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# Comparative Thermokinetics Study of Terpolymeric Resins derived from p-Hydroxyacetophenone, Resorcinol and Glycerol

**Kapse S.K.[1], Hiwase V.V.[2], Kalambe A.B.[1] and Kene J.D.[3]**
[1]Department of Chemistry, Institute of science, Nagpur, MS, INDIA
[2]Department of Chemistry, Arts, Commerce and Science College, Arvi, Dist. Wardha, MS, INDIA
[3]V.N.I.T., Nagpur, MS, INDIA

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## Abstract

*The terpolymeric resins abbreviated as PARG-I and PARG-II were synthesized by polyphosphoric acid (PPA) catalyzed polycondensation of p-hydroxyacetophenone, resorcinol and glycerol in 1:1:3 and 2:1:4 molar proportions respectively. The resins were characterized by various physico-chemical methods such as elemental analysis, IR, $^1$H NMR, UV-Vis and non-aqueous conduct metric titration. The thermokinetic parameters were determined using Freeman-Carroll and Sharp-Wentworth methods. The order of degradation was determined by FC method and confirmed by SW method.*

**Keywords**: Polycondensation, resin, terpolymer, thermal degradation, freeman-Carroll, sharp-wentworth, thermokinetic parameters.

## Introduction

Terpolymeric resin has been attracting much attention of materialists since last two decades owing to interesting properties superior than copolymer that can fulfill the demand of modern society. These include toughness, resilience, low density, high and low melting points, ability to be molded, conductivity, resistance etc. These resins reported to have an application such as high resistivity materials, thermal blankets, thermal control paints, circuit boards, lubricants, paints and insulating coatings, resistors, semiconductors, protective coating on aviator machine parts and many other applications at elevated temperature and ion-exchange. Thermally stable terpolymeric resins consequently have great potential besides the challenges regarding ease of manufacturing, thermal stability and mechanical strength, durability, separation and purification etc. In recent year considerable interest has been made to improve the quality of the polymer by co-polymerization most probably terpolymerization either by modifying methods or by introduction of a variety of functional monomers. The study of the thermal degradation of terpolymer resins has recently become subject to interest. Terpolymeric resins having good thermal stability have enhanced the scope for development of any polymeric materials[1-8].

Michael *et al* studied the thermal decomposition behavior of p-hydroxyquinoline-guanidine-formaldehyde terpolymers. Thermal decomposition curve which showed two decomposition steps (265-475$^o$C and 540-715$^o$C). Freeman-Carroll and Sharp-Wentworth methods were used to calculate activation energies and thermal stability[9].

Singru *et al* studied thermal property of p-cresol-oxamide-formaldehyde terpolymers resin. Thermal study of the resin was carried out to determine its mode of decomposition and thermal stability. By using data of thermogravimetry various kinetic parameter like frequency factor (Z), free energy change (F) and apparent entropy(S*) have determined using Freeman-Carroll method[10]. Rahandale *et al* synthesized the copolymer (2, 2'-HBBF). The negative values of entropy (ΔS) indicate that the activated polymer has a more ordered structure than the reactants and the reactions are slower than the normal[11]. The Freeman-Carroll and Sharp-Wentworth methods have been used to evaluate kinetic parameters for these terpolymers[12-13].

The present communication deals with the study of the thermokinetic parameters of PARG-I and PARG-II terpolymeric resin was determined by using Freeman-Carroll and Sharp-Wentworth methods.

## Material and Methods

**Chemicals:** All chemicals were AR grade and chemically pure grade p-Hydroxyacetophenone, resorcinol and glycerol, PPA was procured from SD fine, India. Double distilled water was used for all experiments.

**The synthesis of PARG terpolymeric resins:** The mixture of p-Hydroxyacetophenone (0.1M), Resorcinol (0.1M) and Glycerol (0.3M) was refluxed in the presence of polyphosphoric acid in oil bath at 120 -130$^o$C for 8.0 hrs with intermittent shaking. The brownish product was repeatedly washed with cold distilled water, dried in air and powered. The product was washed with many times with hot water to remove unreacted monomers. The air dried product was extracted with ether to remove copolymer which might be produced along with terpolymer. It was further purified by dissolving in 2% NaOH

solution, filtered and reprecipited by the gradual drop wise addition of 1:1 HCl with constant and rapid stirring in order to avoid the lump formation. The PARG-I resin so obtained was filtered, washed several times with hot distilled water. The yield of terpolymer PARG-I was found to be 74%.

Similarly PARG-II was synthesized and purified by the same method as above. The yield of terpolymer PARG-II was found to be 79%. The tentative structure of PARG terpolymeric resins are shown in figure 1. And synthetic details of PARG terpolymer resins are given in table 1.

**Thermogravimetric analysis (TGA) of PARG resins:** Thermo gravimetric analysis (TGA) of PARG-I and PARG-II terpolymers resin samples were carried out by using Perkin Elmer Diamond TGA/DTA analyzer in the argon environment at Dept. of Material Science, VNIT Nagpur. The polymeric sample was allowed to heat up to $900^0$C at linear heating rate of $10^o$C $min^{-1}$. The Freeman-Carroll and Sharp-Wentworth methods have been employed for the calculation of kinetics parameters of the newly synthesized PARG-I and PARG-II terpolymer resin with the help of the dynamic TGA curve[14-29]. In present work thermo kinetic parameters were determined by using the following methods.

**Freeman - Carroll Method (FC):** In this the kinetic parameters determined by following expression,

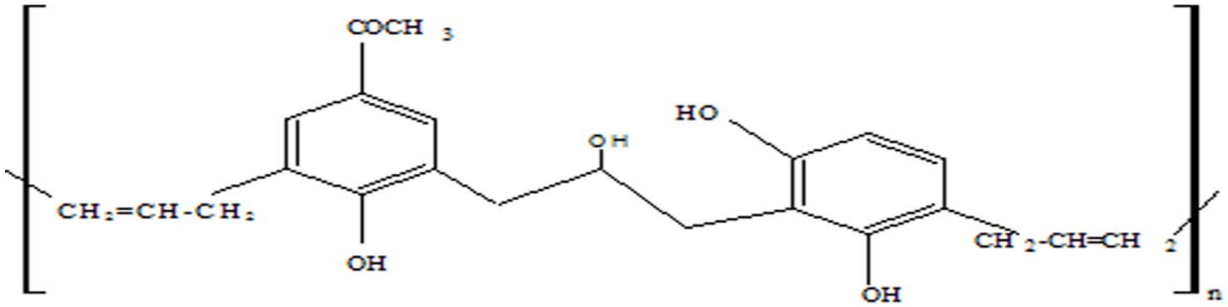
$$\frac{\Delta Log\left(dw/dt\right)}{\Delta Log\left(Wr\right)}=\left[-\frac{Ea}{2.303R}\right]\times\frac{\Delta\left(1/\mathrm{T}\right)}{\Delta LogWr}+n$$

Where, *dw/dt* = Rate of change of weight with time, $W_r$ = Difference between weight loss at completion of reaction and at time t, Ea = Activation energy, n = Order of reaction.

Freeman-Carroll method is more suitable method since the yield is useful to determine the activation energy as well as order of reaction in single determination.

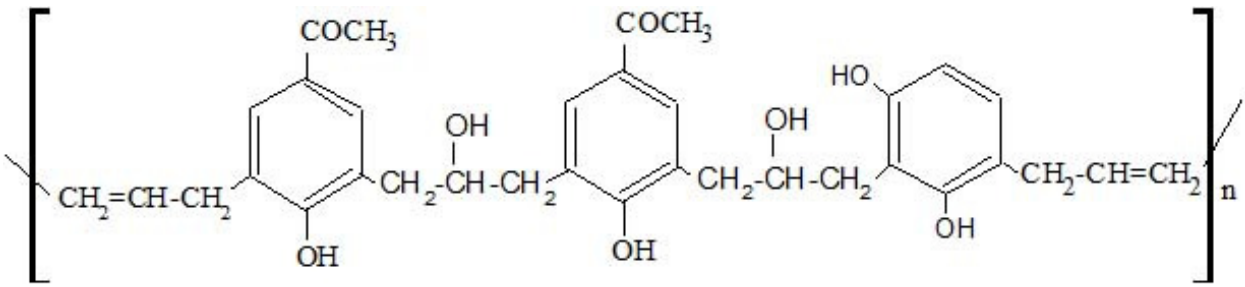
**Table-1**
**Synthesis details of PARG resins**

| Resin | p-Hydroxy acetophenone | Resorcinol | Glycerol | catalyst | Reaction temperature ($^o$C) | Time (Hrs) | Yield |
|---|---|---|---|---|---|---|---|
| PARG-I | 0.1M | 0.1M | 0.3M | PPA | 120-130 | 8.0 | 74% |
| PARG-II | 0.2M | 0.1M | 0.4M | | 120-130 | | 79% |




**PARG - I**

(a)




**PARG - II**

(b)

**Figure-1**
**Tentative structure of PARG-I (a) and PARG-II (b)**

Sharp-Wentworth method (SW): Following expression is used to evaluate the kinetic parameters,

$$\text{Log}\ \frac{(d\alpha / dt)}{(1-\alpha)^n} = Log\ \frac{A}{\beta} - \frac{Ea}{2.303RT}$$

Where, dα/dt is fraction of weight loss with time, n = The Order of reaction, Z = Frequency factor, β = Linear heating rate and α = The fraction of amount of reactant.

Thermogram of PARG-I and PARG-II terpolymer resins are shown in following figure 2 and figure 4 respectively. The initial loss up to 140°C was due to loss of water present in PARG-I terpolymer resin. The decomposition of the resin between 143-343°C was studied. The order of decomposition was found to be 2.2 as determined by Freeman-Carroll method, which was further confirmed by Sharp-Wentworth method. FC and SW method plots of PARG-I terpolymer resin is shown in figure 3. The initial loss up to 150°C was due to loss of water present in PARG-II terpolymer resin. The decomposition of resin between 203-377°C was studied. The order of decomposition was found to be 0.6 as determined by Freeman-Carroll method, which was further confirmed by Sharp-Wentworth method. FC and SW method plots of PARG-II terpolymer resin is shown in figure 5. Thermo kinetic parameters of PARG terpolymer resins are tabulated in table 2.

**Table-2**
**Thermokinetic parameters of PARG terpolymer resins**

| Resins | Methods | Decomposition temperature (°C) | Ea (kJ) | A($min^{-1}$) | ΔS* (J/K) | ΔG* (kJ) | Order (n) |
|---|---|---|---|---|---|---|---|
| **PARG-I** | FC | 143-343 | 42.98 | $4.45x10^2$ | -221.88 | 165.19 | 2.2 |
| | SW | | 44.61 | $6.48x10^2$ | -247.58 | 181.23 | |
| **PARG-II** | FC | 203-377 | 120.01 | $6.49x10^{10}$ | -71.60 | 160.34 | 0.6 |
| | SW | | 118.78 | $8.33x10^{10}$ | -73.0 | 160.25 | |

*FC=Freeman-Carroll method, SW=Sharp-Wentworth method.

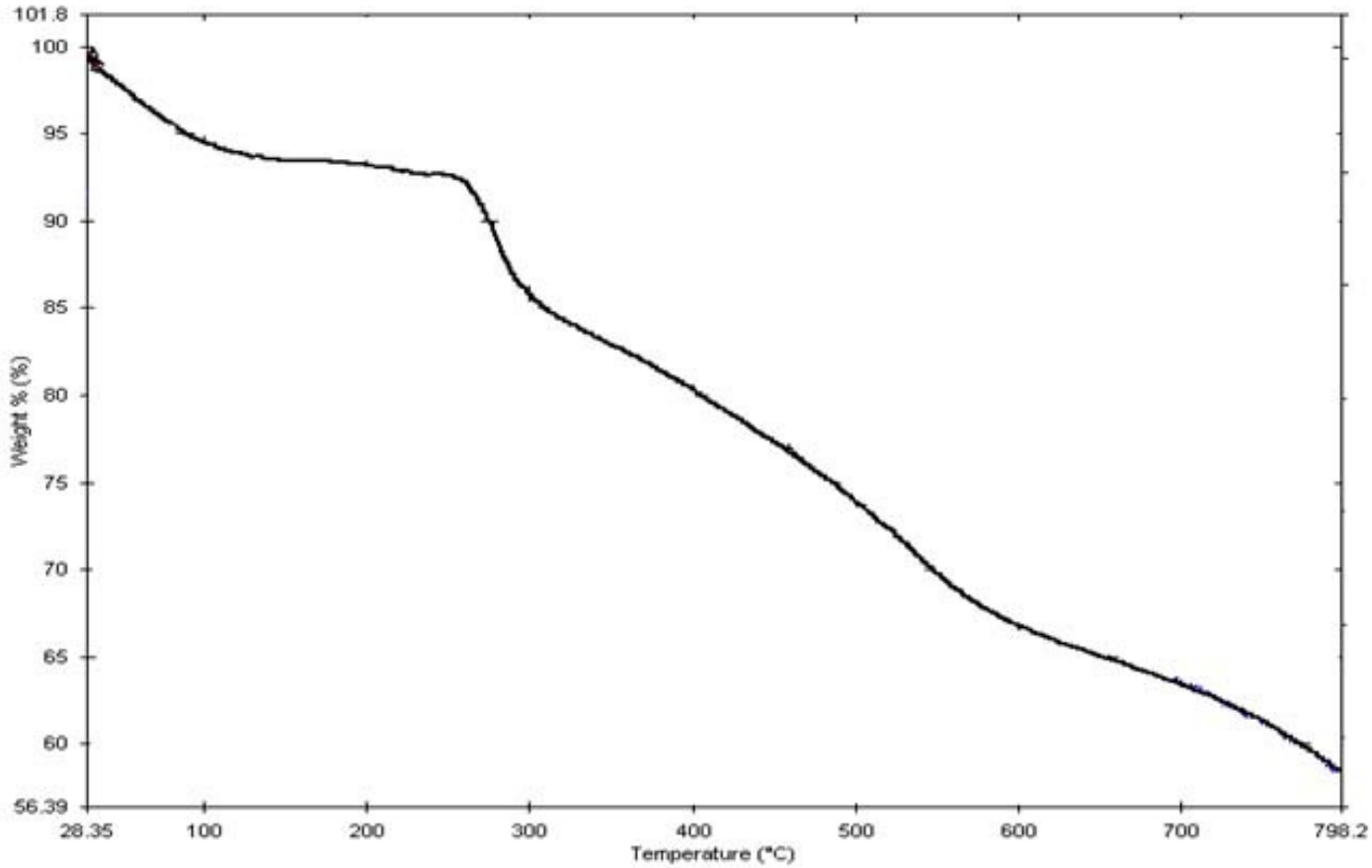



**Figure-2**
**Thermogram of PARG-I**

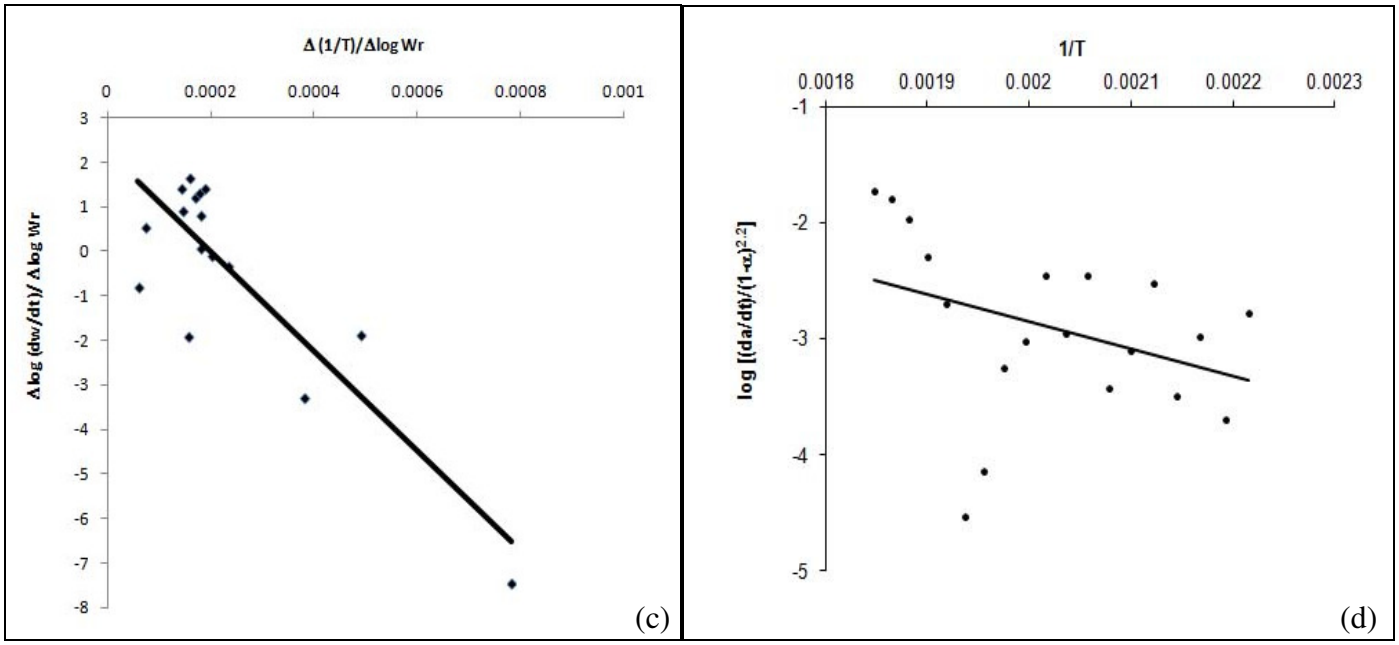



**Figure-3**
**FC plot of PARG-I (c) and SW plot of PARG-I (d)**

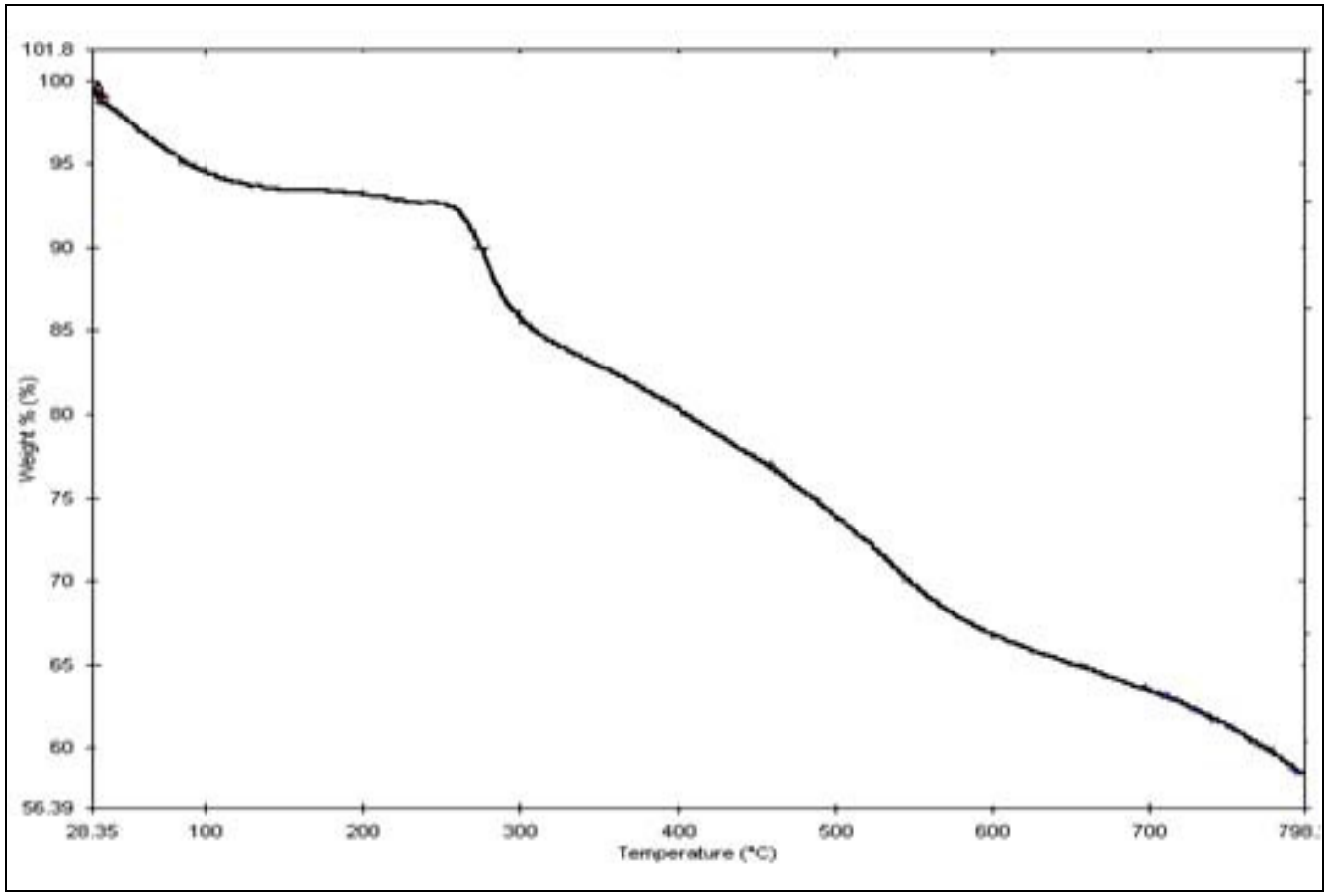



**Figure-4**
**Thermogram of PARG-II**

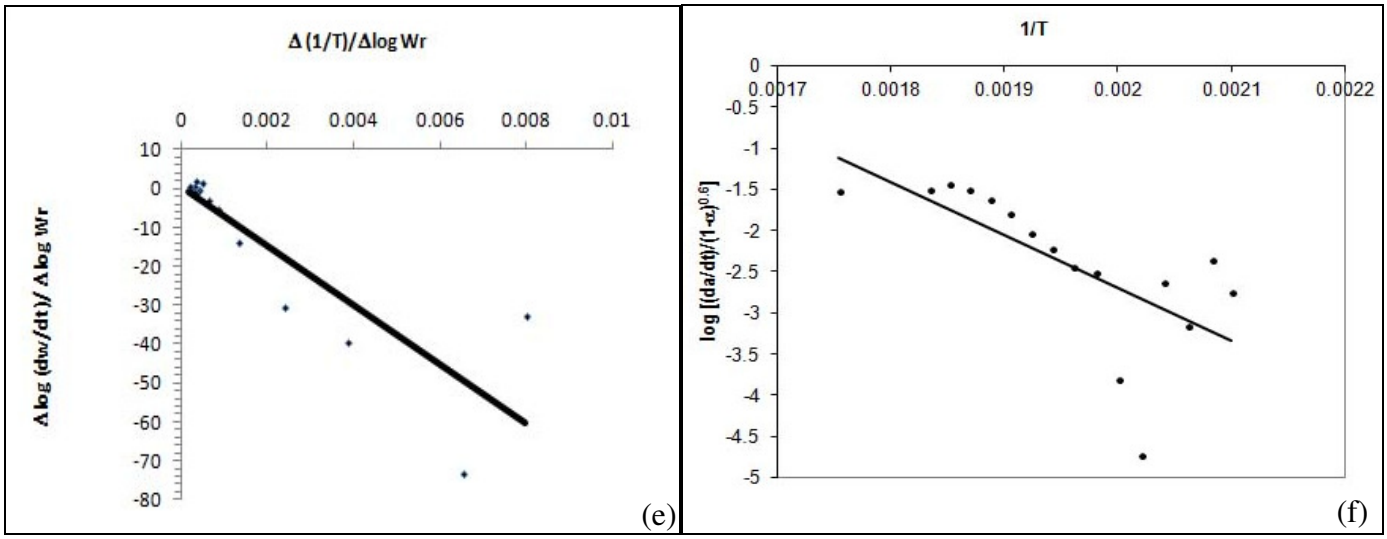



**Figure-5**
**FC plot of PARG-II (e) and SW plot of PARG-II (f)**

## Conclusion

The values of activation energies, apparent entropy, free energy and frequency factor of degradation are determined by Freeman-Carroll and Sharp-Wentworth methods are in good agreement. Low values of frequency factor of PARG-I suggest the slow degradation as compared to PARG-II. More negative entropy values for PARG-I than PARG-II implies highly ordered structure of former than latter one owing to high value of activation energy degradation for PARG-II as compared to PARG-I, it will not be amiss to conclude that PARG-II is more thermally stable than PARG-I. However reverse order followed as for as kinetic stability is concerned. The thermokinetic parameter support to the tentative structures of Terpolymeric resins shown in figure 1.

## References

**1.** Lee K.E., Poh B.T., Morad N. and Teng T.T., Development, characterization and the Application of hybrid materials in coagulation/flocculation of waste water: A review, *Int. J. Polym. Anal. Charac*t., **13**, 95-107 **(2008)**

**2.** Kaushik A. and Singh P., Polyurethanes based on fatty acids with improved--, *Int. J. Polym. Anal. Charact*., **10**, 373-386 **(2005)**

**3.** Masram D.T., Kariya K.P. and Bhave N.S., Electrical conductivity study of resin synthesized from salicylic acid, butylenes diamine and formaldehyde, *Arch. Appl. Sci. Res*., **2(2)**, 153-161 **(2012)**

**4.** Gurnule W.B., Rahandale P.K., Kharat R.B. and Paliwal L.J., Synthesis and characterization of copolymer derived from 2-hydroxyacetophenon, oxamide and formaldehyde, *Prog. Crystal Growth Charct. Mater*., **45**, 155-160 **(2002)**

**5.** Kushwaha A.D., Hiwase V.V., Kalambe A.B. and Kapse S.K., Semiconducting behavior and thermal study of terpolymeric resin derived from p-nitrophenol, resorcinol and formaldehyde, *Arch. Appl. Sci. Res*., **4(3)**, 1502-1510 **(2012)**

**6.** Masram D.T., Kariya K.P. and Bhave N.S., Thermal degradation study of salicylic acid, diaminonaphthalene and formaldehyde, *E.J. Chem*., **6(3)**, 830-834 **(2009)**

**7.** Mathew D., Nair C.P.R., Ninan K.N., Pendent cyanate functional vinyl polymers and Imido-phenolic- triazines thereof: synthesis and thermal properties, *Europe. Polym. J*., **36(6)**, 1195-1208 **(2000)**

**8.** Nakanishi K., Infrared absorption spectroscopy practical, Nolden Day and Nankod, Tokyo **(1967)**

**9.** Michael P.S.P., Barbe J.M., Juneja H.D. and Paliwal L.J., Synthesis, characterization and Thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer, *Europe. Polym. J.,* **43(12)**, 995-5000 **(2007)**

**10.** Singru R.N., Khati V.A., Gurnule W.B., Zade A.B. and Dontulwar J.R., Studies on semiconducting, chelating and thermal properties of p-cresol-oxamide-formaldehyde terpolymer resin, *Anal. Bioanal. Electroche,* **3(1)**, 67-86 **(2011)**

**11.** Rahangdale S., Gurnule W. B., Synthesis, thermal and electrical properties of 2, 2'-HBBF copolymer resin, *Chem. Sci. Trans*., **2(1),** 287-293 **(2013)**

**12.** Freeman E.S. and Carroll B., The application of thermoanalytical techniques to reaction kinetics, The Thermogravimetry evaluation of the kinetics of the decomposition of calcium oxalate monohydrate, *J. Phys. Chem*., **62**, 394-397 **(1958)**

**13.** Sharp J.B. and Wentworth S.A., Kinetic analysis of Thermogravimetry data, *Anal. Chem*., **41**, 2060-206 **(1969)**

**14.** Karunakaran M., Vijayakumar C.T., Magesh C., Amudha T., Terpolymer resin-II thermal and metal ion binding properties of resorcinol-thiourea-formaldehyde terpolymer resin, *IJEST*, **3(1)**, 162-176 **(2011)**

**15.** Vogel A.I., Textbook of practical organic chem, Longman Scientific and Technical, UK (**1989)**

**16.** Basavaraju B. and Naik H.S.B., Synthesis and thermal degradation kinetics of Co (II), Ni (II), Cd (II), Zn (II), Pd (II), Rh (III) and Ru (III) complexes with methylquinolino [3, 2- b] benzodiazepine, *E. J. Chem*., **4(2)**, 199-207 **(2007)**

**17.** Belsare P.U. and Zade A.B., Synthesis and Thermogravimetry analysis of 2, 2'-Biphenol based terpolymer resins, *Chem. Sci. Trans*., **2(4)**, 1136-1147**(2013)**

**18.** Silverstein R.M. and Webster F.X., Spectrometric identification of organic compounds, 6th Edn. John Wiley, New York, **(1998)**

**19.** Ballamy L.J., the IR spectroscopy of complex molecules, John Wiley and Sons. Inc. 142 **(1975)**

**20.** Morrison R.T. and Boyd R.N., "Organic Chemistry", Prentice Hall 4-Pub, Co. Pvt. Ltd. 6. Wardlaw G.M. Hampl J.S., 7th Edn, **(2007)**

**21.** Su W.F., Lee K.E. and Peng W.Y., Thermal properties of phthalic anhydride and phenolic resin-cured rigid rod epoxy resins, *Thermochimica Acta*., **395-398** 392-393 **(2002)**

**22.** Dharkar K.P., Khamborkar A.K. and Kalambe A.B., Thermal degradation analysis of melamine-anilineformaldehyde terpolymeric ligand, *Res. J. Chem. Sci.,* **2(12)**, 11-16 **(2012)**

**23.** Ozwa T.J., Temperature control modes in thermal analysis, *Pure Appl. Chem*., **72(11)**, 2083-2099 **(2000)**

**24.** Ukey V.V., Juneja H.D., Borkar S.D., Ghubde R.S., Naz S., Preparation, Characterization, Magnetic, and Thermal Studies of some chelate Polymers of first series transition metal ions, *Mater. Sci. Engg.* B, **132**, 34-38 **(2006)**

**25.** Coats A.W., Critical investigation of methods for kinetics analysis of thermo analytical data, *J. Thermal Anal*., **7**, 601-617 **(1975)**

**26.** Kapse S.K., Hiwase V.V., Kalambe A.B., Structural and thermokinetic study of resin-I derived from p-hydroxyacetophenone quinhydrone and melamine, *Der Pharma Chemica*, **4(1)**, 460-467 **(2012)**

**27.** Tantry R.N., Janthi K., Harish M.N.K., Angadi S.A.R., Chinnagiri K.K.T., Synthesis and thermal degradation kinetics studies of Benzimidozole substituted metal phthalocyanine through oxadiazole bridge (M=Co, Ni, Cu), *Res. J. Chem. Sci.,* **3(11)**, 36-46 **(2013)**

**28.** G. Indira Devi, Sabu P.G., Parameshwaran G., Thermal decomposition kinetics and mechanism of Co(II), Ni(II) and Cu(II) complexes derived from anthracene carboxaldehyde L-Tyrosine, *Res. J. Chem. Sci.***, 3(9)**, 58-63 **(2013)**

**29.** Thavamani S.S., Rajkumar, Removal of Cr(II), Cu(II), Pb(II) and Ni(II) from aqueous solutions by adsorption on alumina, *Res. J. Chem. Sci.,* **3(8)**, 44-48 **(2013)**