Thermogravimetric Analysis of Tercopolymer Resins Derived From p-Cresol-Dithiooxamide-Formaldehyde Terpolymer Resin (p-CDF)

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ABSTRACT

Tercopolymers were prepared by the condensation of p-Cresol (p-C)-,dithiooxamide(D) and formaldehyde (F) in the presence of hydrochloric acid (2M) as catalyst with varying molar ratio of reacting monomers. Tercopolymers were characterized by their electronic absorption spectra, NMR spectra, IR spectra, elemental analysis and TGA. Molecular weight of tercopolymer were determined by non-aqueous conductometric titration. The kinetic and thermodynamics parameters such as order of reaction, energy of activation, frequency factor, entropy charge, free energy change and apparent entropy change have been determined. Freeman Carroll and Sharp Wentworth method have been applied for the calculation of kinetic parameters while the data from the Freeman-Carroll method have been used up to determine various thermodynamics parameters. The static (isothermal) TG data were analyzed by use of Sharp-Wentworth method were calculated and it was observed that the p-CDF-IV was more stable than those of p-CDF-I, p-CDF-II and p-CDF-III. This prediction on the basis of static TG data is an agreement with the prediction based on the activation energies and initial decomposition temperatures calculated from the dynamic TG curves.

KEYWORDS-Tercopolymers, Synthesis, Resin, Thermal degradation, Kinetic parameters

INTRODUCTION

Polymers are one of the chief products of modern chemical industry. They are high molecular weight compound containing covalent bonds as the force holding together atoms or smaller molecular fragments. Polymers are macro molecules built up by the linkage of small molecules (monomers) by chemical bond into a long chain. Polymer have influenced our life style in such away that it would not be wrong to say that we are in polymer age. For example, house-hold utensils, clothes, furniture, automobile,space aircraft etc. Research on polymers or giant molecules has been carried out due to their importance, currently attached to the problem of producing material with high temperature resistance. These are so frequently use by people that a common man calls them by names like plastics, fibres, rubbers resins etc. Thermally stable materials are used as high

temperature lubricants, surface coatings, adhesives, fibres, elastomers, construction materials required in high speed aircrafts and space vehicles.

The fundamental concept that high polymers are actually high molecular weight compounds containing covalent bonds as the force holding together atoms or smaller molecular fragments was generally accepted until 1930. The high molecular weight sounds like rubber, silk cellulose, proteins, resins and gums were known to the chemists since long and were believed to be made of colloidal aggregates of small molecules which were held together by some undefined binding force. As the term implies, macromolecular science deals with compounds whose characteristic properties depend mainly on the extraordinary large size of the molecules and synthetic polymeric or macromolecular compounds lies between 104 and 107 polymeric materials received attention and importance only in the recent years. Polymer whether Synthetic or man made are used in daily life in the form of plastics fibres. rubber, paints and coatings. Condensation of phenol or hydroxybenzoic acid with formaldehyde in presence of acid afforded a polymer, while condensation of hydroxybenzoic acid and urea/thiourea with formaldehyde /trioxane in presence of acid yields a terpolymer. These terpolymers are reported to have better acid resistance, better thermal stability and electrical properties than those of phenol-formaldehyde type copolymers. The terpolymers can be used as adhesives, abrasives, binders, fibers. chemical resistant, insulates surface coatings, flocculent, ion-exchangers, antioxidants, semiconductors, dyes, rectifiers, fungicides in plants and living tissues, hair fixatives, hardening, agents, molding materials, fire resistant, thermal and thermo-oxidative stable products etc.

Metal containing conducting polymers are a new and interesting class of materials that combine some of the redox properties of the conducting polymer and some of those of the metal ions. A large number of such polymers have been synthesized and studied and have been found to be of interest because the electronic, optical and catalytic properties of the complexes produced are combined in a processable form. The conventional polymers with an organic backbone are characterized by high viscosity and longrange elasticity, useful for their applications in technology but they suffer from a disadvantage that most of them break down on heating in air below 250°C commercial products. The polyethylene, polyamide, polyester, fiber etc. are well known examples of organic polymers. The high density polyethylene so formed is relatively hard, still and consists of mainly straight chains.

Tercopolymer are macromolecular entities which form an integral part of the backbone. Tercopolymers are found to be amorphous powder or crystalline resinous in nature and form special class of polymers which are widely known for their uses. Condensation of phenol or hydrobenzoic acid with formaldehyde in presence of acid afforded a polymer, while condensation of hydrobenzoic acid and biuret with formaldehyde or trioxane in presence of acid as catalyst yields a Tercopolymer. This tercopolymers in general are found to be insoluble in most of the common organic solvent and are fuseableto clear melts. These Tercopolymer have better thermal stability and electrical properties than those of phenol - formaldehyde type copolymers. The tercopolymers can be used as ion-exchangers, semi-conductors, antioxidants, hardening agents, molding materials, rectifiers, dyes, fungicides in plants and living tissues.

The rapidly expanding field of tercopolymers are interestingly attracting attention by scientists and has undergone spectacular growth during the last few years. Tercopolymer are thermally more stable and therefore suitable for withstanding high temperature.

In this paper we describe the study of Freeman-Carroll and Sharp-Wentworth methods to evaluate activation energy and thermal stability of newly synthesized tercopolymer resin. Kinetic parameters have been determined by the application of Freeman-Carroll and Sharp-Wentworth methods. The p-APDF terpolymer resins have been synthesized by the condensation process and purified. These are yellow color and are soluble in DMF, DMSO, aqueous KOH, and NaOH and insoluble in almost all organic and inorganic solvents.

EXPERIMENTAL

Chemicals : All the chemicals used were of Analytical R. grade.

Instruments used:

The apparatus required for a thermogravimetric analysis consists of the components.

1) A sensitive analytical balance.
2) A furnace.
3) A furnace temperature controller program
4) A recorder which provide a plot of sample. The plot is known as thermogram.

This is the entire experimental set-up for the thermogravimetric analysis, known as thermobalence. A wide range of commercial instruments are available and all of these have many common features. The thermograms of the terpolymer resins under present investigation were carried out at Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Anand, Gujarat.

Synthesis of p-Cresol(p-C)–Dithiooxamide(D)–Formaldehyde (F) Terpolymer Resin.

The four different types of p-CDF terpolymer resins have been successfully synthesized and abbreviated as given in Table 1.

Synthesis of p-CDF-I terpolymer resin

The new terpolymer resin p-CDF-I was synthesized by condensing para cresol (1.08 g, 0.1 mol) and dithiooxamide (1.20 g, 0.1 mol) and formaldehyde (7.50 ml, 0.2 mol) in molar ratio of 1:1:2 in the presence of 2M (200 ml) HCl as a catalyst at 122ºC ± 2ºC for 5 hrs in the round bottom flask attached with water condenser and was heated in oil bath with occasional shaking to ensure thorough mixing. The temperature of oil bath was controlled by dimerstat. The resinous cream product obtained was removed immediately as soon as the condensation reaction was over. The reaction is shown as follows in Fig. 1.

Purification of Resins :

The separated terpolymer resin was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove p-cresol-formaldehyde copolymer which might be present along

with p-CDF terpolymer. The product so obtained was further purified by reprecipitation technique. For this purpose, the terpolymer resin was dissolved in 10% aqueous sodium hydroxide solution, stirred well, filtered, and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v concentrated hydrochloric acid/distilled water) with constant and rapid stirring to avoid lump formation. The process of re-precipitation was repeated twice. The terpolymer sample p-CDF-I thus obtained was filtered and washed several times with hot water, dried in air, powdered and kept in vacuum desicator over silica gel. The yield of the terpolymer resin was found to be 81%. The reaction is shown as follows.

Similarly other terpolymer resins p-CDF-II, p-CDF-III and p-CDF-IV were synthesized by varying the molar ratios of the starting materials viz. (2:1:3), (3:1:4)

and (4:1:5), respectively with little variation of experimental conditions. The samples, yields and reaction details are tabulated in Table 1.
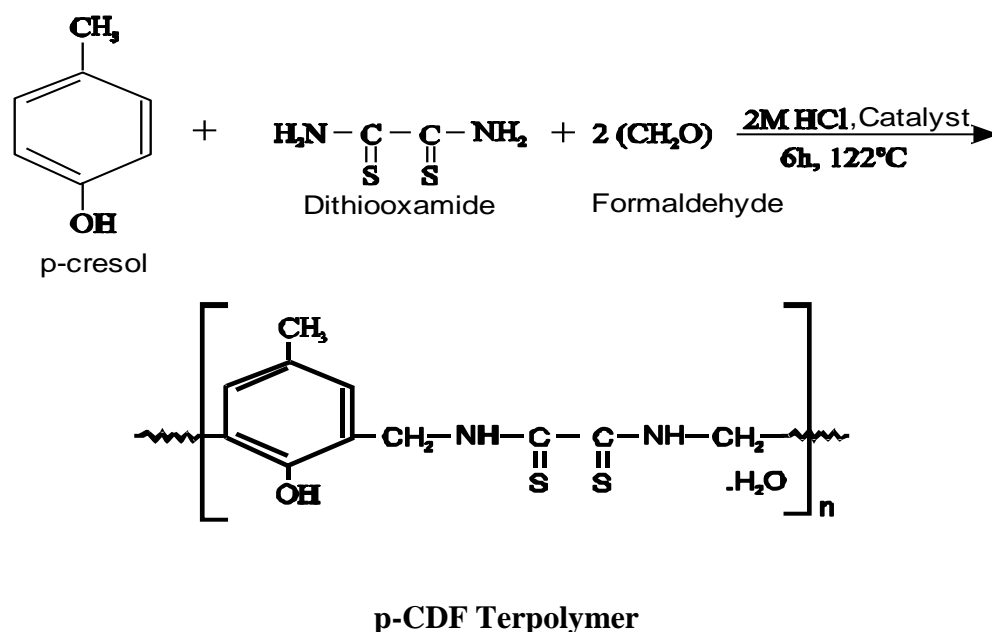

p-CDF Terpolymer

Fig. 1 Reaction and Suggested Structure of Representative

p-CDF-I Terpolymer Resin

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a technique in which we study the decomposition of mass at various temperatures. In TGA a sensitive balance is to be used to follow the weight change of the sample as a function of temperature and the thermogravimetric curves (thermograms) were recorded between mass losses versus temperatures. TGA study gives the information of the sample composition, its thermal stability, its thermal

decomposition and kinetic parameters. The thermograms of all newly synthesized terpolymer samples were recorded on Perkin Elmer Purix TGA, DTA-7 thermal analyzer at heating rate of 10ºC per minute and in nitrogen atmosphere up to 800ºCat Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Anand, Gujarat.

Determination of Thermodynamic Parameters

Thermogravimetry is useful technique to study the thermal stability of polymers. It gives useful information of polymer properties. In this technique, change in weight of polymer sample is observed with increasing temperature. At low temperature (100 -150ºC) there is a loss of only moisture while at higher temperature, polymer starts degrading. The temperature range from which polymer starts degrading and to the certain temperature at which it decomposes completely is called decomposition temperature range. In many polymers, TGA curve follows relatively the simple sigmoid path. The shape of TG curve depends upon the following thermodynamic kinetic parameters.

1) Order of reaction 'n'
2) Frequency factor 'A'
3) Activation energy 'Ea'
4) Change in the entropy 'ΔS'
5) Free energy change 'ΔF'
6) Apparent entropy 'S*'

The value of these parameters can be of major importance in the elucidation of mechanism involved in polymer degradation and in estimation of thermal stability. TG curves may be complex, if a material degrades by multistep mechanism. Numbers of methods have been proposed for estimating kinetic parameters from TGA studies [5, 6]. These methods are Freeman-Anderson [3], Coats and RedFem [2], Broido [1], Sharp-Wentworth [7], Freeman-Carroll [4] methods etc. All these methods are based on the assumption that thermal and diffusion barriers are negligible and Arrhenious equation is valid.

In the present investigation Sharp-Wentworth and Freeman-Carroll methods have been employed for determination of thermodynamic parameters of thermal degradation of the synthesized and purified terpolymer resins with the help of non-isothermal pattern.

Table 1

Synthesis and Physical Data of p-CDF Terpolymer Resins

Terpolymer Resin Abbreviation	Reactants			Molar ratio	Catalyst 2M/HCl (ml)	Reflux Temp. (K)	Time (hr)	Yield (%)	Melting point (K)
	Para cresol p-C (mol)	Dithiooxamide D (mol)	Formal dehyde F (mol)						
p-CDF-I	0.1	0.1	0.2	1:1:2	200	393	5	77	434
p-CDF-II	0.2	0.1	0.3	2:1:3	200	393	5	80	439
p-CDF-III	0.3	0.1	0.4	3:1:4	200	393	5	85	447
p-CDF-IV	0.4	0.1	0.5	4:1:5	200	393	5	87	451

p-Cresol-Dithiooxamide-Formaldehyde Terpolymer Resin (p-CDF)

The p-CDF terpolymer resins which are synthesized taking various molar ratios of monomers in 4 different ratios. They are found to be in green colour and are soluble in DMF, DMSO, aqueous KOH, NaOH and are insoluble almost in all other organic and inorganic solvents.

RESULTS AND DISCUSSION

Thermogravimetric Analysis (TGA)

Decomposition patterns (Thermograms) of synthesized four p-CDF terpolymer resins are shown in Fig. 5, 6, 7 and 8. A brief account of thermal behavior of these terpolymer resins is given below. But for reason of economy of space the thermal data of only one representative case p-CDF-I has been given in Table 3 for Freeman-Carroll method. The thermograms were recorded in the temperature range of 40ºC to 800ºC, showing three stages of degradation reaction. By studying TG of p-CDF terpolymer, indicates that these terpolymers are thermally stable at elevated temperature.

Thermogravimetry of p-CDF-I terpolymer resin

Thermogram of p-CDF-I is shown in Fig. 5 and depicts three stages of decomposition in the temperature range of 40ºC to 800ºC, after initial loss of water molecule (6.42% found and 6.66% calculated). First decomposition step starts from 125-360ºC which represents the degradation of -CH$_3$ group attached to aromatic benzene nucleus and hydroxyl group (18.20% found and 18.25% calculated). Second step decomposition starts from 360ºC to 410ºC corresponding to 66.42 mass loss, which may be due degradation of aromatic benzene nucleus, and dithiooxamide against calculated 66.05% loss. Third step decomposition starts from 410ºC to 800ºC (93.34% found and 100% calculated) leaving behind carbon moiety. The thermal degradation may be due to increasing thermal vibration, which increasing molecular strain due to increasing cross linking and ultimately unstability increases. Therefore to maintain stability the molecule undergoes degradation at each temperature range.

Thermogravimetry of p-CDF-II terpolymer resin

Thermogram of this polymer depicts three decomposition stages with initial loss of water molecule (4.64% found and 4.61% calculated) in temperature range of 40 – 150ºC. First step of decomposition starts from 150ºC and end to 370ºC, which may be due to degradation of two methyl groups (-CH$_3$) and two hydroxyl groups attached to two aromatic benzene rings (20.71% found and 20.96% calculated) due to increasing strain in the molecule by increasing temperature. Second step of decomposition starts from 370ºC and end to 520ºC corresponding to complete loss of two aromatic benzene nucleus and side chain attached to it (99.02% found and 100% calculated) leaving behind carbon moiety. The molecule undergoes degradation due to increasing unstability and to maintain the stability.

Thermogravimetry of p-CDF-III terpolymer resin

Mass loss curves shows three stages of decomposition with initial loss of water molecule (3.14% found and 3.57% calculated) in the temperature range of 40 – 160ºC. First step starts from 160ºC to 360ºC (22.21% found and 22.61% calculated), may be due to loss of three methyl and three hydroxyl groups of aromatic nucleus, due to increasing the strain and by increasing cross linking. Second step starts from 360ºC to 600ºC (67.14% found and 67.26% calculated), may be due to loss of three aromatic benzene nucleuses, due to increasing unstability by increasing thermal vibrations. Third step starts from 600ºC to 800ºC (84.23% found loss and 84.62% calculated loss), may be due to loss of side chain of triazine ring consequently, residue may be assigned as 1, 3, 5 triazine (15.77% found and 15.38% calculated). The molecule undergoes degradation due to unzipping strain and unstability developed due to increasing cross linking and increasing thermal vibration.

Thermogravimetry of p-CDF-IV terpolymer resin

The decomposition curve depicts three steps in degradation after loss of crystalline water molecule (2.10% found and 2.40% calculated). First step of degradation starts from 180ºC to 360ºC, which may be due to degradation of five methyl and four hydroxyl groups attached to four aromatic benzene nuclei (23.64% found and 23.92% calculated), may be due to increased strain in the molecule. The second step starts from 360ºC to 640ºC (77.16% found and 77.55% calculated), which may be due to degradation of four aromatic benzene nuclei. The third step decomposition starts from 640ºC to 8000ºC corresponding (89.06% found and 89.24% calculated), may be indicated the decomposition of side chain ($-CH_2-NH$) attached to triazine ring. Consequently the residue is left over, corresponding to 10.94% found and 10.76% calculated may be due presence triazine ring. The increasing temperature may develop the strain in the molecule which causes the degradation in the molecule.

By using thermal decomposition data the graphs were plotted by applying Sharp-Wentworth method (Fig.2) . The thermal activation energy plot and Freeman-Carroll plots for p-CDF terpolymer resin have depicted in Fig. 3 and 4 respectively. The thermodymanic parameters have been calculated on the basis of thermal activation energy by using Freeman-Carroll method. The various kinetic parameters such as change in the free energy (ΔF), change in entropy (ΔS), frequency factor (Z), apparent   entropy (S*) and order of the reaction (n) are given in Table 2.

Table 2
Results of Thermogravimetric Analysis of p-CDF Terpolymer Reins

Terpolymer resins	Half Decomposition Temp. (K)	Activation Energy Ea, (KJ)/mol		Entropy change ΔS (J)	Free energy ΔF (KJ)	Frequency factor (Z) (Sec.$^{-1}$)	Apparent entropy (S*) (KJ)	Order reaction (n)
		FC	SW					
p-CDF-I	683	23.68	22.97	-8.11	2.57	16.95	-11.26	1.03
p-CDF-II	773	27.15	28.56	-8.14	2.58	17.62	-11.32	1.05
p-CDF-III	783	35.34	34.89	-8.76	2.76	18.72	-11.41	1.07
p-CDF-IV	802	37.94	38.72	-8.91	2.89	19.21	-11.72	1.09

SW – Sharp-Wentworth Method;   FC – Freeman–Carroll Method

Table 3

Thermogravimetric Data and Decomposition Temperature Range of

p-CDF Terpolymer Resins

Terpolymer Resins	Loss of crystalline water molecule		Decomposition step, temperature range (ºC), mass loss (%) and species degraded						Mass of residue left over (%)
			First Step (loss of methyl & hydroxyl group)		Second Step (loss of aromatic phenyl nucleus)		Third Step (loss of side chain of dithiooxamide)		
	Temp. range (ºC)	Mass loss (%)	Temp. range (ºC)	Mass loss (%)	Temp. range (ºC)	Mass loss (%)	Temp. range (ºC)	Mass loss (%)	
p-CDF-I	40-125	6.42(F) 6.66(C)	125-360	18.20(F) 18.25(C)	360-140	66.42F) 66.01(C)	410-800	99.34(F) 100.00(C)	0.66(F) 0.00(C)
p-CDF-II	40-150	4.64(F) 4.61(C)	150-370	20.71(F) 20.96(C)	370-520	70-34(F) 70.06(C)	520-800	99.02(F) 100.00 (C)	0.98(F) 0.00 (C)
p-CDF-III	40-160	3.57(F) 3.52(C)	160-390	22.49(F) 22.35(C)	390-550	76.77(F) 76.96(C)	550-800	99.56(F) 100.00 (C)	0.44(F) 0.00 (C)
p-CDF-IV	40-165	2.49(F) 2.85(C)	165-395	23.21(F) 23.20(C)	395-570	81.06(F) 81.27(C)	570-800	97.41(F) 100.00 (C)	2.59(F) 0.00 (C)

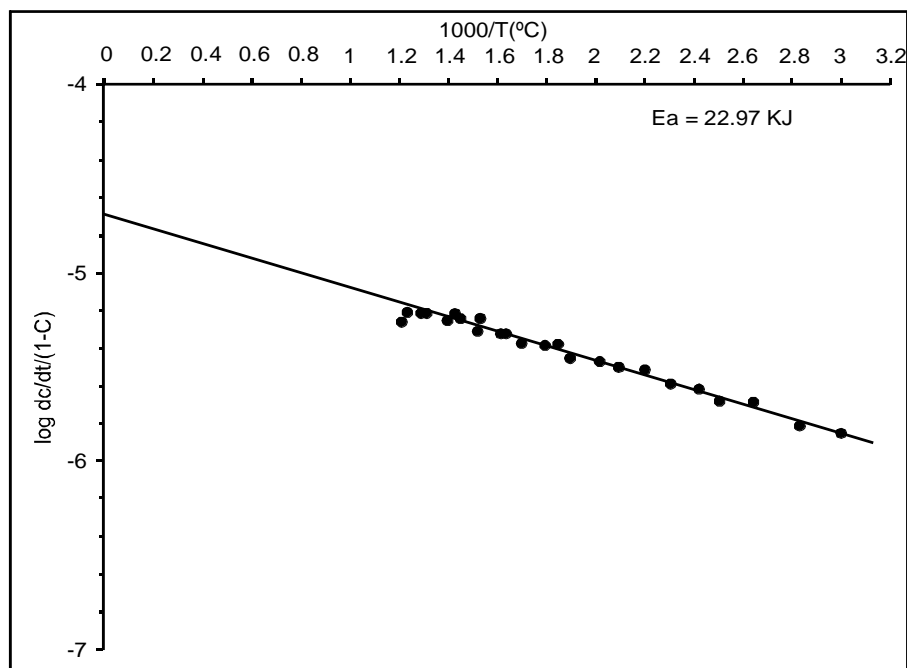Sharp - Wentworth Plot of Terpolymer - p-CDF-1

Fig.2 Sharp-Wentworth Plot of p-CDF-I Terpolymer Resin
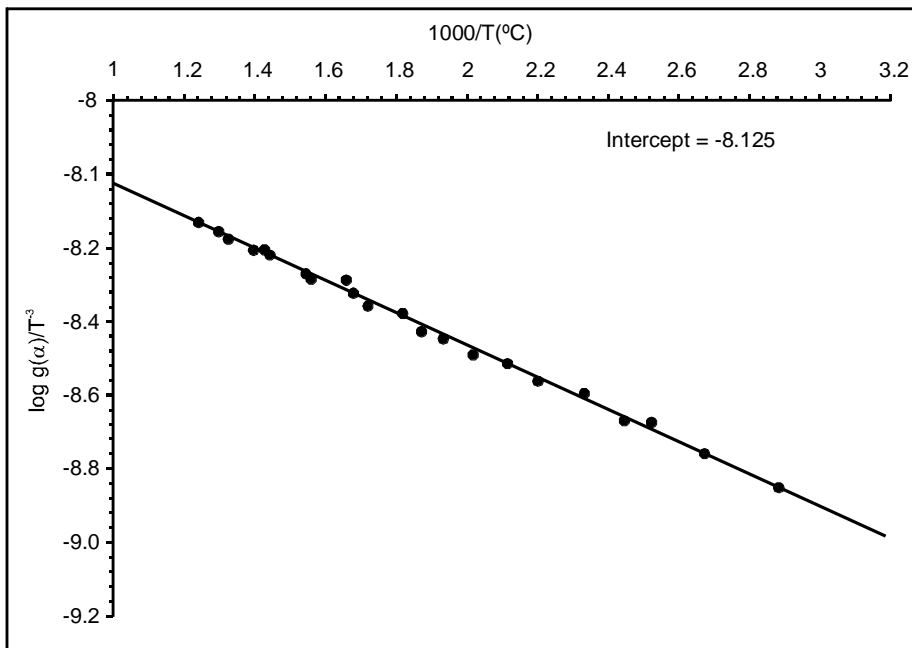
Freeman-Carroll Plot of Terpolymer - p-CDF-1

Fig.3 Thermal Activation Energy Plot(Freeman-Carroll Plot)

of p-CDF-I Terpolymer Resin

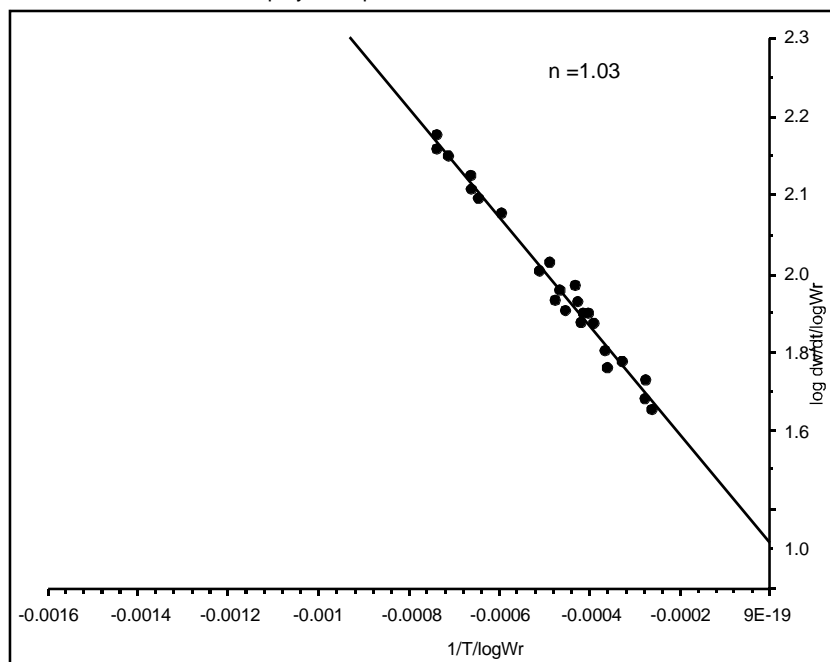Freeman-Carroll Plot of Terpolymer - p-CDF-1

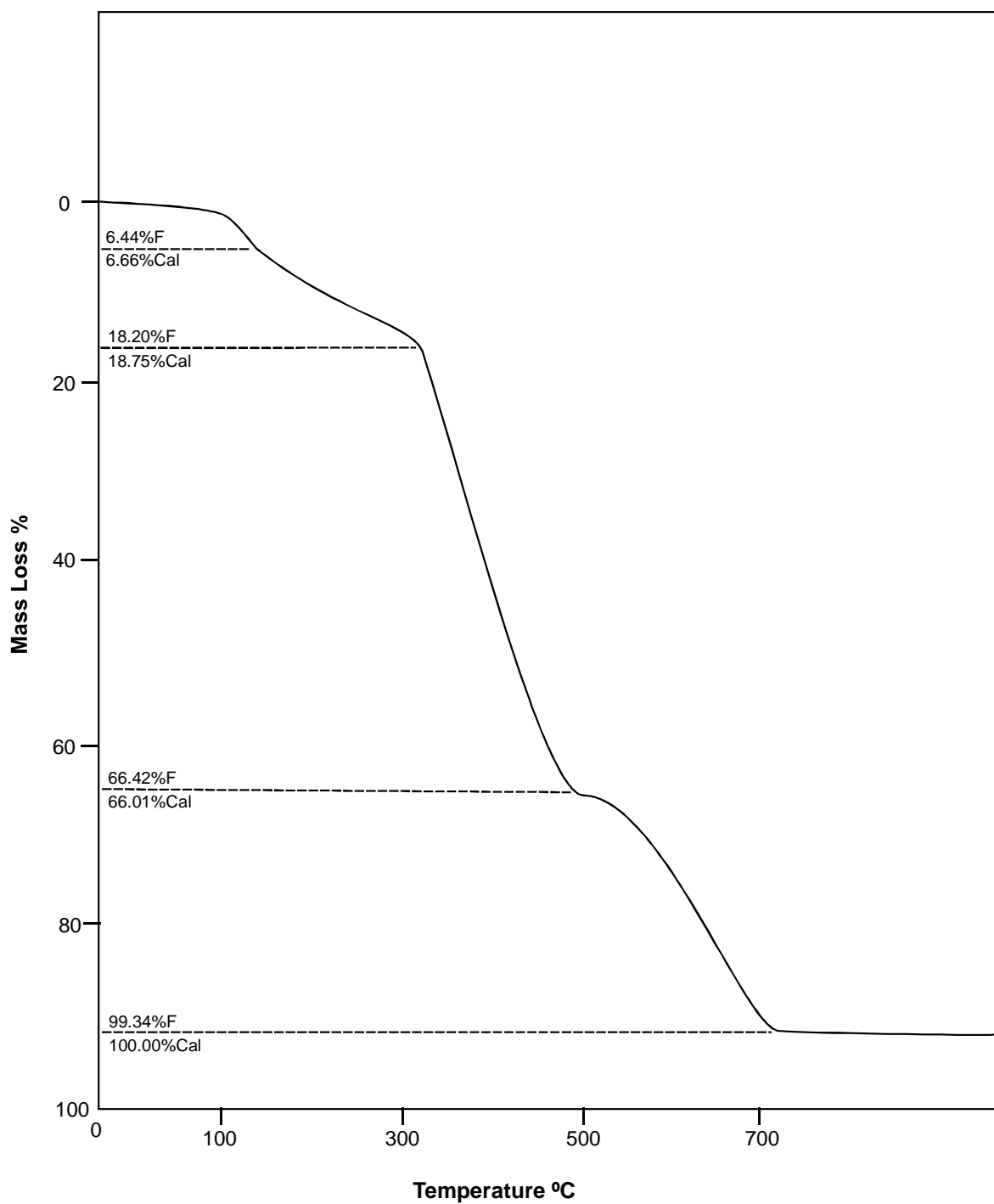**Fig.4 Freeman-Carroll Plot of p-CDF-I Terpolymer Resin**

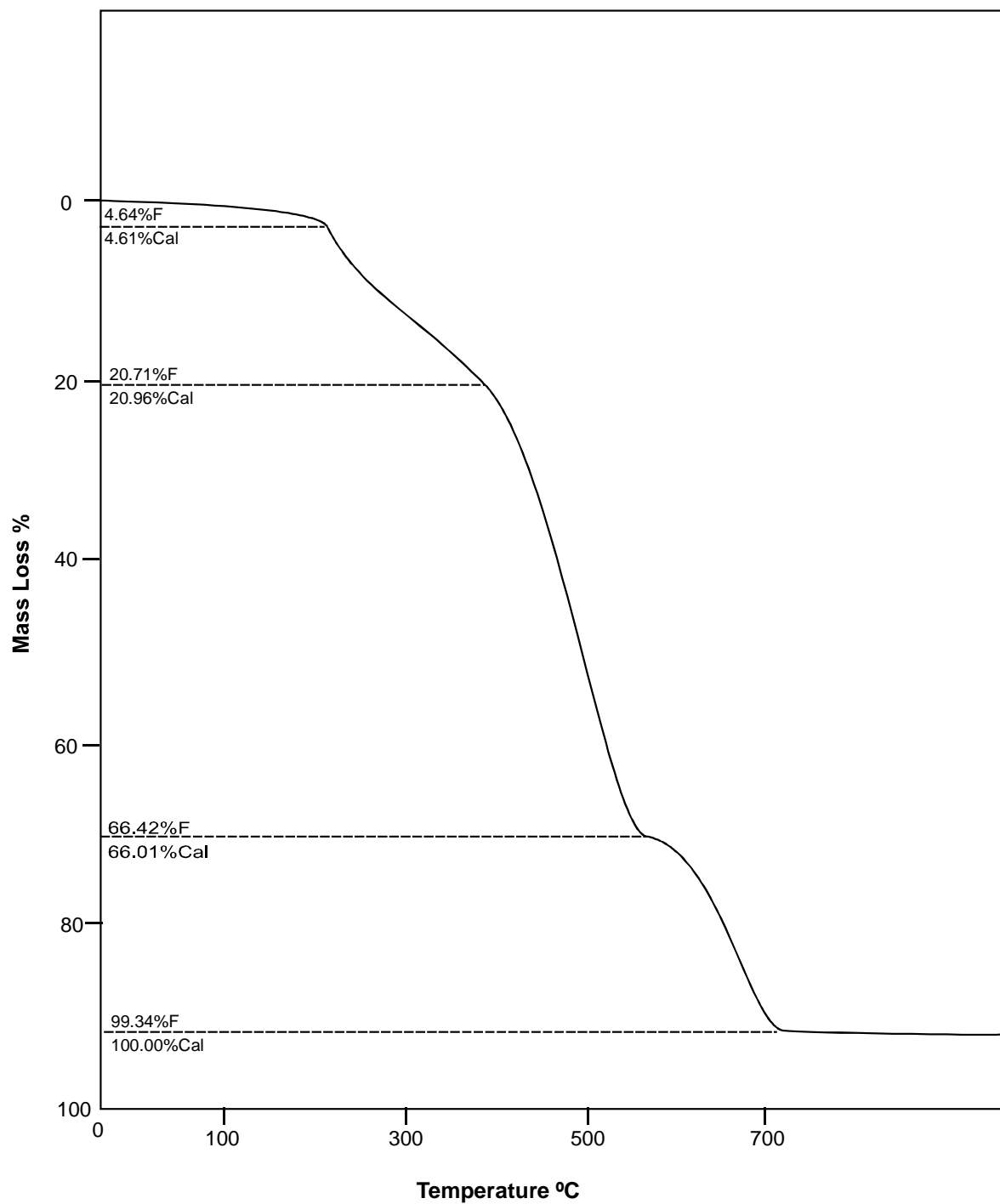**Fig. 5 Decomposition Pattern of p-CDF-I Terpolymer Resin**

Fig. 6 Decomposition Pattern of p-CDF-II Terpolymer Resin

Fig. 7 Decomposition Pattern of p-CDF-III Terpolymer Resin

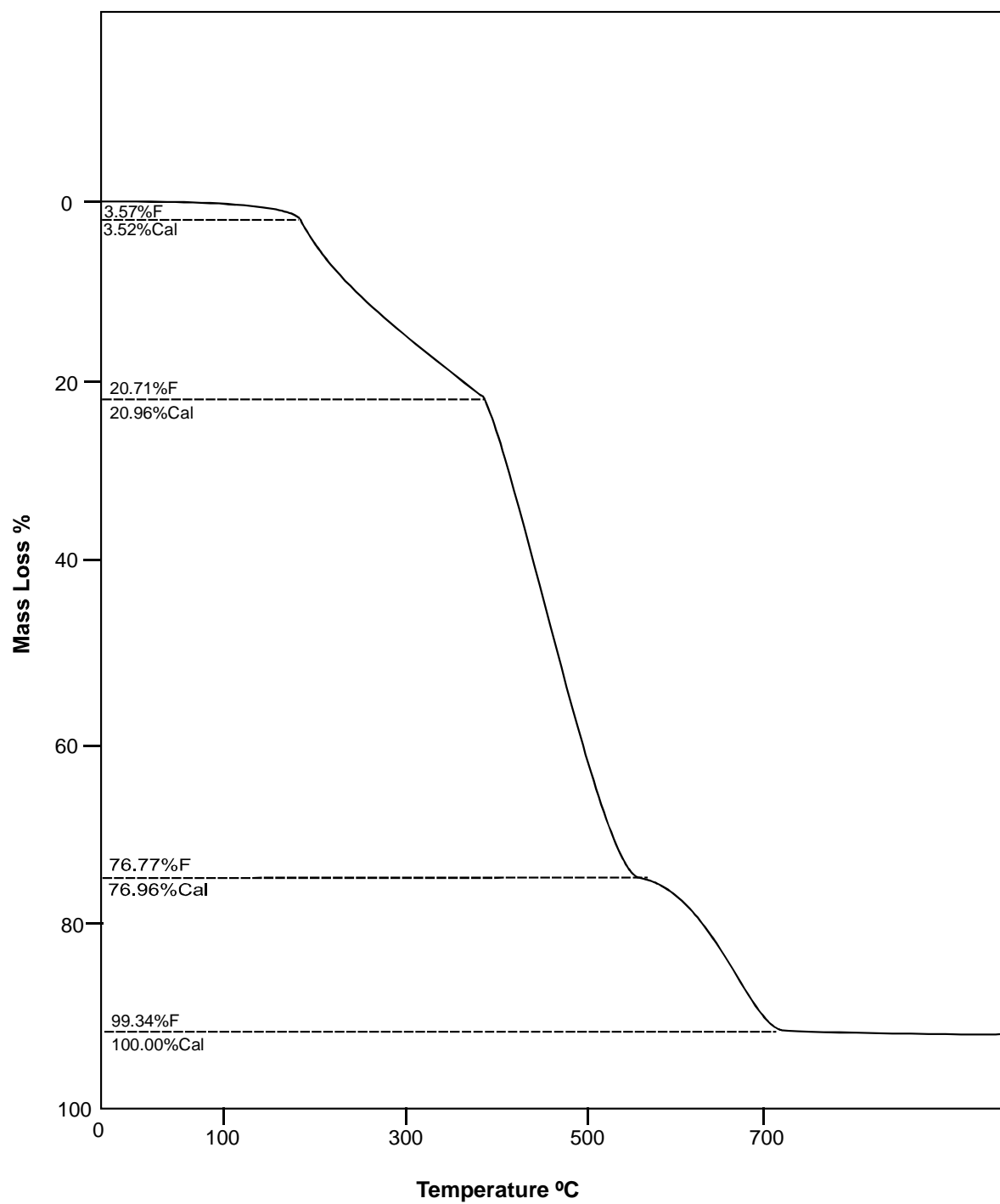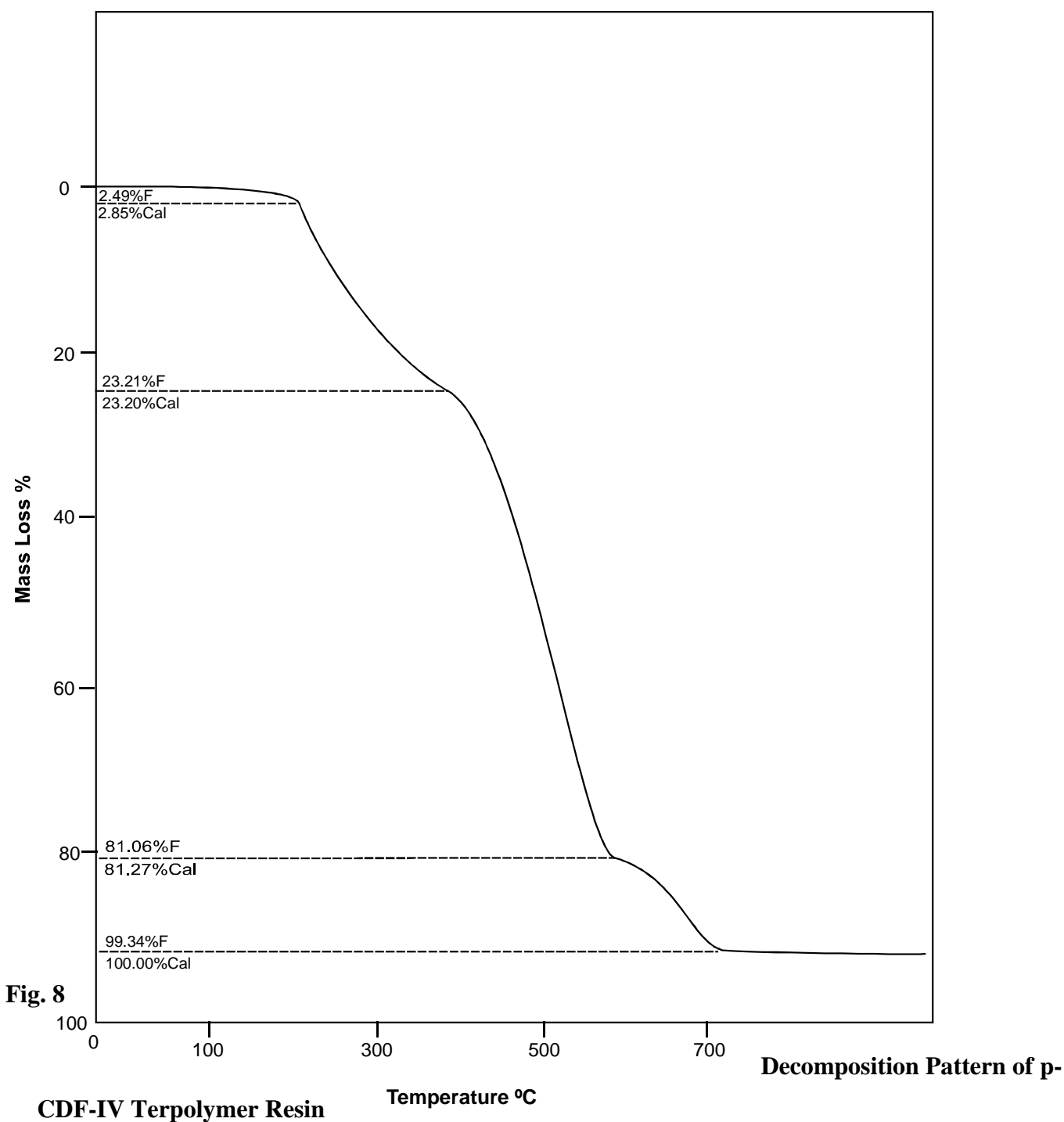**Fig. 8**   **Decomposition Pattern of p-**
CDF-IV Terpolymer Resin

The decomposition process is three steps process in which there is a initial mass loss due to slow evolution of water molecule which may be entrapped in the terpolymer molecule in the form of crystalline phase [9]. In the first step methyl and hydroxyl groups may be degraded, in second step aromatic benzene nuclei degraded, in third step side chain of dithiooxamide is degraded and consequently residue of dithiooxamide is left behind after complete degradation reaction. The degradation may be due to the strain developed in the resin molecule by increasing temperature. To decrease the strain and to maintain stability, terpolymer undergoes degradation.

The activation energy calculated by both Sharp-Wentworth and Freeman-Carroll methods are found in good agreement. The sequence of thermal stability is found to be p-CDF-I <p-CDF-II <p-CDF-III <p-CDF-IV. The sequence reveals that as molecular weight of terpolymer resin increases, the thermal stability also increases. But the thermal stability is independed on the molecular weight and in fact depend upon thermal activation energy, initial and half decomposition temperatures, which may be supported by the increasing order of melting points [9, 12, 8, 13, 14]. The thermodynamics parameters have been calculated from the data of Freeman-Carroll method, found to be nearly comparable for four p-CDF terpolymer resins, this indicating the common mode of decomposition reaction mechanism.

The frequency factor (Z) is the factor which gives the information of rate of frequency of the reaction speed. The values of Z for p-CDF terpolymer samples are found to be low, indicating that the rate of decomposition reaction may be slow which may also be supported by the negative value of change in entropy (ΔS). The negative value of ΔS indicates the order of disorder is less i.e. the decomposition may be carried out with more orderly, indicating slow rate of decomposition. Also, with the Sharp-Wentworth method and Freeman-Carroll method the plots obtained are not perfectly linear at all temperatures. At some range of temperature, the lines are found to be straight, which indicates the decomposition reaction is not perfectly first order, throughout the complete reaction. In certain range of temperature, the decomposition reaction might be first order. Therefore, we assumed the first order kinetic of decomposition reaction (n=1) by neglecting some abnormal points [11, 10]. As the thermal decomposition reaction is very complicated, no remarkable conclusion can be obtained from the thermal study of p-CDF terpolymer resins.

On the basis of all the physico-chemical and spectral evidences and foregoing results and discussion the most probable structures have been proposed for p-CDF terpolymer resins under investigations as shown in Fig. 9.
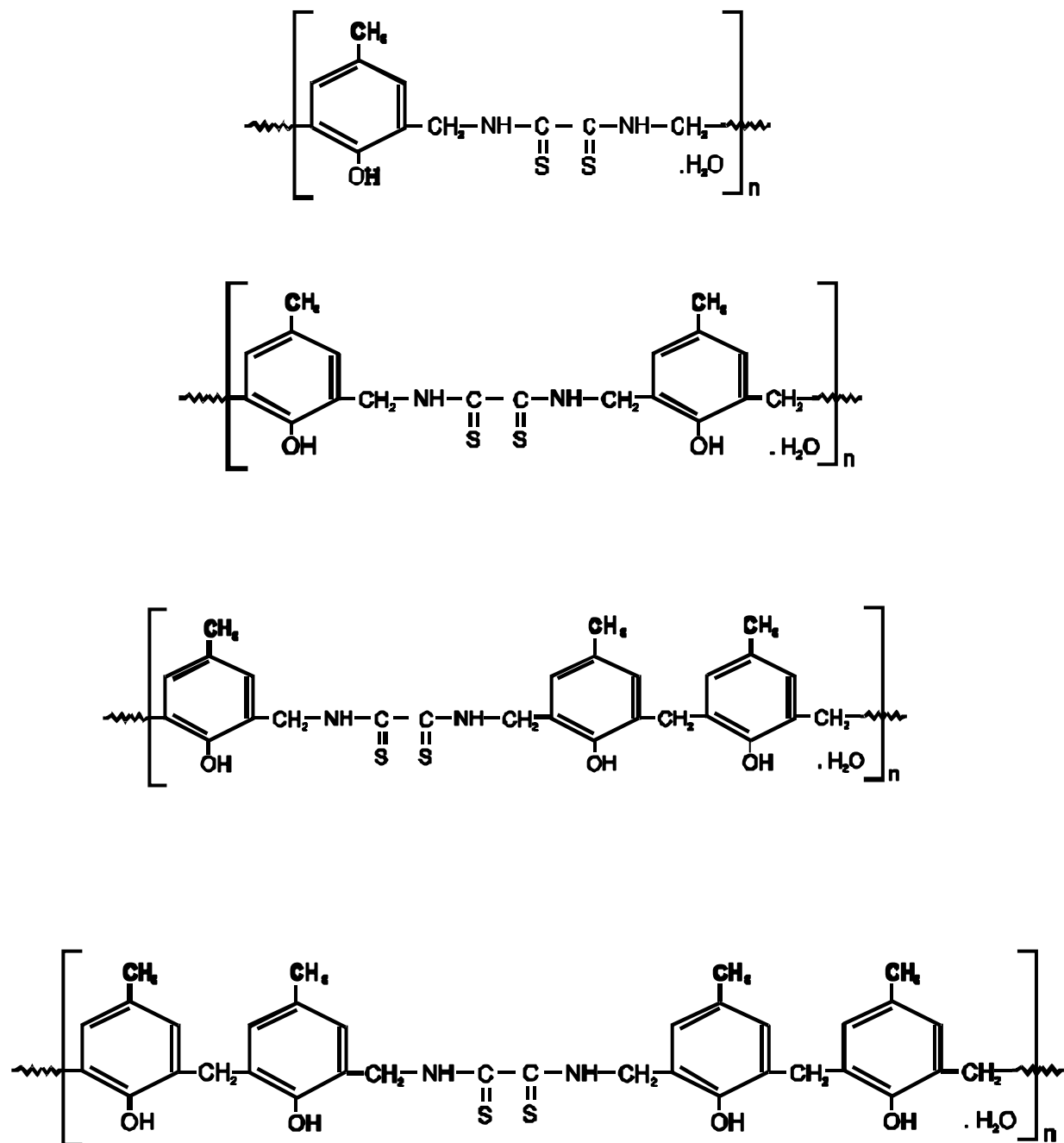
Fig. 9. Structures of p-CDF Terpolymer Resins

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