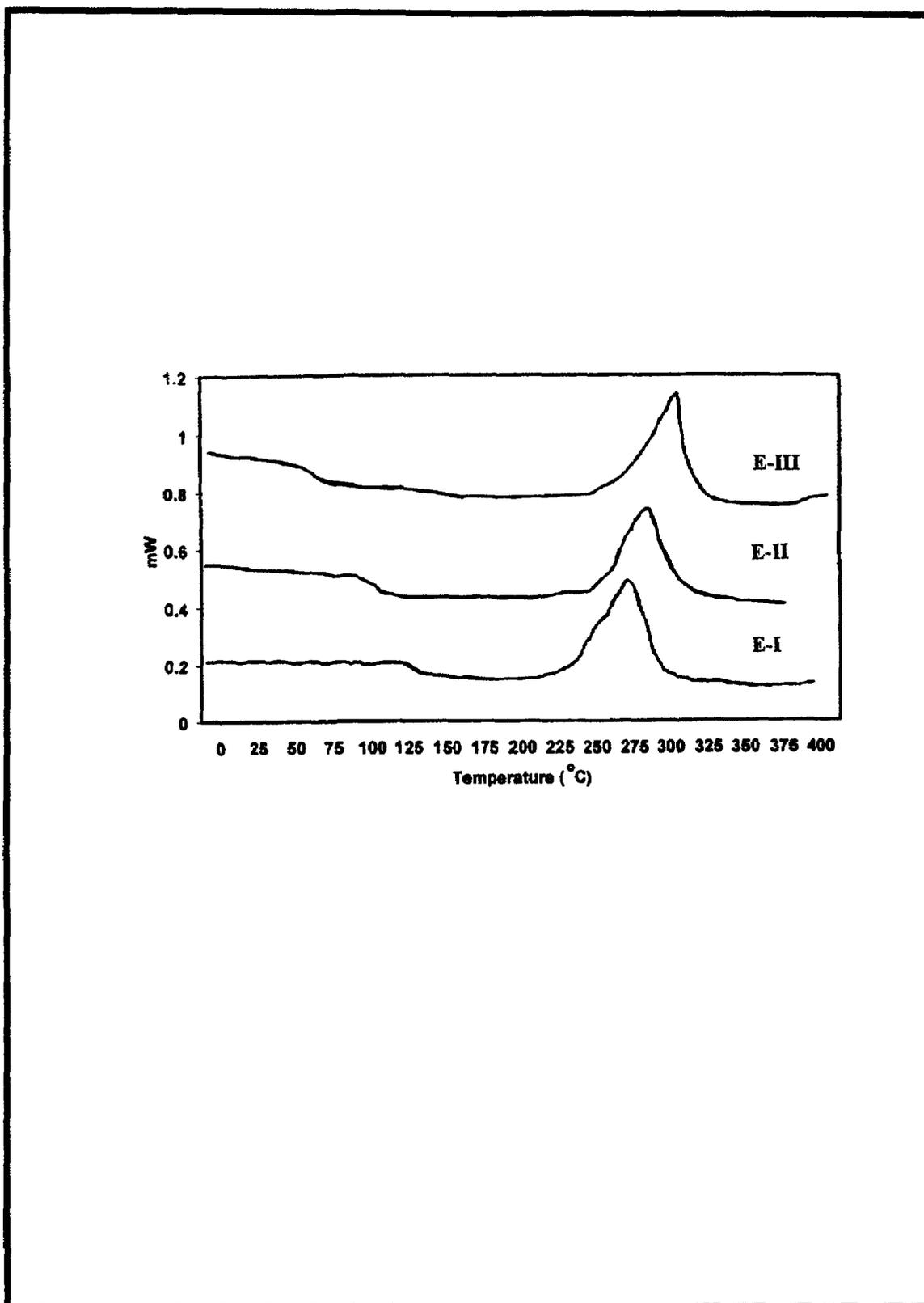
In order to know the influence of the side substituents on the flexibility of epoxy resin chains, and the relationship between the size and polarity of the side residue on the flexibility of epoxy resins, we have analyzed the glass transition temperatures ( $T_g$ ) and melting temperatures ( $T_m$ ) from DSC measurements as indicated in experimental section.  $T_g$  of the polymer is important for the intended application. This transition temperature is defined as being the temperature or range of temperature at which the polymer passes from a hard and often brittle stage (glass) to a resistant stage of the rubber type. The applicable  $T_g$  values were determined from the points of intersection of the extrapolated baseline at the low temperature end and the tangents to the curve at the inflection point and determine the applicable exothermic heats of reaction ( $\Delta H$ ). DSC thermograms of the cured epoxy resins with PEHA and PDA were represented in *Figures (3.19 and 3.20)*. The cured epoxy resins with PDA show an exothermic peak and endothermic peak. The cured epoxy resins with PEHA show only exothermic peak. The endothermic peak at 142 °C is produced from melting of PDA. The exothermic peak was observed at 218 °C and 250 °C for cured epoxy resins with PDA and PEHA, respectively. The exothermic peak comes from curing reaction of epoxy resins with amine.

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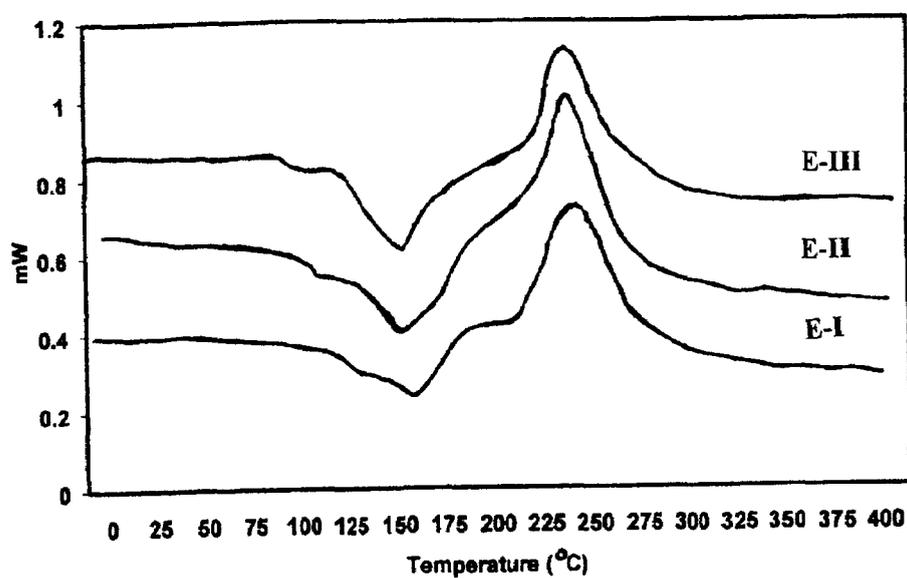
The glass transition temperatures of these resin systems were measured by differential scanning calorimetry or DSC, as indicated in *Table (3.8)*. Careful inspection of T<sub>g</sub> data of the prepared Schiff base epoxy resins of I- VII reveals that the prepared epoxy resins have high values more than 100 °C except polymer VII and III that have 90.3 and 54.21 °C, respectively. This can be referred to introducing of CH<sub>2</sub> groups as spacer groups of polymer backbone will induce some flexibility in the resin backbone. The T<sub>g</sub> of polymeric system has multifunctional dependence on the micro- structural characteristics of high molecular weight macromolecules [238,239]. The higher T<sub>g</sub> values are related to strong dipolar interaction between side substituents of the polymeric chain. While, the glass transition temperature of low molecular weight compounds depends on the intermolecular interaction of individual molecules exclusively, being controlled by the molar volume and dipolar connectivity, hydrogen bonds, and Van der Waals interactions between molecules. This was observed in the epoxy resin III that possesses lower T<sub>g</sub> value and that was referred to the lower interactions of epoxy groups at P- position when imine groups at o- position (structure III).

**Table (3. 8): Thermal Properties of Schiff Base Epoxy Resins.**

<b>Epoxy Resins</b>	<b>Tg (°C)</b>	<b>Δ H (J/g)</b>
<b>E-I</b>	110.5	26.36
<b>E-II</b>	117.6	36.47
<b>E-III</b>	54.21	50.14
<b>E-IV</b>	104.3	39.62
<b>E-V</b>	115.8	37.47
<b>E-VI</b>	113.5	48.56
<b>E-VII</b>	90.3	63.88



**Figure (3.19): DSC Thermograms of the Cured Epoxy Resins E-I- E-III with PEHA.**



**Figure (3.20): DSC Thermograms of the Cured Epoxy Resins E-I- E-III with PDA.**

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### **3-3.CURING OF EPOXY BINDERS BASED ON SCHIFF BASE DERIVATIVES:**

The curing stage is the second step in the preparation of thermoset polymers. In this stage epoxy polymers are considered structoterminal or structopendant depending on whether cross-linking occurs through the epoxy end groups or the hydroxyl groups. The prepolymer is structoterminal when polyamines or polyamides are used for cross-linking; in this case, curing involves the opening of the epoxide groups. Hardening occurs primarily through the hydroxyl groups when an anhydride is used as cross-linking agent; in this situation, epoxy prepolymer is considered as structopendant. The curing mechanisms of epoxy binders and the structures of cured epoxy with amines, amides and anhydride have been thoroughly studied and the systems of epoxy resins with different types of hardeners are used extensively in many industrial application [240,241]. Curing agents are either catalytic or corrective catalytic curing agent functions as an initiator for epoxy resin homopolymerization, where the corrective curing agent acts as a comonomer in the polymerization reactions.

The curing agent can react with the epoxy and pendent hydroxyl groups on the resin backbone by way of either an anionic or cationic mechanism. Catalytic curing agents can be used for homopolymerization, as a supplemental curing agent

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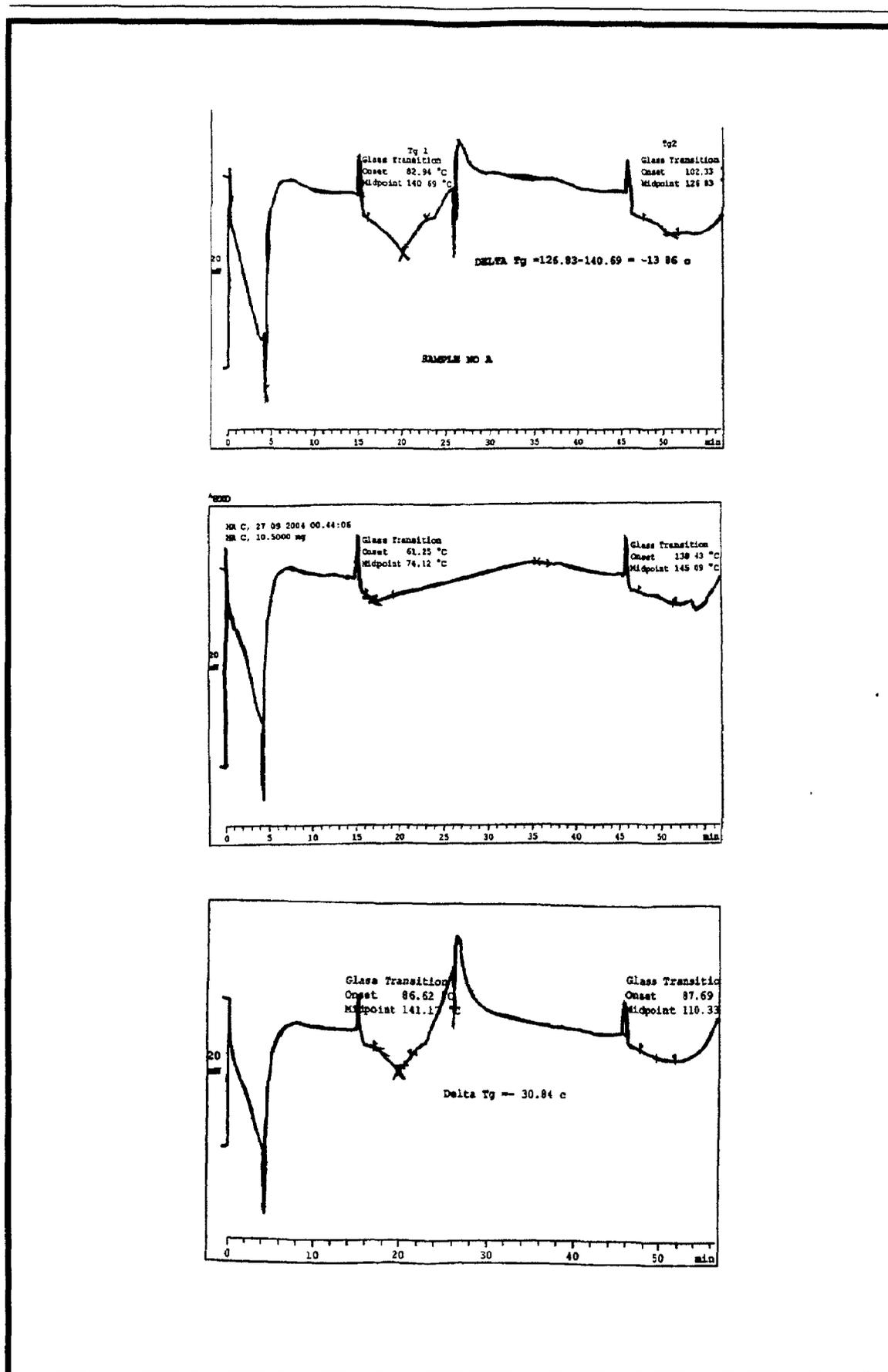
with polyamines or polyamides , or as accelerators for an anhydride cured system catalytic cures are initiated by Lewis acids e g, boron trihalides , and Lewis bases, e.g., tertiary amines.

Several methods based on data of dynamic mechanical analysis (DMA) [242] rheological measurement, near infrared analysis [243] and thermal differential scanning calorimetry (DSC) were used to study the relation and curing kinetic mechanisms. The reactivity of epoxy binders to be cured, and the properties of the end products, affects the choice of curing system. The type and concentration of curing agents may be able to control the length of cross-links (cross-link density), and consequently the mechanical properties of the cured epoxy resins. In the present work we have used DSC measurements to evaluate the curing exotherms of the prepared epoxy resins with both PDA and PEHA curing agents. In this respect, the cured epoxy resin samples were heated and scanned from 25 to 150 °C and then immediately cooled at 25 °C. Tg values are reported as Tg2. While the temperatures of the heated resins from 25 to 285 °C followed by cooling to 25 °C are reported as Tg1. The change in Tg value was determined as the differences between Tg2 and Tg1. The percentage of cured epoxy conversion, c, can be calculated using the formula:

$$C = (\Delta H - \Delta H_1) / (\Delta H) \times 100 \quad (3.1)$$

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Where  $\Delta H$ ,  $\Delta H_1$  values (J/g) are exothermic heat of reaction for thermal scan of cured epoxy and cured coat at 285 °C, respectively. The results of a typical set of DSC experiments conducted on epoxy resins are reproduced in *Figure (3.21)*. The data of Tg1, Tg2 and curing conversion of curing agents of the prepared epoxy resins with PEHA and PDA were determined and listed in *Tables (3.9-3.10)*. In order to provide standards of comparison for calorimetric degree of cure and fixed degrees of crosslinking, Barton [244] prepared a series of epoxy resins in which the curing agent was varied between 74 and 100% of the stoichiometric amount. These resins were fully cured and their Tgs determined by DSC and thermal expansion measurements. From the DSC data the inflection points in scans at 20 K/min were taken as Tg, but the effect of heating rate on Tg was small - a change from 20 to 50 K/min caused a reduction in Tg of only 3.5 K. The dependence of Tg on curing agent concentration was approximately linear. From iso-thermal experiments at various cure temperatures and times, samples of known calorimetric fractional conversion, C values were obtained. It was shown that Tg was a very sensitive index of the degree of cure; during the final 10% of the curing reaction the Tg increased by 70 K.



**Figure (3.21): DSC Thermograms of Cured Schiff Base Epoxy Coatings with PEHA (I,III and VII).**

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The same author [245] has applied the same procedure of assessing the dependence between  $T_g$  and the degree of cure to another system. In this case the DSC measurements of  $T_g$ , did not provide a very precise estimate of the degree of cure above 70% conversion, and the results were complicated by the appearance of two transitions at high degrees of cure, due to the hetero-phase nature of the cured resin. Careful inspection of data listed in *Tables (3.9-3.10)*, reveals that the cured epoxy resin with PDA has high cured percentage values than that determined for PEHA, and this indicates that the reactivity of the prepared epoxy resins towards aromatic amines is much higher than aliphatic amines at higher temperatures. It is well known that aromatic amines act as hardener for epoxy resin and require elevated temperatures to complete curing reaction because their lower electron donating during the reaction with epoxy resins [246]. This indicates that the cured epoxy resins crosslinked with PDA have high crosslink density than that cured with PEHA at elevated temperature due to tendency of PEHA to form Epoxy dangling chains which are not completely cured. It was also observed that the cured epoxy resins with PDA have high  $T_g$  values than that cured with PEHA. This can be attributed to the higher crosslink density resulting from reaction of epoxy resins with PDA curing agent [247]. The glass transition of these resin systems were measured by DSC as indicated in *Tables (3.9-3.10)*. The initial scan was

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performed to 150°C and the T<sub>g</sub> was taken as the onset of the baseline change. The second scan was conducted to 280°C and was used to check for possible increases in T<sub>g</sub>. Using this method, we were able to determine that the glass transition temperatures of the resin systems before and after post-cure. It was observed that the data of T<sub>g</sub> of the epoxy resins also increased during post-cure. This phenomenon was observed and has attributed it to an increase in molecular weight due to uncontrolled chain extension, and to the removal of solvent [248]. The T<sub>g</sub> of cured resins was increased after post-cure. We must remark here that T<sub>g</sub> values do not correlate with thermal stability. In other words, 'stiffer' resins are not automatically more stable than softer resins. For example, Schiff base polymer VII resin (T<sub>g</sub> = 90.3°C) possesses a higher thermal stability than all the epoxy resins. We may also note that cured resin VII will be shown to possess a higher thermal stability than resin I, in spite of its much lower T<sub>g</sub> value.

**Table (3. 9): Thermal Properties of Cured Schiff Base Epoxy Resins with PEHA.**

<b>Epoxy Resins</b>	<b>Tg<sub>1</sub> (°C)</b>	<b>Tg<sub>2</sub> (°C)</b>	<b>T cure (°C)</b>	<b>Conversion (%)</b>
<b>E-I</b>	126.38	140.96	244	83.2
<b>E-II</b>	118.5	154.3	245	66.4
<b>E-III</b>	74.12	145.3	242	56.3
<b>E-IV</b>	125.4	145.3	245	64.1
<b>E-V</b>	135.4	135.77	248	70.9
<b>E-VI</b>	146.5	183.36	243	63.4
<b>E-VII</b>	110.33	141.1	250	90.1

<sup>1</sup> glass transition temperature of first run (from 25 to 150 °C).

<sup>2</sup> glass transition temperature of second run (from 25 to 285 °C).

**Table (3. 10): Thermal Properties of Cured Schiff Base Epoxy Resins with PDA.**

<b>Epoxy Resins</b>	<b>Tg<sub>1</sub> (°C)</b>	<b>Tg<sub>2</sub> (°C)</b>	<b>T<sub>m</sub> (°C)</b>	<b>T cure (°C)</b>	<b>Conversion (%)</b>
<b>E-I</b>	136.23	139.51	142	218	96.4
<b>E-II</b>	129.5	132.41	140	217	87.5
<b>E-III</b>	105.12	109.45	143	218	90.43
<b>E-IV</b>	145.4	145.9	144	219	89.12
<b>E-V</b>	125.4	127.8	145	216	94.32
<b>E-VI</b>	156.5	157.9	143	215	95.75
<b>E-VII</b>	127.33	128.45	143	224	98.5

<sup>1</sup> glass transition temperature of first run ( from 25 to 150 °C).

<sup>2</sup> glass transition temperature of second run (from 25 to 285 °C).

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### 3-4. EVALUATION OF CURED EPOXY RESINS IN COATING APPLICATION:

Epoxy resins form one of the most important widely used in such diverse applications as surface coatings; adhesives for printed circuit boards; in the potting of electronic components; as rigid foams; adhesives; and in the manufacture of fiber-reinforced composites for value added applications. In all of these materials, a cure process is involved, during which the epoxy resin is converted into a thermoset network. Epoxy resins provide durable coatings of high mechanical strength with good adhesion to many substrates. Solvent-and chemical-resistant films are obtained by curing at ambient and at elevated temperatures. Low molecular weight liquid or solid epoxy resins are dissolved in solvents at room temperature to cure with amines. The curing usually takes 7 days; resin and hardener components are packed separately. Amine – cured systems are suited for marine and maintenance coatings where corrosion resistance is required. The working pot life of amine-epoxy resins systems depends on the curing agent, solvent, accelerators, and temperature. Normal stoichiometry employs equivalent weight of amino hydrogen per equivalent weight of epoxy resins, but in practice, the best performance may be given by other ratios. It is usually a major good in epoxy coatings to maximize pot life and minimize cure time at ambient temperature. In this respect, the curing and application

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of our prepared epoxy resins and hardener based on Schiff base epoxy resins at ambient temperature are another goals of this work.

### **3-4-1. Relationships between Cured Epoxy Resin Structure and their Mechanical Properties:**

Cured thermoset polymers are more difficult to analyze than cured thermoplastic. They are insoluble and generally intractable. However, properties are influenced by factors at the molecular level, such as backbone structures of epoxy resin and curing agent; nature of covalent bond developed between the epoxy resin and the curing agent during the cross-linking; and density of cross linking, i.e., degree of cure Epoxy resins have a wide and increasing use in industry owing to their unique combination of properties. The absence of volatile byproducts and low shrinkage during cure results in good molding characteristics, and the minimization of internal stresses give the thermoset excellent mechanical properties. Furthermore, the cured resins possess outstanding chemical resistance and they have high adhesive strengths due mainly to the generation of polar hydroxyl groups during cure. For these purposes the mechanical properties of cured resins have tested by determining the impact, pull-off adhesion and bending.

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The curing experiments, reported here, were formulated as solvent-based liquid coatings. In this respect, epoxy resins were mixed with curing agents based on both PDA and PEHA at ratio 4:1 (wt of epoxy: wt of hardener), the mixed ratios are dissolved in 10% of MEK (wt% base and hardener) to dissolve polyamine hardeners. Then, these samples were sprayed (by using air spray gun) with wet film thickness, WFT, 225  $\mu\text{m}$  on blasted steel panels. The tests for measuring the mechanical properties were evaluated after 24h at ambient temperature (25° C). The data of mechanical properties (pull-off adhesion, impact, bending and pencil hardness) for cured epoxy resins with curing agents were tabulated in *Tables (3.11 and 3.12)*. The data reported on pull-off adhesions indicate that all cured epoxy resins with PDA have superior adhesion properties with steel than that cured with PEHA. This can be attributed to the formation of highly crosslinked epoxy networks when PDA was used as hardener. It was also found that cured epoxy resins based on Schiff base polymer VII have excellent adhesion of steel. This can be attributed to the high epoxy functionality of this resin, which produces high hydroxyl groups when cured with PDA or PEHA hardeners. It has been demonstrated that the presence of small controlled amounts of terminal hydroxyl groups can have beneficial effects on adhesion [249]. The excellent adhesion of the prepared epoxy

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resins can be referred to the ability of the Schiff base resins to form stable coordination bond with steel.

The mechanical properties of coatings films were determined with impact and T- bend tests. It was noted that the cured epoxy resins based on PDA possess excellent impact and bend resistance. While cured epoxy resins with PEHA pass impact resistance but it fails with T- bend tests. This behavior indicates that the cured epoxy resins with PEHA will produce low crosslinked networks. These behaviors indicate that the type of cross-linking agent affect the mechanical properties of coatings. This leads to speculate that the high crosslinking density networks possess good mechanical properties of the formed network. The mechanical properties of resin systems can also be used to estimate the degree of cure [250-252]. This was observed by the variation of hardness results (by pencil test) from softer (minimum crosslinks) to hardener coatings (maximum cross- link- density). The results of hardness test agree with the data reported on curing exotherms of epoxy resins that determined from DSC measurements.

**Table (3. 11): Adhesion Tests of Cured Schiff Base Epoxy Resins.**

Epoxy Resins	X-Cut		Pull-off (MPa)	
	PEHA	PDA	PEHA	PDA
<b>E-I</b>	4A	5A	3.5	5
<b>E-II</b>	3A	4A	1.5	2
<b>E-III</b>	3A	4A	1	1.5
<b>E-IV</b>	3A	4A	2	3.5
<b>E-V</b>	3A	4A	1	1.5
<b>E-VI</b>	4A	4A	3.5	5
<b>E-VII</b>	5A	5A	4	5

**Table (3. 12): Mechanical Properties of Cured Schiff  
Base Epoxy Resins.**

Epoxy Resins	T-bending		Impact Resistance (j/mm)		Hardness	
	PEHA	PDA	PEHA	PDA	PEHA	PDA
E-I	FAIL	PASS	3.5	10	2H	2H
E-II	PASS	PASS	10	10	3H	2H
E-III	PASS	PASS	10	7.5	3H	3H
E-IV	FAIL	PASS	3.5	7.5	2H	2H
E-V	FAIL	FAIL	3.5	10	HB	4H
E-VI	FAIL	PASS	3.5	10	HB	4H
E-VII	FAIL	PASS	7.5	15	3H	5H

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### **3-4-2. Evaluation of Chemical Resistance for Cured Resins:**

Durability of coats may be defined as the capacity of paint to endure; that is, to remain unchanged by environment and events. Effects of environmental conditions have an enormous effect on durability, and test methods for developing and monitoring the performance of coating systems are always designed to simulate conditions of usage. They are usually designed to accelerate the degradative processes to which coatings are subjected. The reason for this acceleration of the degradation processes is to provide early warning of coatings failure. There are two types of test methods to evaluate the durability of coatings chemical resistance test and mechanical tests. In the previous section we have evaluate the mechanical tests of the present types of cured epoxy based on Schiff base epoxy resins. In the present section we have discuss the chemical resistance test, which have described in experimental section. In this respect the coated panels have subjected to chemical environments (alkali, acid, solvent and salt spray) to study the durability of coats. The data of alkali, acid, solvent resistance and water resistance were determined for cured epoxy systems based on PDA listed in *Tables (3-13) – (3-17)*. The reason for coating failure are legion nevertheless some reasons for failure are readily identifiable, and attempts can be made to compact them. Architectural coatings based on

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autoxidizable binders have the seeds of degradation. The oxidation process does not stop when the film has dried. Oxidation proceeds, giving an increasingly crosslinked film. The adequacy of durability of modern exterior glass coat is due to a careful choice of binder, which aims to keep the oxidizability of the film to the minimum, maximizes the extensibility of the film while maintaining adequate hardness, among other considerations. It will be clear that the requirements to be met include both chemical resistance and optimum mechanical properties. Failure of coating systems will be due to either of these factors or to a combination of them. We shall now discuss an extensive range of tests and the data of tests that have been devised to give an indication of the probable performance of coating films appropriate to its durability. The failure of test indicates that the coating films losses their adhesion with panels.

**Table (3.13): Water, Acid, Alkali and Solvent Resistance in Addition to Rub Test of Epoxy Resin Cured with PDA.**

<b>Resin No.</b>	<b>Water resistance</b>	<b>Acid resistance</b>	<b>Alkali resistance</b>	<b>Solvent resistance</b>	<b>Rub test</b>
<b>E-I</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>
<b>E-II</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>
<b>E-III</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>
<b>E-IV</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>
<b>E-V</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>
<b>E-VI</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>
<b>E-VII</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>	<b>EX</b>

**Table (3.14): Water Resistance Data of epoxy resins cured with PDA.**

Resin No.	Immersion period " Days "					
	1	2	7	14	21	30
E-I	EX	EX	EX	EX	EX	EX
E-II	EX	EX	EX	EX	EX	EX
E-III	EX	EX	EX	EX	EX	EX
E-IV	EX	EX	EX	EX	EX	EX
E-V	EX	EX	EX	EX	EX	EX
E-VI	EX	EX	EX	EX	EX	EX
E-VII	EX	EX	EX	EX	EX	EX



**Table (3.16): Alkali Resistance Data of Epoxy Resins  
Cured with PDA.**

Resin No.	Immersion period " Days "					
	1	2	7	14	21	30
<b>E-I</b>	EX	EX	EX	EX	EX	EX
<b>E-II</b>	EX	EX	EX	EX	G	P
<b>E-III</b>	EX	EX	EX	EX	G	G
<b>E-IV</b>	EX	EX	EX	EX	EX	G
<b>E-V</b>	EX	EX	EX	EX	G	P
<b>E-VI</b>	EX	EX	EX	EX	G	P
<b>E-VII</b>	EX	EX	EX	EX	EX	EX

**Table (3.17): Solvent Resistance Data of Epoxy Resins  
Cured with PDA.**

<b>Resin No.</b>	<b>Immersion period “ Days “</b>					
	<b>1</b>	<b>2</b>	<b>7</b>	<b>14</b>	<b>21</b>	<b>30</b>
<b>E-I</b>	EX	EX	EX	EX	EX	EX
<b>E-II</b>	EX	EX	EX	EX	EX	EX
<b>E-III</b>	EX	EX	EX	EX	EX	EX
<b>E-IV</b>	EX	EX	EX	EX	EX	EX
<b>E-V</b>	EX	EX	EX	EX	EX	EX
<b>E-VI</b>	EX	EX	EX	EX	EX	EX
<b>E-VII</b>	EX	EX	EX	EX	EX	EX

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Solvent resistance may be tested for very different reasons. Tests of resistance to petrol and diesel fuel are carried out on compositions that may be expected to encounter contact or intermittent splashing with these liquid, e.g. motor vehicle finishes, storage tanks, etc. The use of polar solvents such as ketones is often used to assess the degree of cure of a crosslinked network for solvent resistance; methyl isobutyl ketone or acetone is recommended. In addition to immersion testing, solvent resistance may be assessed by a solvent rub test. In this respect acetone have used to determine the degree of curing of the present coating systems by both immersion and rub methods. The failure of tests was determined either by disruption or dissolution of the coating films from panels. Generally, solvent resistance depends primarily on polarity of cured network resins. Non-polar polymers show solvent resistance to water, acetone and other polar solvents, whereas polymers containing sites for hydrogen bonding are most affected by moisture humidity and polar solvent [253]. Moreover, the molecular weight and crosslink density of polymer networks are directly related to its resistance to solvent attack. This is due to the thermodynamic relation between polymer network structures and solvent [254]. Crosslinking is the ultimate structural factor in preventing a polymer from dissolving in a solvent. Although this cannot completely eliminate the effects of polarity and hydrogen

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bonding, it raises molecular weight to the size of an infinite network, preventing “individual polymer” chains from dissolving in the solvent. The higher the degree of crosslinking indicates the less free volume and segmental mobility remain available in the polymer. So that solvent molecules can hardly penetrate the crosslinked network at all. The crosslink density can be controlled by change type of curing agents and functionality of epoxy resins [255], in this respect, it was found that the all prepared epoxy resins cured with both PDA and PEHA have good solvent resistance. This can be attributed to increasing of crosslink density by increment of epoxy functionalities, although the epoxy polarity is increased by increment of epoxy functionalities [256]. The high solvent resistance of the cured epoxy systems based on PDA and PEHA indicates the solvent (MEK), used to solublize polyamine hardener, and is not trapped in the cured system [257,258].

Whereas most conventional structural materials are subject to severe attack by many aqueous acids and bases, most organic polymers are relatively resistant to these corrosive environments. Only specific functional groups in the polymer may cause sensitization to such reagents. The acidic phenolic hydroxyl group in phenolic resins remains sensitive to alkali even after final cure [259]. The acetal group in cellulose, polyformaldehyde and polyvinyl acetals is very sensitive to

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hydrolysis by aqueous acid [260]. Polyesters, polyamides, and polyurethanes may be hydrolyzed by acid or alkaline catalysis [261]. In the present systems the structure of network based on Schiff base as epoxy binders and PDA or PEHA as curing agents, have imine and ether groups, which are sensitive to both aqueous acidic and alkaline solutions. The data of acid and alkali chemical resistance for cured epoxy resins with PDA indicate that these networks possess high resistance to alkaline and acidic aqueous solutions, although they have polar groups. The high alkaline and acidic resistance can be referred to high crosslink density of networks due to high epoxy functionalities. This can be attributed to high crosslink density of network decreases their exposure to environment (262, 263). It was also observed that the cured epoxy resins based on PEHA at mixing ratios (4/1) show defects with both alkaline and acidic aqueous solutions. This can be attributed to the lower crosslink density of network and increase the attack of polar groups of network and dangling chains to acidic and alkaline solutions.

### **3-4-3. Testing Corrosion Resistance of Coating:**

Previous tests showed that the cured epoxy resin with aromatic amine has a relatively chemical resistance than that cured with aliphatic amine. The attention was drawn to study the corrosion resistance in an attempt to prove and confirm this

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speculation. Evaluation by accelerated salt spray (fog) testing was carried out to verify these results. Salt spray tests are probably the most common tests applicable to corrosion resistance and the most controversial [264]. It is well established that salts such as sodium chloride can cause rapid corrosion of ferrous substrates, and it is useful to have information on the behavior of a particular system in protecting such substrate from corrosion both with intact and damaged coating films [265- 267]. However, they are well established, and, despite the problem of reproducibility, are quite useful guides to performance in the absence of longer-term corrosion data. They are this unlikely to be discarded. They are considered to be unrealistic by some workers because of the degree of acceleration of the corrosion process that they achieve and the variability of the extent of damage that is inflicted in some of the tests. There are two tests: the continuous salt spray test and the intermittent. In the present work the continuous salt spray test was used, as described in experimental section, to study the effect of salts on the properties of coating films. The duration times of tests were determined for all cured epoxy systems with PDA and listed in *Tables (3.18) – (3.20)*. The test was stopped after 500 hours. Panels of the cured epoxy system I to VII with PDA as curing agent showing different degrees of corrosion are presented in *Figure (3.22)*.

**Table (3.18): Evaluation Degree of Blistering of Schiff's Epoxy Resins Cured with PDA after Salt Spray Duration (500 h).**

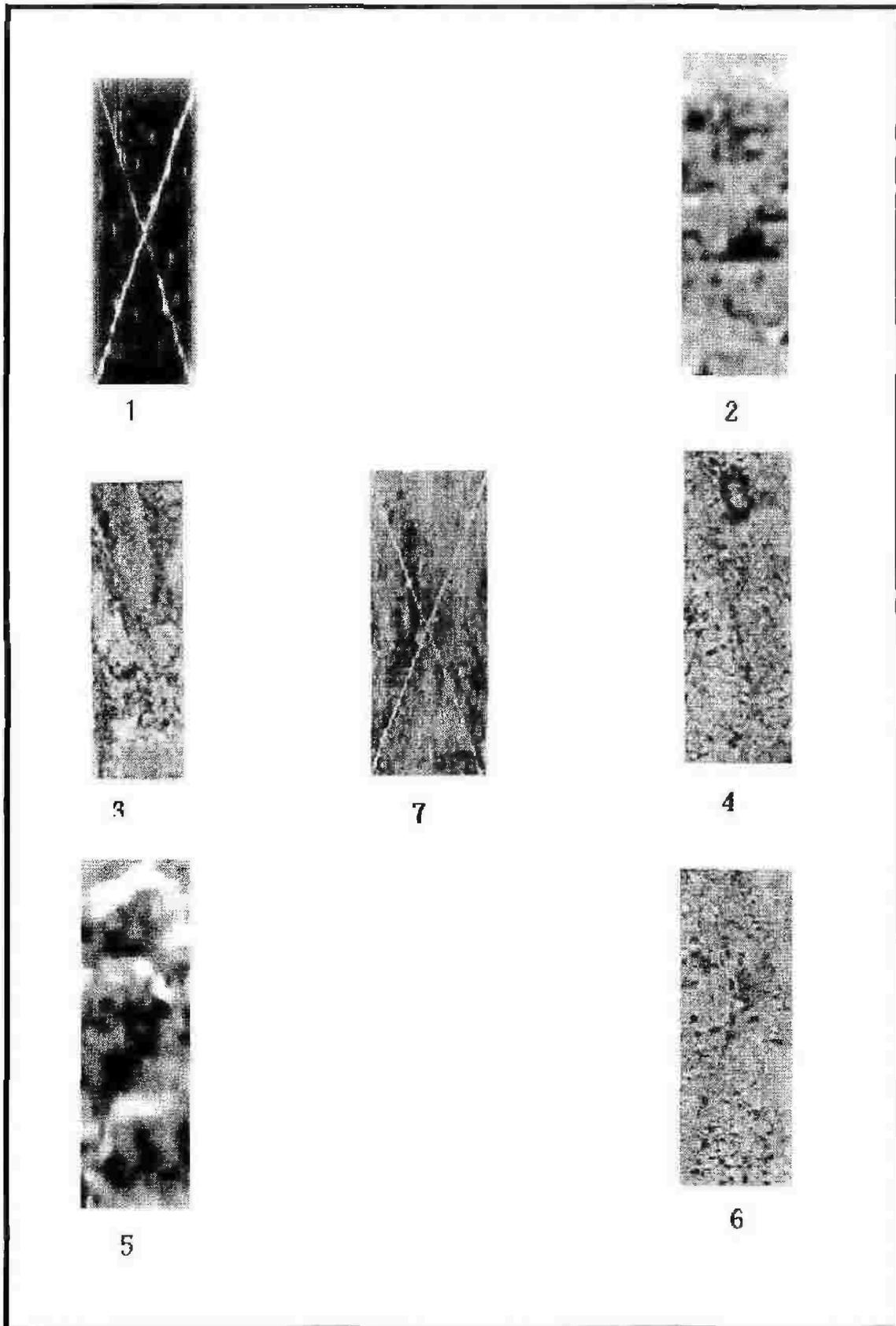
RESIN No.	DEGREE OF BLISTERING	
	SIZE	FREQUENCY
E-I	10	-
E-II	8	M
E-III	8	F
E-IV	10	-
E-V	8	F
E-VI	8	F
E-VII	10	-

**Table (3.19): Evaluation Degree of Scribe failure of Schiff's Epoxy Resins Cured with PDA after Salt Spray Duration (500 h).**

<b>RESIN No.</b>	<b>DEGREE OF SCRIBE FAILURE</b>	
	<b>MILLIMETERS</b>	<b>RATING NUMBER</b>
<b>E-I</b>	0	10
<b>E-II</b>	1.8	7
<b>E-III</b>	1.5	7
<b>E-IV</b>	1.4	7
<b>E-V</b>	2.1	6
<b>E-VI</b>	1	8
<b>E-VII</b>	0	10

**Table (3.20): Evaluation Degree of Rusting of Schiff's Epoxy Resins Cured with PDA after Salt Spray Duration (500 h).**

RESIN No.	DEGREE OF RUSTING	
	RUST GRADE	RUSTING %
E-I	10	0.01
E-II	8	0.1
E-III	9	0.03
E-IV	10	0.01
E-V	7	0.3
E-VI	9	0.03
E-VII	10	0.01



**Figure (3.22): Salt Spray Resistance of Cured Epoxy Resins (I-VII) with PDA after 500 h of Exposure Period.**

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There are three ways to express the results of the accelerated salt spray test after exposure for 500 hours. The first one is the degree of blistering (Size & frequency), the second is the degree of scribe failure and the third is the degree of rusting. The results of salt spray indicate the strong adhesion of coatings by increase of epoxy functionalities. Coating performance was consistently improved for each exposure time for both coatings. This can be attributed to relationships between coating properties and performance. In this respect the adhesion of substrate with coat is the main problem for coating failure [268]. Cracking, flaking scaling or blistering due to under rusting (the latter often being accompanied by brown discoloration of the film) is due to mechanical action by the products of corrosion.

The most familiar corrosion of this type is the rusting of iron exposed to moist atmosphere or water [269, 270]. The initial penetration of rust through the protective coating film is based on the coating constituents [271]. The coating constituents must be able to resist the transfer of ions through the coating and be able to expand and contract with the underlying surface over which it is applied. These ions are chloride, sulfate carbonate, or similar ions, which, on penetrating the film, would start under, film corrosion. So the coatings must be highly adhere to the substrate and must have excellent resistance to water, ionic passage, osmosis, chemical

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weather and electrodosmosis [272- 275] . Resistance to osmosis and electrodosmosis greatly affect coating life. In this respect water or dilute salt water are directed to the coating, they are semi permeable membranes, to which the principle of osmosis definitely applies. If the steel surfaces contain chlorides, sulfates or other ions (on which the coating is applied) will increase water penetration through the coating and leads to blistering and coating failure. So the strong adhesion is required to overcome the physical action of osmosis and electrodosmosis. Strong adhesion also prevents moisture vapor from passing through the coating and condensing in a poor area of adhesion, leading to a blistering of coating. This is of particular significance when it comes to the choice of suitable coating systems. In our epoxy systems it was observed that increasing of epoxy functionality increases the adhesion of coat with steel. This can be referred to the curing of epoxy groups with polyamide hardeners produce hydroxyl groups. It has been shown that the concentration of resultant hydroxyl group has a deleterious effect on the adhesion of the epoxy coating to the steel metal [276]. Careful inspection of data indicates that Schiff base epoxy based on structure VII and I show excellent salt spray resistance. This can be attributed to the ability of these resins to form stable adhesion with steel due to high epoxy functionality and their ability to form coordination bonds with steel [277].

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Accordingly, these epoxy materials are used in petroleum pipeline, tanker and marine coatings, linings for petroleum tanks and tankers, salt barges and ships, general chemical tankers, as well as exterior coatings for the bottoms, boot-topping, and decks.