CHAPTER V

THERMAL ANALYSIS

General Survey

Thermal methods of investigation, generally referred to as thermal analysis or thermoanalytical techniques, have found wide applications in recent years(1). These may be defined as experimental methods for characterizing a system (element, compound or mixture) by measuring changes in physico-chemical properties as a function of increasing temperature with time(2). The chief methods generally used are :

(1) Thermogravimetry (TG)
(2) Differential thermal analysis (DTA)
(3) Differential scanning calorimeter (DSC)
(4) Thermomechanical analysis (TMA)
(5) Electrothermal analysis (ETA)
(6) Thermal depolarization analysis (TDA)
(7) Depolarized light intensity analysis (DLI)
(8) Thermo-optical analysis (TOA)
(9) Evolved gas analysis (EGA) and
(10) Evolved gas detection (EGD).

These techniques provide informations relating to certain physical and chemical phenomena, which are listed below :-

Physical change	Chemical changes
Crystalline transition	Chemisorption
Second order transition	Desolvation (dehydration)
Fusion	Decomposition

Vaporisation
Sublimation
Absorption
Adsorption
Desorption
Dielectric parameter
Light intensity

Oxidative degradation
Solid-state reaction
Solid-gas reaction
(Oxidation or reduction)
Volatile product

Thermogravimetry (TG) monitors the weight changes in a sample as function of temperature. It is also considered to be one of the most important methods for studying polymer stability. It gives information concerning the thermal stability and composition of the original sample, the composition and stability of intermediate compounds and the composition of the residue.

However, there are other unique applications of this technique not well recognized, such as determination of additives e.g. plasticiser content in poly (vinyl butyral) resin(3,4), characterization of polymer blends and copolymers(3,5,6). TG has also been used for studies on flame retardance (7-12), crosslinking (13,14), track resistance (15), and thermal life(16,17). This dynamic method provides more rapid measurements over a wide temperature range. For Investigation of complex systems, it is often desirable to couple TG with other analytical techniques such as DTA, gas chromatography (GC), mass spectroscopy, Infra red (IR) spectroscopy, thermomechanical analysis (TMA), Electrothermal analysis (ETA), thermooptical analysis (TOA) and thermo-evolution analysis (TEA).

In classical kinetic studies the reaction is carried out at a constant temperature as a function of time. Substances of comparatively simple structure are generally studied and standard measuring techniques are usually adequate.

In the field of polymer science, the chief use of TG has been to study the thermal decomposition of polymeric materials. Isothermal thermogravimetry has been used for this purpose since 1949, when Jellinek(18) first studied the pyrolysis of polystyrene in vacuum with quartz thermobalance. Modorsky(19) applied the isothermal technique to the study of polymer pyrolysis. Since 1959, the non-isothermal thermogravimetry is employed to study the thermal decomposition of polymers.

To obtain meaningful results from thermogravimetry , it is necessary to consider the effects of the following factors on weight loss or gain in weight as function of temperature or time.

(1) Amount, film thickness, or particle size of sample.
(2) Speed at which weight changes are recorded.
(3) Shape of the crucible containing the sample.
(4) Rate of heating
(5) Change in the density of ambient atmosphere.

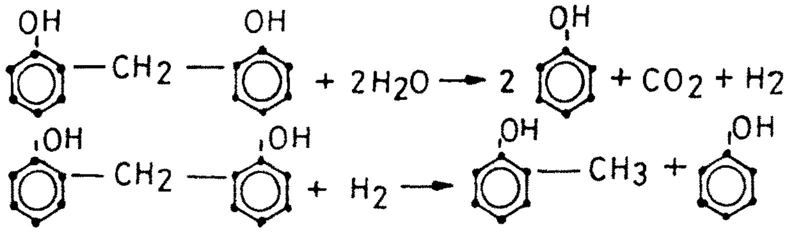
Molecular weight, size distribution, structure of chain ends, existence of branches, presence of weak links and inclusion of impurities may have a pronounced influence on the pyrolysis of sample. However, it is possible to measure or to approximate some of these parameters for some linear polymers.

The above description provides a brief review of some of the dynamic thermal methods more commonly used recently. As mentioned previously thermal analysis is now generally recognized as one of the basic analytical tools for polymer characterization. Polymerization and curing of monomeric systems can also be studied with the help of many thermal techniques with respect to enthalpy changes or kinetics and mechanism. In the other direction, depolymerization and decomposition of polymers under controlled conditions can also be investigated and so also the analysis of reaction products, using any of the techniques described earlier.

Thermal Analysis of phenolic Resins

In all the work to which references have so far been made, the structure of the resins has been determined by the isolation of definite compounds from the condensation. The problem has also been approached by a study of the thermal decomposition products of the cured resin, or by a study of the products obtained by prolonged digestion with sodium hydroxide.

In 1921 Herzog (20) digested various phenolic resins with sodium hydroxide, and found that part of the phenol could be recovered. Allen, Mehrag, and Schmidt(21) heated the cured resin in an autoclave, at 300^{0}C for several hours with 10-15 % sodium hydroxide. The hydrolysis product contained a greater proportion of higher boiling phenols than did the material from which the resin was made. Often phenols were formed which did not occur free in the original material. A considerable amount of hydrogen was also found. While the mechanism of the reaction was not completely explained, it is evidently connected with the rupture of methylene bridges. The net effects may be illustrated by the following equations in which the simplest methylene bridged compound dihydroxydiphenylmethane is chosen as an example.



Megson(22) made a thorough study of the thermal decomposition of novolacs. The resin, after washing with hot water to remove catalyst, excess of formaldehyde and water soluble phenols, was decomposed in a distillation flask by heating upto 450^{0}C. The distillate was collected and the various fractions were identified. Phenol and cresols were obtained from pure phenol-formaldehyde novolacs; from cresol resins, higher methyl homologues of the original phenol were in general obtained, together with dihydroxy-dairylmethanes and substituted xanthenes. the yield of p-cresol was small compared to the ortho isomer; this was interpreted as meaning either;

(1) that p-substitution was of less frequent occurrence than o-substitution,

(2) that decomposition took place more readily at ortho linkages, or

(3) that the resin contained a high proportion of o-linkages,

brought about by preferred condensation in the ortho position.

Waterman and veldman(23) criticized the results of thermal decomposition, largely on the ground that, when a decomposition product like phenol has formed, two hydrogen atoms are required on the spot where the rupture has taken place. If these hydrogen atoms are not available, noncontrollable reactions may occur. To overcome these objections , waterman and veldman decomposed the resin under hydrogen pressure, in the presence of molybdenum catalyst. The principle products from a novolacs were phenol, benzene, cresols and toluene. From resoles, the yield of these products were much less, and ratio of cresols to phenol was much greater.

Megson's work, in general , fully supported the hypothesis that the novolacs resins consist of complex mixture of long chain molecules connected by methylene bridges. These conclusions have been confirmed(24) by studies on the thermal decomposition of 3,5-bis-hydroxymethyl-p cresol.

Ouchi and Honda(25) pyrolyzed several types of phenolformaldehyde resins in vacuum and found that the volatiles formed consisted of methane, carbon monoxide, hydrogen and water. As the number of methylene bridges increased, the amount of methane increased and the carbon monoxide and the water content decreased. It was also found that a large percentage of the carbon atoms in the bridges remained in the residual carbon.

Since oxidation is not easily controlled, more work has been done to understand its mechanism (26). When films of cured resin were aged in air at 200^0C, the rapid appearance of carbonyl group was found in the infrared spectrum along with a decrease in methylene content. Subsequently increase in aldehyde groups and acid groups were found. Since hydroxyl content did not decrease until much later, an initial degradation process was proposed in which the methylene carbon was first oxidized through the carbonyl, aldehyde and acid derivatives before chain scission occured. At this point quinone method might be formed.

Heron(27) used TG - isothermal and gas chromatography techniques for the study of the pyrolysis of phenolformaldehyde resin in air and in inert atmospheres and found that there were two stages in the oxidation of phenolformaldehyde resin, based upon TG curves.

Heating under vacuum or in an inert atmosphere(28) produced the darkening of colour but little or no change in the infrared spectrum was observed. Thus, there are other non-oxidative reactions which produce free radicals in the resin leading to the colour producing changes. Furthermore, measurements of intensities of colour changes during air oxidation of film of varying thickness showed the oxidation to be a surface phenomenon (29) . Studies of the rate of oxidation gave an activation energy of 19.5 Kcals/mole (30). The rate change at about 180^0C, suggested that quinonoid structure was formed primarily above 170^0C. An increase in the rate constants as the amount of reacted formaldehyde is increased gave further support that the methylene groups are being oxidized. Furthermore, a resin based on bisphenol-A (with methyl groups in place of hydrogen atoms of the usual methylene link) was oxidized at only half the rate of phenol based resins. No difference was found in relative case of quinonoid formation at either ortho or para position.

Wenlandt and Hoiberg(31) have studied the thermal analyses of various organic acids. The DTA and TG curves of 5-amino salicylic, 5-nitrosalicylic, acetylsalicylic, 5-bromo salicylic, salicylhydroxamic, α , β - dibromo succinic, m-cresoxyacetic, p-bromomandelic, d-camphoric, diphenic, picric, 2-4 dimethoxy benzoic, m-hydroxybenzoic, 3-4 dihydroxybenzoic , 4-hydroxy, 3-methoxy benzoic acid and tropic acid were obtained from ambient to 350^{0}C. The DTA curves are useful for indentifying the acids.

Jeffrey(32) used TG curves to study the thermal stability of phenolformaldehyde resin in air and offered a generalization that thermal stability decreased with increasing molecular weight of the meta-substituted phenol. In the case of para-substituted phenol, because the number of active portions of the phenol has been reduced from three to two, crosslinking can not as with the meta phenols and reduction in thermal stability is to be expected. The TG of alkyl-substituted phenol-formaldehyde resin showed a large peak at 440^{0}C . After the maximum weight loss has occurred, a steady rate of weight loss was obtained which was attributed to the burning off of a carbonaceous residue.

Learmonth and Wilson(33) studied the thermal stability of differentially catalyzed phenolic resins in the presence of oxygen by means of TG and DTA-techniques. They observed that three different types of DTA curves were obtained.

Pyrolysis of cured one-step resins to 600^{0}C was found to produce water, paraformaldehyde, carbon dioxide, carbon monoxide, methane and some aromatic products(34). The water and paraformaldehyde did not form below 400^{0}C and their presence at 600^{0}C can be accounted for as a result of splitting out of methylol groups. The presence of benzene and toluene indicated that some hydroxyl group has been split off, these would provide a source of oxygen for oxidative reactions. Above 450^{0}C char or carbonaceous residue was formed and carbon monoxide was liberated. The mechanism is apparently through a quinone-type intermediate involving some ring scission and subsequent condensation although there is little analogy for the fragment.

Popov and co-worker(35) also studied the thermal behavior of phenol-formaldehyde resin in air by DTA and TG techniques. In the presence of hexamethyltetramine, the rate of weight loss was less and residue remained, and DTA thermograms of novolacs resins were similar in several ways. The resol resins appeared to harden at lower temperature than the novolacs.

On the basis of carbonyl formation determined by means of infrared techniques Conley(36) found, that the partially cured phenol-formaldehyde resin gave a value of E of 19.5 Kcal/mole whereas the fully cured phenol-formaldehyde resin gave a value of E of 15.6+/- 3.9 Kcal/mole over a temperature range of about 140^{0} - 220^{0}C . It appeared that the initial oxidative degradation weight loss might be associated with the formation of carbonyl compounds.

High-temperature degradation of alkali-catalyzed polycondensates (37) was studied by monitoring changes in elemental composition as a function of time and temperature. The resin, once fully cured at elevated temperatures, all degrade identically despite differences in their phenol-formaldehyde content of the resins.

With the need for more heat resistant materials, studies of the rate of decomposition and products of decomposition have been intensified. TG(38) and DTA(39,40) techniques, long used with inorganic molecules (41), have been applied by a number of workers to phenolic resins. The products of pyrolysis have been studied by vapour-phase chromatography and mass spectrometry and changes in the resin itself have been followed by surveys of infrared spectra. The results of conley and his coworkers(42) have provided the most complete analysis of the degradation of phenolic resins. In his work on the curing and subsequent degradation of phenolic, conley(42) examined the products of phenolic, infrared spectroscopy, differential thermal analysis, and thermogravimetric analysis. Cured phenolic resins have been found more heat resistant than polyesters or epoxy resins but less so than silicone are of interest.

(1) The range from room temperature upto 500^{0}C and

(2) the range from 500^{0}C to 1000^{0}C or higher.

In the lower range there were significant differences noted(41) between the reaction of heat of uncured one-step and two-step resins as might be expected. The one-step resins first showed a slight endotherm when the temperature was increased to 110^0C- 120^0C in the DTA tests. Then an endotherm followed as the resin continued to cure, probably due to the water formed in the reaction. Two step resins showed an endotherm(43) at 80^0C possibly related to the melting of the temperature of the reference material at 150^0C - 155^0C as the resin reacted with hexamethyltermine.

Degradation of the resin began above 230^0C and was endothermic. At about 440^0C another endothermic peak appeared, which might be due to condensation of aromatic rings after the loss of methylene bridges and as a beginning of char formation(44). Weight loss during the period upto 400^0C was significant, but was minor compared to the loss as the temperature was increased to 800^0-1000^0C. Differences were reported to be small between one - and two -step types of phenolic resins in the way in which they lose weight in the high temperature range after they have been cured.

Korahak and co-worker (45) investigated the thermal and thermoxidative degradation of novolac oligomers at 150^0C-900^0C, The properties of oligomers started to change at 300^0C- 400^0C, where the weight losses increased, the oxygen content decreased and oligomers became insoluble in acetone and sodium hydroxide. Gas-liquid chromatography showed that the liquid products obtained after the solidification of the oligomers contained especially water, phenol and cresols. The changes observed in the IR spectra during the treatment originate from a thermoxidative degradation of polymers where in the first place the methylene groups are oxidized to keto groups which produce quinoid and carboxylic groups. The changes observed in the IR spectra indicated the occurrence of transformation of polymeric H-bonds into dimeric bonds. The cross-linking of novolacs proceeds essentially by condensation processes of phenolic hydroxy groups by which aromatic ether bonds were formed. This process facilitated by the transformation of polymeric H bonds with dimeric bonds.

Ouchi(46) observed that on pyrolysis of phenolformaldehyde resin at temperature upto 700^0C, there was no change in the IR-spectrum upto 300^0C, however above this temperature, the hydroxy absorption began to decrease, indicating the diphenyl ether type linkages between C_6H_6 nuclei with the elimination of water. Above 400^0C the changes which occurred in the spectra suggested that dibenzyl ether structures decompose to benzylphenyl ethers and that xanthenes or diphenylene oxide type o-groups are probably formed. Upto 500^0-550^0C methylene bridges decomposed to form C:O or CH_3 groups. Above 500^0C the diphenylether type linkages decomposed rapidly and polysubstitution of benzene nuclei increased. From 600^0C upwards, the aromatic H is also eliminated and the spectra became structure less, perhaps because of the condensation of aromatic nuclei. The oxygen left at this stage may be present as inner-ring-O, as in diphenylene oxide.

The degradation of phenol-formaldehyde polycondensates was investigated by mass spectrometric thermal analysis. The thermal oxidative mechanism proposed by Conley(47) was confirmed. Phenolic homologue products of thermal scission of methylene phenyl bonds, showed high activation energies; oxidative products had activation energies comparable to or slightly higher than that for oxidation of methylene bridges to carbonyl compounds.

The kinetics(48) of decomposition of the phenolic resin and the properties and composition of the gaseous, liquid and solid degradation products were studied. The gases continued CO_2,CO,H, CH_4,C_2H_4,MeOH and HCHO vapour. The liquid products included upto 54 components, 50 % of the dark liquid was phenol and cresols. The liquid mixture also contained MeOH, H_2O, xylenol, naphthols, diphenyl methane and triphenyl methane.

The rate at which each of the products of decomposition is evolved, has been measured by a mass spectrometric analysis in the temperature range from 250^0 to 800^0C (49). The general degradation of phenolic resins is a first-order reaction, the decay being proportional to the amount of active polymer remaining.

Gutsalyuk(50) studied the thermal degradation of hardened phenol-formaldehyde novolacs. At low temperature, loss of weight occurred due to evolution of 5-6% low molecular weight compound and the resins was decomposed at higher than 300^0C. Gaseous and liquid decomposition products were formed at 360-600^0 and at higher than 600^0C, the yield of these compounds became constant.

Thermogravimetry for the determination of kinetic parameters of thermal degradation behaviour of various polymers including polystyrene, epoxy phenolic resin, polyurethanes and poly (tetrafluoro ethylene), has been reviewed by Reich and Levi(51).

Thermogravimetric studies have been reported(52) on the stabilities of resins made from diphenylol propane and formaldehyde. When the aliphatic hydrogen atoms of diphenylol propane were entirely substituted by fluorine atoms, stability of the resins formed with formaldehyde was enhanced but the carbon residue was similar to unsubstituted bisphenol resins. When the central groups of the diphenylol derivative was tetrafluorodichloro prophylidene, the resulting resin was less stable. It was found that the addition of polytetrafluoroethylene to phenolic resins inhibited degradation to a significant extent.

Fleming(53) investigated the thermal properties of a number of nitrosubstituted and analogous non nitro substituted epoxide polymers dramatic increase in char yield and decrease in maximum rate of weight loss were observed for the nitro substituted systems compared to their non-nitrated analogues. These effects were enhanced when highly functional and highly aromatic epoxide resins were used. The sample size and heating rate employed had pronounced effects upon the amount of char formed during thermal degradation. Analysis of char residues indicated hetero ring formation for the nitrosubstituted systems during pyrolysis.

The effect of varying the nature of crosslinks in phenolic resins has been studied by Learmonth(54). Thermal analysis showed that the methylene bridge was stronger under non-oxidative conditions than the isopropylidene linkage. The results were somewhat affected by the degree of cross linking.

The isothermal decomposition of a phenolic resin(55) in a phenolic-carbon cloth composite was measured at approximately 0.1 to 0.2 torr pressure over the temperature range of 105^0 to 718^0C. The kinetics were initially first order and in the later stages second order. An analytical technique was provided for calculating the maximum quantity of resin which would volatilize during decomposition thereby obviating the necessity of measurements for extended time periods. Plots of equilibrium constant versus the reciprocal absolute temperature showed that two equilibria were involved, one which predominates upto 352^0C and the other above this temperature. The heats of reaction were: 2.2 and 15.3 Kcal/mole. The first value has been considered to be associated with hydrogen bonding and the second with the decomposition and oxidation activation energies.

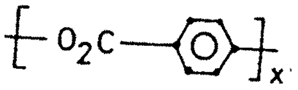
It has been also reported that the primary short time (<=0.6Sec) pyrolysis(56) products of phenol-formaldehyde resin at 800^0C were benzene, toluene,xylene, water,hydrogen,methane,carbon monoxide, carbon dioxide and unsaturated hydrocarbons resulting from side reactions of primary products.

The hardening of novolacs(57) by hexamine was studied at pressure upto 5000 kg/cm^2. The application of pressure DTA method to the thermal curing of some dioxymethylated parasubstituted phenols indicated that the endothermic peak observed at about 75^0C at ambient pressure was due to the melting of the substance and formation of ester bonds.

Kinetic data(58) for thermal degradation of polymers like teflon, polyethylene delrin acetal and phenolic resins reinforced with glass or carbon fiber were obtained from dynamic thermogravimetric studies, processed with the a id of computer. The results agreed with the activation energies and Arrhenius frequency factors obtained under static conditions.

On heating at 40^0C polymer fibers(59) link polyacrylinitrile and phenolic adhesives liberated organic solvents and impurities. On further heating to 123^0 to 200^0C the polymer underwent thermal degradation and gave off carbon monoxide, formaldehyde and hydrogen cyanide. Volatile substances were identified by gas chromatography or spectrophotometry. The polycondensation(60) of ph_2-O-salicylic acid and formaldehyde in the presence of sulfuric acid at 100^0C gave heat resistant diphenylether-salicylic acid - formaldehyde oligomers. On heating it readily underwent crosslinking and thus at temp.300^0C it is susceptible to degradation than Iditol.

Jellinek and Fujiwara (61) have mentioned that the activation energy of thermal degradation of poly (p-oxybensoate) (Ekonol) in vacuum is 59.6Kcal/mole and with approximately 30% volatilize formation.



The degradation preceded by an induction period resulting from poor heat conductivity of Ekonol. the main degradation products are PhOH,CO,CO_2 and unmodified compound having molecular weight 200.

The reaction followed first order kinetics. The precise mechanism is not established. The thermal stability of Ekonol is intermediate between those of poly(tetra-fluroethylene) and polyethylene.

Kinetic parameters of the nonisothermal addition condensation of m-xylene-CH_2O system were studied by Lee(62). The DTA curves were analyzed by the Borchardt-Denials method(63). The reaction is reported to be second order. The activation energy has been reported to be second order. The activation energy has been reported to be: 23.3Kcal/mole and the frequency factor $6.6x10^{13}$ 1/mole-min.

Theories for the Evaluation of Kinetic Parameters for TG Measurement

Thermal methods of analysis involve those techniques wherein the dependence of a property of a substance is measured as a function of temperature. Accordingly four broad divisions of the techniques may be recognized viz. techniques depending on change in energy, in weight, in dimension and those involving evolved volatiles.

Thermogravimetric (TG)

Pyrolysis of many polymers yield the TG curve which follows a relatively simple sigmoidal curve. In such a case weight of the sample decreases slowly as reaction begins, then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction gets completed. The shape of the curve depends on the kinetic parameters viz., reaction order (n), frequency factor (Ao) and activation energy (E).

The values of these parameters have been shown to be of major importance to elucidate the mechanisms involved in polymer degradation (64,65) & to estimate thermal stability (66). It should however, be noted that the expressions employed to evaluate these parameters are in general valid for fluid system and it would be worthwhile to check their validity solid-state reactions.

These parameters, therefor, would not be much significance unless substantiating evidence is presented for the validity of the expression applied to the solid-state reactions.

Thermogravimetric curves obtained for polymers are not always simple. If degradation of material occurs by a multistage mechanism involving rate controlling steps of similar order with activation energies of similar magnitude, a relatively simple trace may be yielded. Such a trace will provide an overall activation energy for the degradation of the sample. The TG trace, however, will involve two or more sigmoids provided the value of activation energy of the rate controlling steps have values greater then zero. These kinds of sigmoidal traces may be analysed to evaluate Ao and E by methods similar to those employed for TG traces possessing single sigmoid. However, in the cases where the values of E for the rate controlling steps are quite close, one reaction may overlap another and the analysis of TG curves may become difficult. The values of kinetic parameters thus obtained will be overall ones and may be little importance to elucidate the mechanism involved in the pyrolysis. It is, therefore, necessary to complement TG studies with DTA and with chromatographic, IR and mass spectrographic methods.

Generally, in the evaluation of kinetic parameters TG methods are preferred over isothermal ones because of the following reasons.

(1) TG methods require relatively fewer data. The temperature dependence of the volatilization rate may be determined over various temperature ranges from the results of a single experiment. To achieve same thing from isothermal methods, several separate experiments are required to perform.

(2) The continuous recording of weight loss versus temperature ensures that no features of the pyrolysis kinetics are overlooked.

(3) A possible source of variation in the estimation of kinetic parameters usually observed with isothermal methods, is avoided in TG method by employing a single sample for the entire thermograms.

(4) In the isothermal method, a sample may undergo premature reaction which in turn may create difficulty in the proper analysis of the kinetic data.

A major disadvantage of the TG method is precise temperature control of kinetic experiments compared to isothermal methods.

For estimation of kinetic parameters from TG traces several so called exact methods have been proposed. All these methods involve two important assumptions that the Arrhenius equation is valid. Since small quantities of material are employed in TG studies, the thermal and diffusion barriers would be negligible.

Broido Method(67)

The weight of the sample, wt., subjected for thermal analysis, at time t is related to the fraction of the number of initial molecules not yet decomposed, y, by the equation.

$$y = \frac{N}{N_o} = \frac{W_t - W_\alpha}{W_0 - W_\alpha} \qquad ....(1)$$

Wt. = is the active weight at any times, t,

W_α = is the weight of material at the end of pyrolysis.

Wo = is the weight of the material taken initially.

for isothermal pyrolysis the reaction rate is given by

$$\frac{dy}{dt} = - ky^n \qquad .....(1a)$$

$\frac{dy}{dt}$ is the rate of reaction,

k is specific rate constant,

n is the order of reaction.

It is assumed that the specific rate, k, is related with absolute temperature according to Arrhenius equation

$$K = A_o \ e^{-E/RT} \qquad \text{..........(1b)}$$

and if the temperature, t, is linear function of t, i.e.,

$$T = To + B_t \qquad \text{.....(1c)}$$

Then combination of Eq. (1a) to (1c) gives,

$$\frac{dy}{y^n} = - \left(\frac{A_o}{B} \right) e^{-E/RT} \, dT \qquad \text{......(2)}$$

The TG curve for such a reaction represents Eq.(2) integrated from To at which y = 1, thus,

$$\int_y^1 \frac{dy}{y^n} = A_o \int B \int_{T_o}^{T} e^{-E/RT} \, dT \qquad \text{.......(3)}$$

for first order Eq. (3) becomes

$$\int_y^1 \frac{dy}{y^n} = \int_y^1 \frac{dy}{y} = \ln y = \ln \ (1/y) \qquad \text{...(4)}$$

According to Vallet(68) Z=E/RT reduces the integration to that for the expression (20) vallet(68) has tabulated the rapidly changing J(Z) and the slowly varying s(Z) for values of Z from 1 to 200 thus covering the range of interest of most problems

$$j \ (z) = \ z^{-2} \ e^{-2} \ dz = z^{-2} \ e^{-z} \ s(z) \qquad \text{....(5)}$$

Especially for a simple first order reaction, y, has been computed from the equation

$$\ln Y = - \frac{A_o E}{BR} \ J \ (Z) \qquad \text{.....(6)}$$

By integrating and taking logarithms of Eq. (4) one obtains

$$\ln(\ln(1/y)) = (E/RT_m+1)\ \ln T + \text{constant} \qquad \ldots.(7)$$

Where Tm is the temperature of maximum reaction rate. A plot of ln (ln (1/y)) versus in T yields a straight line whose slope is related to the energy of activation.

Employing approximations given by Horowitz and Metzger(69),

$$\text{viz.,}\ e^{-E/RT} = e^{(-E/RTm)}\ (Tm/T) \backsimeq e^{(-E/RTm)}\ (z-T/Tm)$$

and
$$e^{-E/RT} \backsimeq (T_m/T)^2 \quad e^{(-E/RTm)}$$

Broido obtained Eq. (8) and (9) respectively

$$\ln(\ln(1/y)) = (E/RT^2{}_m)T + \text{Constant} \qquad \ldots.(8)$$

$$\ln(\ln(1/y)) = -E/R\ (1/T) + \text{Constant} \qquad \ldots.(9)$$

Eq.(9) was found to be the most accurate of three integrated equations via., (7), (8) and (9).

For the order of reaction n=2, Eq. (10) has been prosed.

$$\ln(1-y)/y = -E/R(1/T) + \text{Constant} \qquad \ldots.(10)$$

Thus the slopes of plot of ln (ln(1/y)) and of (ln (1/y))/y versus 1/t for n=1 and n=2 respectively, should yield the energy of activation.

TGA OF RESIN SAMPLES

Each resin samples is finely powdered and sieved upto 100 mesh size. The same amount of the sample has been employed for analysis. The sample has been taken in platinum boat. The analysis has been carried out in nitrogen at a heating rate of 10^0C mi.$^{-1}$ (RH) on Thermal Analyzer DT : 30 shimadzu

The TG thermograms are shown in fig. 5.1.1 to fig. 5.1.4, fig.5.2.1 to fig. 5.2.2 and fig. 5.3.1 to fig. 5.3.2 . The TG data are analysed by the method of broido (67) to estimate the characteristic temperature parameters like initial decomposition temperature, for 50% decomposition and final decomposition temperature. Also activation energy (EA) are determined by broido method. Such an analysis also indicates whether the degradation occurs in a single step or in more steps. These data are presented in table-T-A, table-T-C and table-T-AC.

Result of TGA.

Examination of the TGA data reveals the following.

(1) For poly(vinyl alcohol) - aromatic phenolic derivative series.

Figures 5.1.1 to fig. 5.1.4 describes the thermal decomposition of these series, the starting decomposition temperature observed between 200^0C to 300^0C depending upon the nature of resins. These resins are thermally stable up to 800^0C to 900^0C depending upon the nature of the resins. For the resin Poly-A-Anthra, Poly-A-Galli, Poly-A-pyro, Poly-A-BRes single stage decomposition was observed. While for resins Poly-A-pHyBe. Poly-A-8Hyqui, Poly-A-Sali and Poly-A-Hyqui double stage decomposition was observed.

Their thermal stabil [illegible] were in the following order.

Poly-A-Hyqui < Poly-A-pyro < Poly-A-Galli < Poly-A-βRes
< Poly-A-Anthra < Poly-A-sali < Poly-A-PHyBe < Poly-A-8Hyqui

Examination of the Figures 5.1.1 to fig. 5.1.4 reveals that the reaction taking place when the resin samples are heated.

This is revealed by the fact that the points forming the Broido plots do not run linearly over the whole range of study. From these plots certain region in which the points lies on a linear plot are selected. This region is employed for the estimation of energy of activation of the degradation reaction. The values of EA are shown in Table-T-A . These values lie in the range from 9.09 to 13.8 K_{cal}/mole.

(2) For poly(vinyl chloride) - Aromatic phenolic derivaties series.

Examination of the TG data reveals the following.

The major change in the resin samples starts when heated between 100^0C to 900^0C depending up on the nature of the resin. Decomposition of polymer continue upto 800^0C.

Their thermal stabilities are in the following order.

Poly-C-pHyBe < Poly-C-Anthra < Poly-C-Pyro < Poly-C-Galli ≍
Poly-C-βRes < Poly-C-Hyqui < Poly-C-Sali < Poly-C-8Hyqui

The values of EA are shown in Table-T-C. The activation energy (EA) value obtained by Broido method for the resin varies from 17.32 to 41.57 K_{cal}/mole.

(3) For poly(vinyl acetate) - Aromatic phenolic derivatives series.

Examination of the TG data reveals the following.

The major change of the resin samples when heated commence at some temperature between 300^0C to 400^0C depending upon the nature of the sample. They are thermally stable up to 900^0C. At 900^0C in most of case 40 to 60 % decomposition taking place. Their thermal stabilities are in the following order.

Poly-AC-Hyqui < Poly-AC-pyro < Poly-AC-βRes < Poly-AC-PHyBe
< Poly-AC-Sali < Poly-AC-Galli < Poly-AC-Anthra

The activation energy (EA) values obtained by Broido method for the resins varies from 20.78 to 40.50 K_{cal}/mole.

TABLE-T-A

Result of TG data by method of Broido

Resin	Method of Broido % wt. loss at ^{0}C								
	$200^{0}C$	300^{0}	400^{0}	500^{0}	600^{0}	700^{0}	800^{0}	900^{0}	Energy of activation EA K_{cal}/mole
Poly-A-Anthra	2.8	5.5	22.2	37.5	57.5	77.0	93.5	99.0	10.5714
Poly-A-Galli	5.0	8.0	16.5	26.5	40.0	58.5	80.0	97.0	10.312
Poly-A-PHyBe	2.5	8.0	17.0	24.5	43.5	79.0	93.5	93.5	13.332
Poly-A-Pyro	4.5	8.0	15.0	24.0	42.0	68.0	90.5	96.5	10.1886
Poly-A-8Hyqui	3.0	5.0	20.5	28.5	45.0	73.0	91.0	91.5	13.8/10.50
Poly-A-Sali	2.0	10.0	22.0	29.0	62.0	84.0	84.5	84.5	10.90/6.41
Poly-A-Hyqui	3.5	12.5	27.5	39.0	58.0	82.5	93.0	94.0	9.09
Poly-A-βRes	3.0	4.5	13.0	26.5	51.0	78.0	89.0	90.0	10.5

TABLE-T-C

Result of TG data by method of Broido

Resin	Method of Broido % wt. loss								
	200^{0}C	300^{0}	400^{0}	500^{0}	600^{0}	700^{0}	800^{0}	900^{0}	Energy of activation EA K_{cal}/mole
Poly-C-Anthra	1.2	9.5	16.2	23.5	41.0	69.5	80.5	80.5	22.17
Poly-C-Galli	3.5	5.5	8.5	14.5	17.5	45.5	66.5	87.5	23.49
Poly-C-PHyBe	11.5	10.0	26.0	32.5	38.0	48.5	55.5	63.5	17.32
Poly-C-Pyro	8.5	10.5	17.0	25.0	58.0	68.5	75.0	80.5	22.86
Poly-C-8Hyqui	2.5	3.5	11.5	16.0	19.0	24.5	36.0	51.5	41.57
Poly-C-Sali	2.0	6.0	18.0	26.5	35.5	51.0	77.0	58.0	31.67
Poly-C-Hyqui	12.5	22.0	41.0	48.5	15.5	66.0	74.0	80.0	28.44
Poly-C-βRes	5.0	6.5	11.0	20.5	49.0	90.0	98.0	99.0	23.49

TABLE-T-AC

Result of TG data by method of Broido

Resin	Method of Broido % wt. loss								
	200^0C	300^0	400^0	500^0	600^0	700^0	800^0	900^0	Energy of activation EA K_{cal}/mole
Poly-AC-Anthra	2.5	3.5	10.0	22.2	41.0	50.5	54.0	59.5	40.50
Poly-AC-Galli	6.0	8.0	10.5	15.5	23.0	31.5	39.0	45.0	29.80
Poly-AC-PHyBe	2.0	4.0	9.0	15.0	26.5	45.5	50.5	55.0	27.71
Poly-AC-Pyro	5.5	7.5	13.0	22.0	33.5	41.5	52.0	62.0	23.27
Poly-AC-Sali	2.5	3.5	7.0	17.5	27.5	45.0	48.5	51.0	29.34
Poly-AC-Hyqui	4.0	5.5	9.0	15.5	28.0	36.5	43.5	49.0	20.78
Poly-AC-βRes	3.5	4.0	8.0	15.0	23.0	30.0	38.5	46.0	26.59

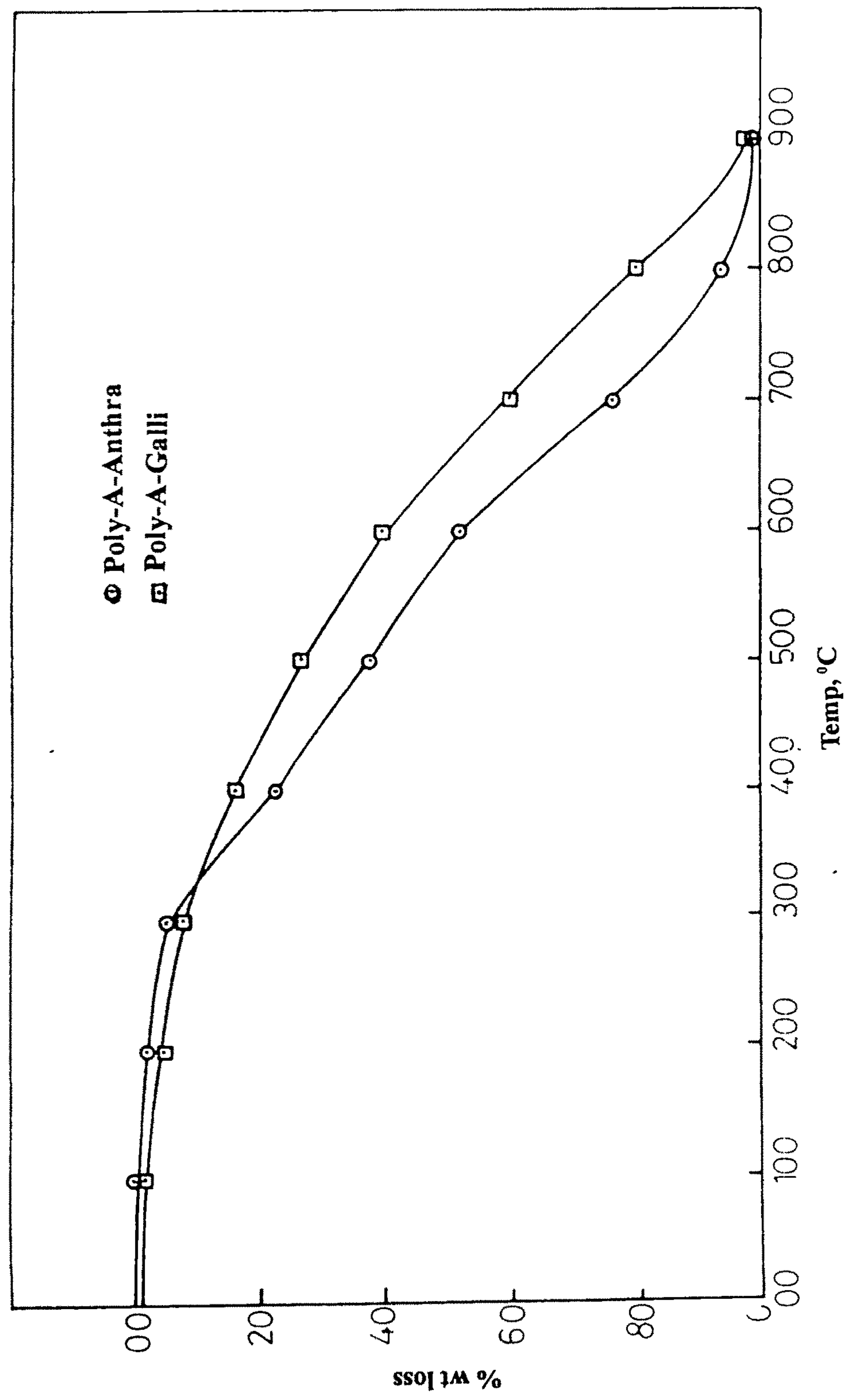

Poly-A-Anthra
Poly-A-Galli
% wt loss
00
20
40
60
80
100
Temp, °C
00
100
200
300
400
500
600
700
800
900

Fig. 5.1.1

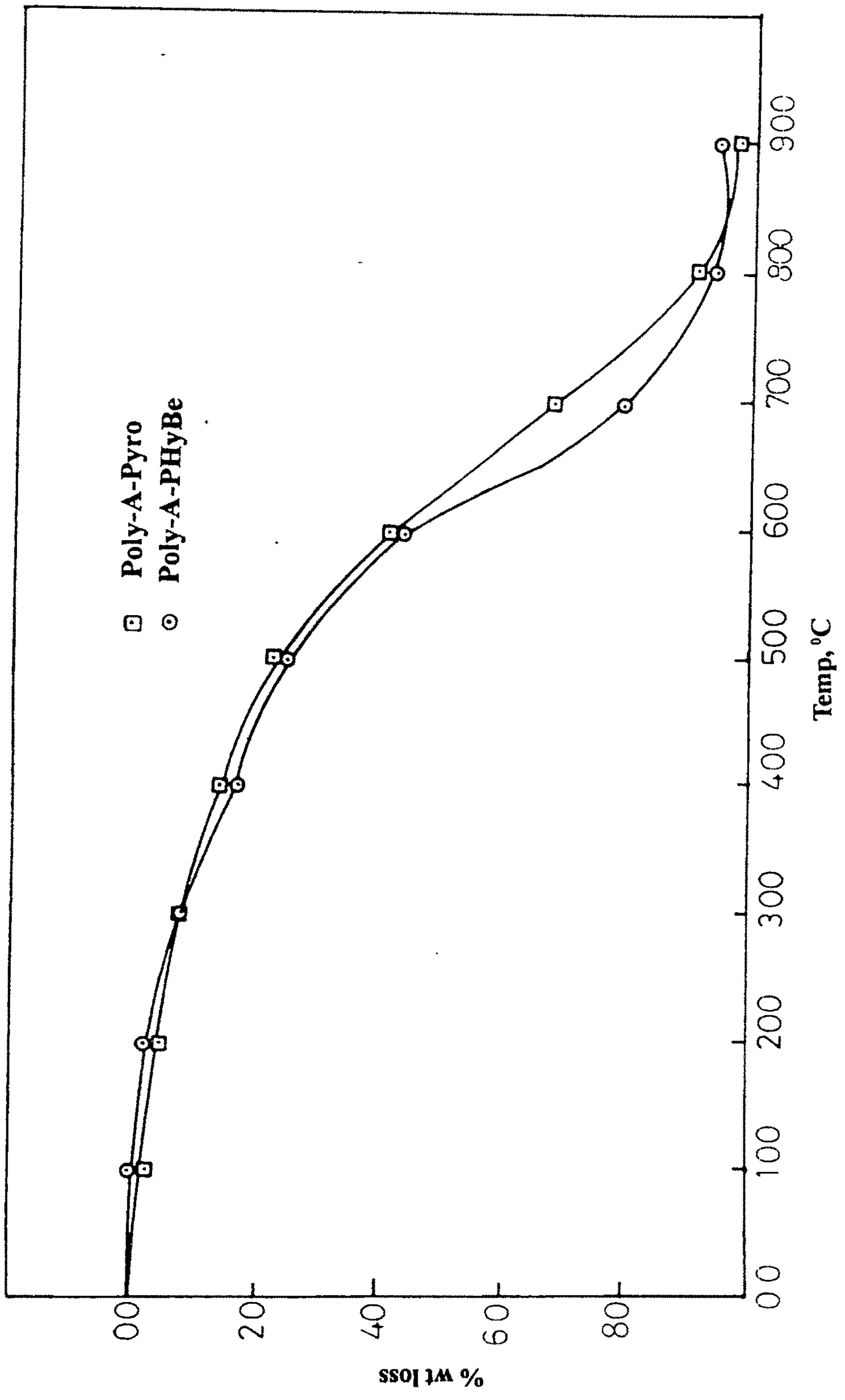

Poly-A-Pyro
Poly-A-PHyBe
% wt loss
00
20
40
60
80
Temp, °C
00
100
200
300
400
500
600
700
800
900

Fig. 5.1.2

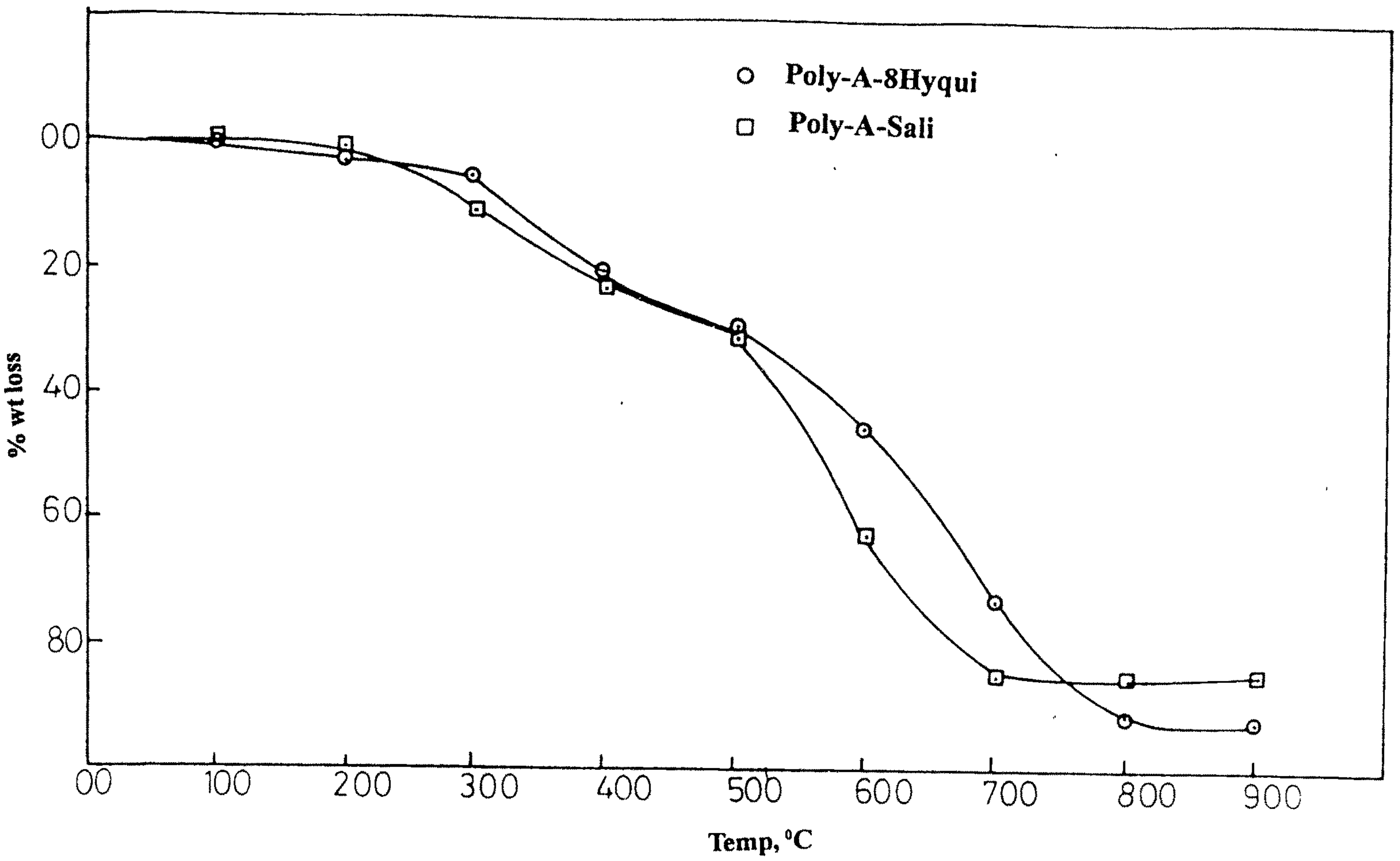

○ Poly-A-8Hyqui
□ Poly-A-Sali
% wt loss
00
20
40
60
80
00
100
200
300
400
500
600
700
800
900
Temp, °C

Fig. 5.1.3

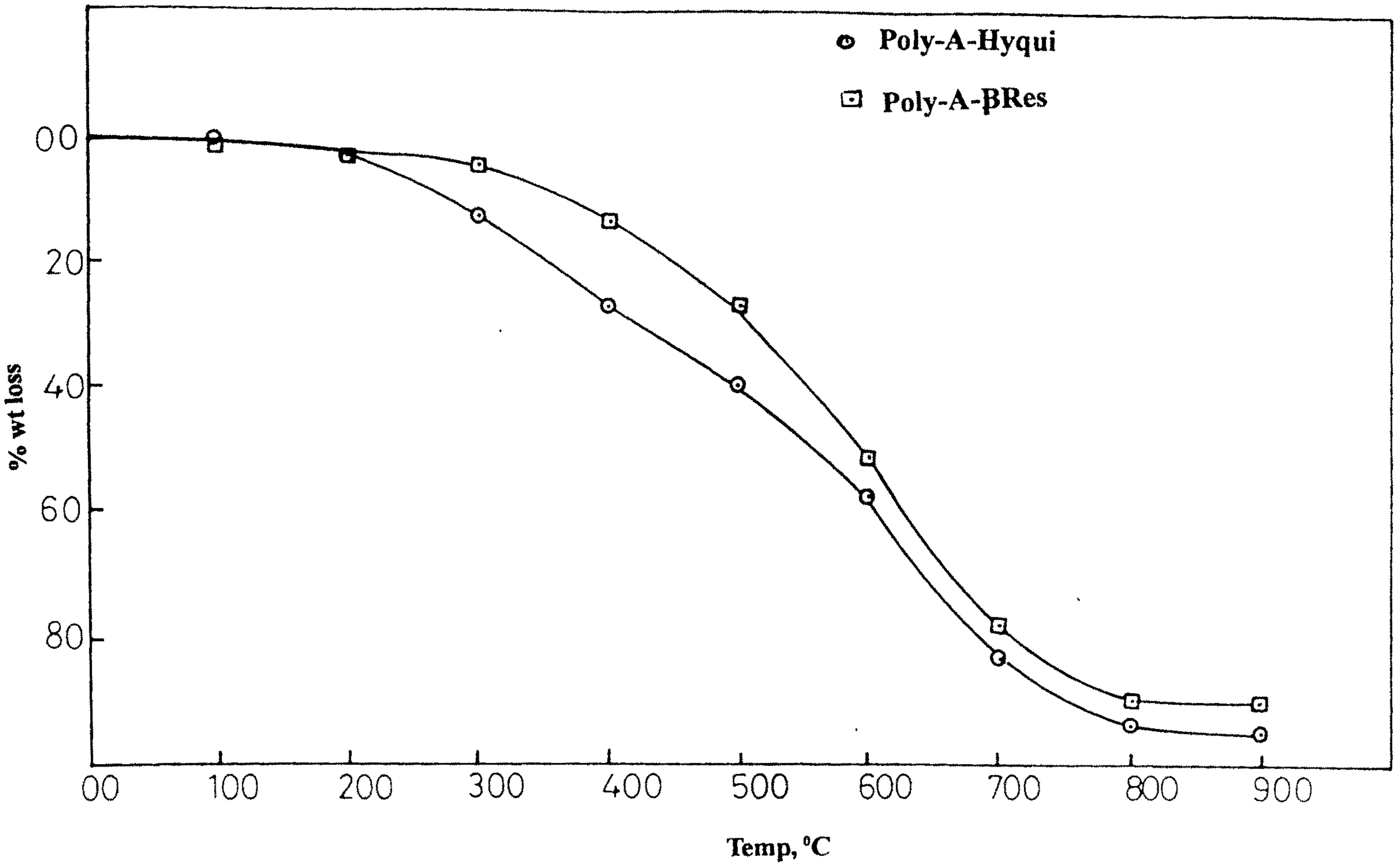
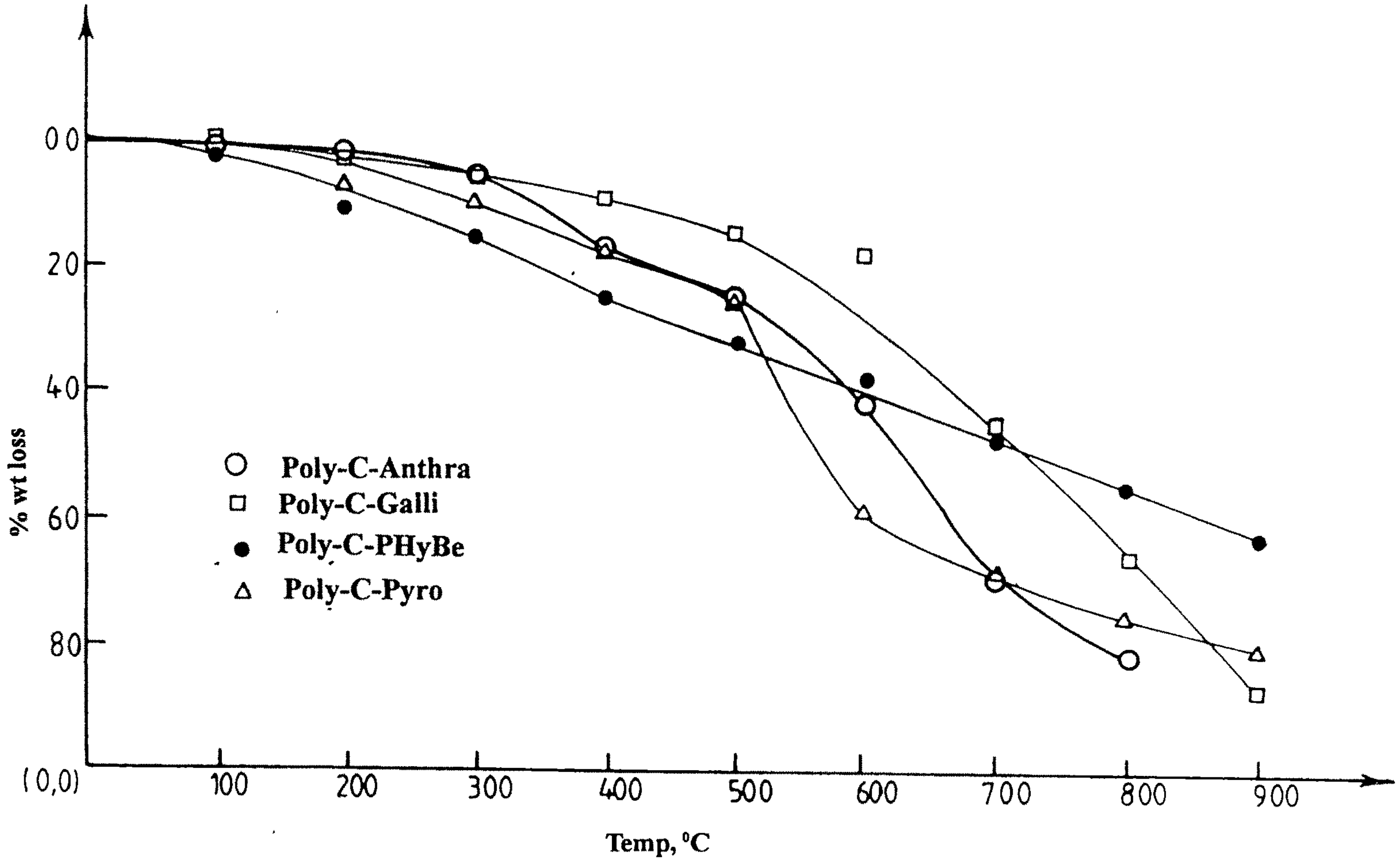

Poly-A-Hyqui
Poly-A-βRes
% wt loss
00
20
40
60
80
00
100
200
300
400
500
600
700
800
900
Temp, °C

Fig. 5.1.4



% wt loss
0 0
2 0
4 0
6 0
8 0
(0,0)
100
200
300
400
500
600
700
800
900
Temp, °C
○ Poly-C-Anthra
□ Poly-C-Galli
● Poly-C-PHyBe
△ Poly-C-Pyro

Fig. 5.2.1

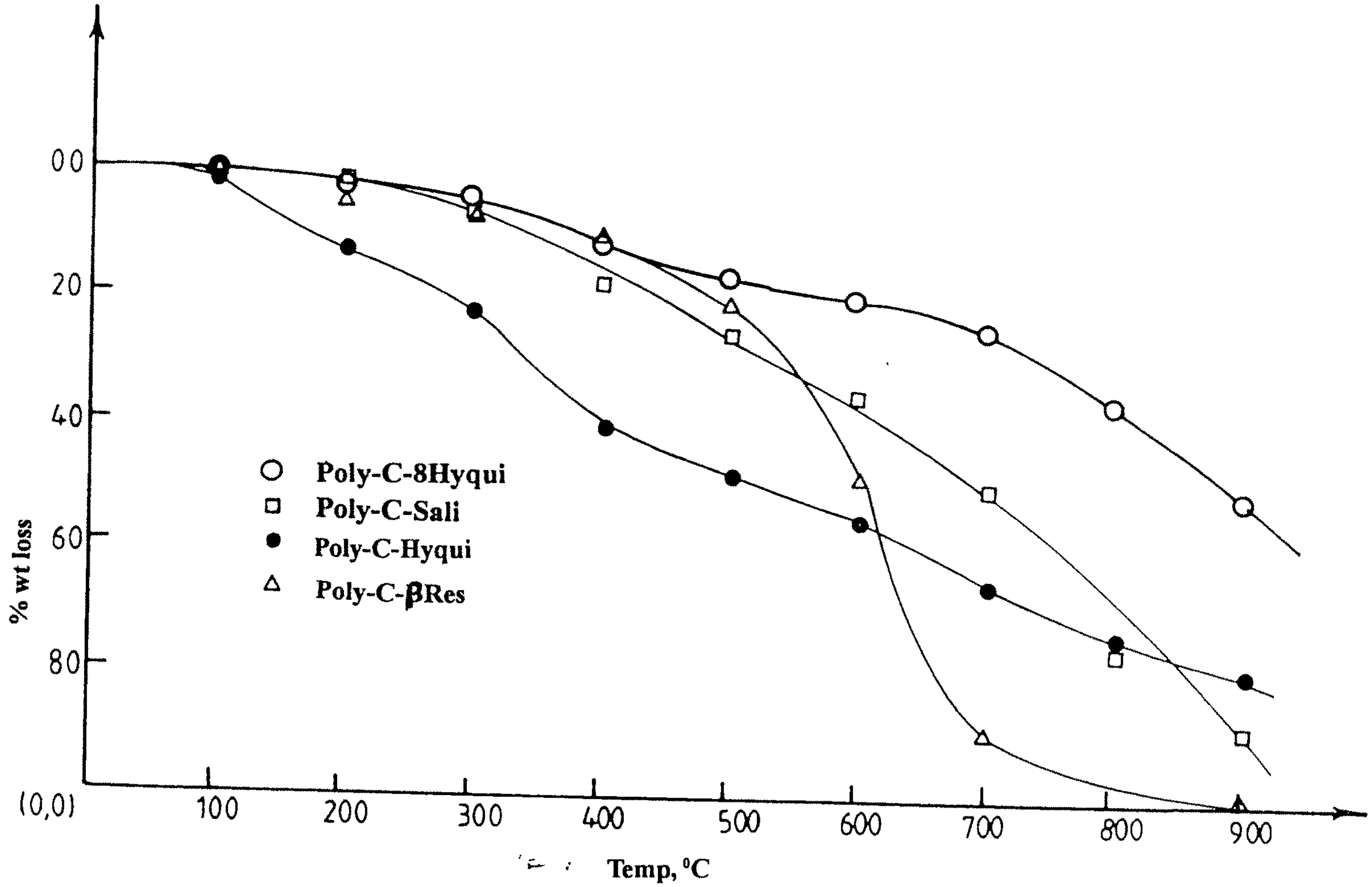

% wt loss
00
20
40
60
80
(0,0)
100
200
300
400
500
600
700
800
900
Temp, °C
○ Poly-C-8Hyqui
□ Poly-C-Sali
● Poly-C-Hyqui
△ Poly-C-βRes

Fig. 5.2.2

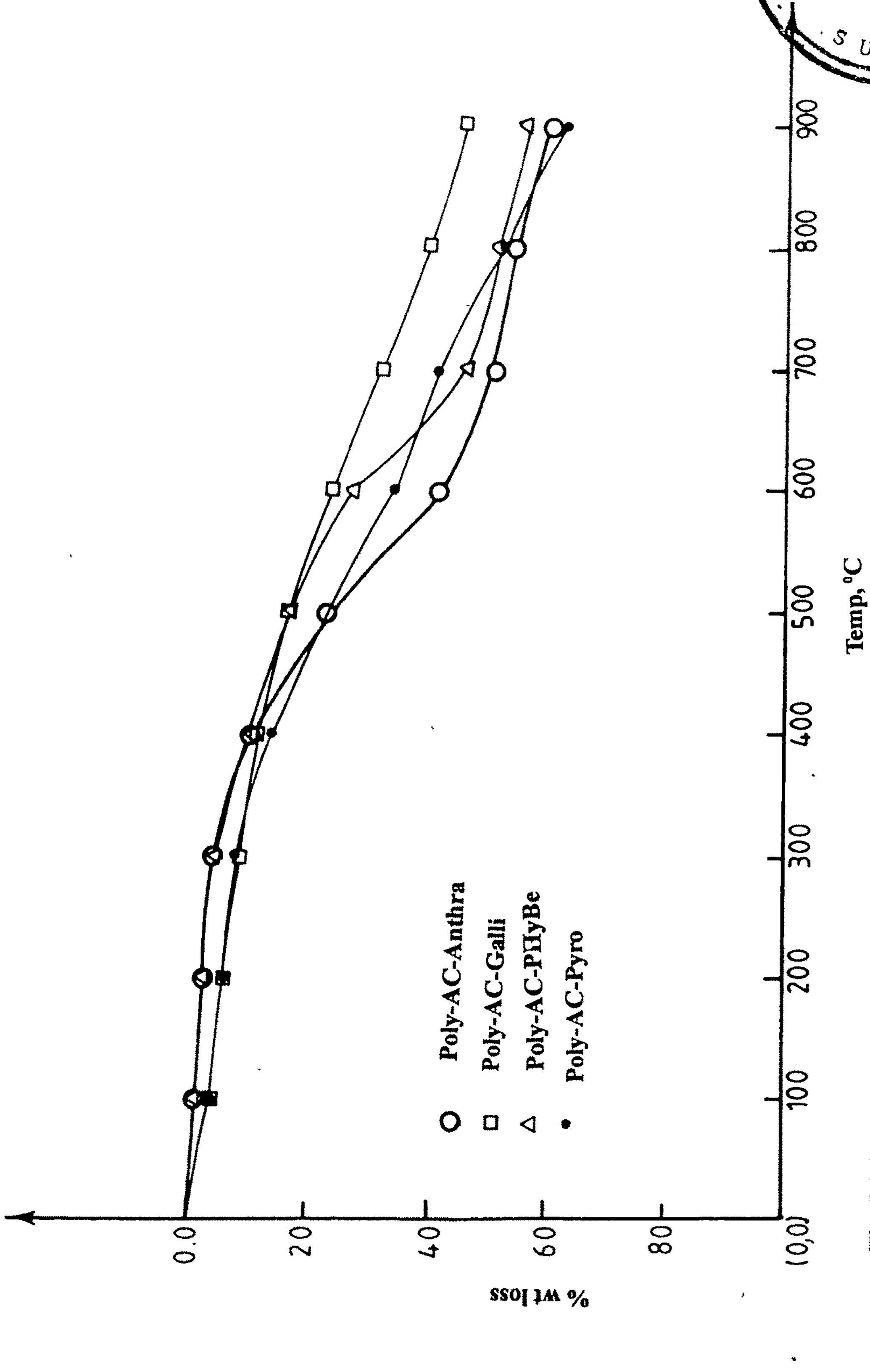

% wt loss
0.0
20
40
60
80
(0,0)
100
200
300
400
500
600
700
800
900
Temp, °C
○ Poly-AC-Anthra
□ Poly-AC-Galli
△ Poly-AC-PHyBe
● Poly-AC-Pyro

Fig. 5.3.1

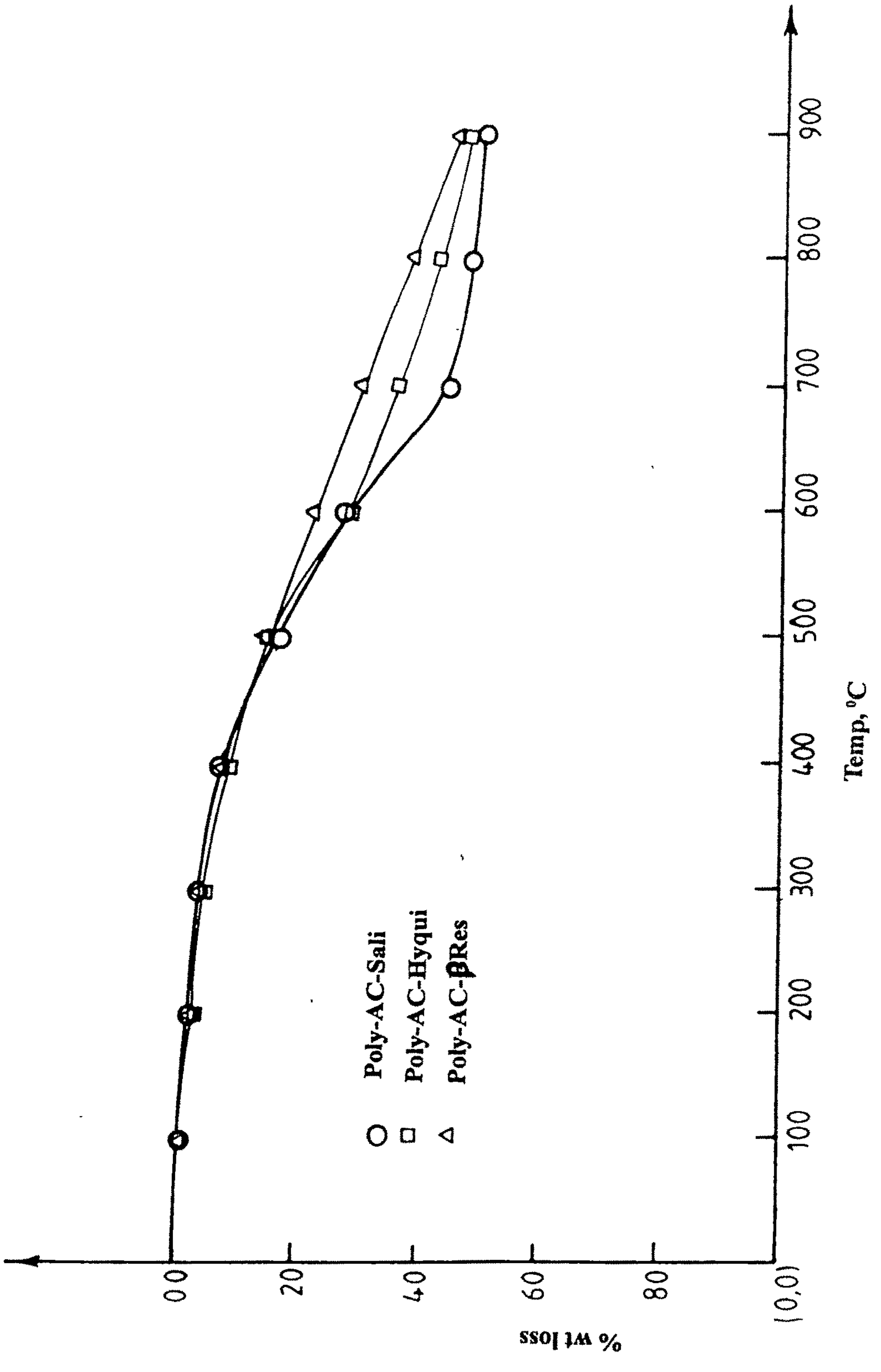

% wt loss
0.0
20
40
60
80
(0,0)
100
200
300
400
500
600
700
800
900
Temp, °C
○ Poly-AC-Sali
□ Poly-AC-Hyqui
△ Poly-AC-βRes

Fig. 5.3.2