

NON-ISOTHERMAL KINETIC AND THERMODYNAMIC STUDIES ON POLYESTERS AT DIFFERENT VISCOSITY AVERAGE MOLECULAR MASSES

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ABSTRACT

Non-Isothermal kinetics of solid-state decomposition of Polybisphenol-A-Carbonate [PC; (M_t : $1.5 - 3.68 \times 10^4$) and polymethyl metacrylate [PMMA M_w : $1.55-3.52 \times 10^4$] has been investigated under nitrogen atmosphere in view to study the effect of molecular mass on their thermal decompositions in solid state. Thermal data deduced through simultaneous thermogravimetric-differential thermal analysis-differential thermo gravimetry [TG-DTA-DTG] was used for calculations of thermodynamic parameters through Horowitz-Metzger and coats-Redfern methods, kinetics and mechanism of degradations of each polymer at different molecular masses. [PC] showed two step decomposition with slower rate than [PMMA], which showed single step decomposition at each of molecular mass ranges. It was observed that ester linkages in [PC] backbone provided satisfactory over [PMMA] which contain ester linkages in side chain, to Horowitz-Metzger, coats-Redfern methods kinetic equations of solid-state decompositions. In general, Horowitz-Metzger methods have shown greater values of energy of activation than Coats-Redfern methods for [PC]. Both of methods have provided a wide difference in frequency factor but almost same entropy change in most of the cases* Thermodynamic and kinetic data were mostly satisfied for first order and zero order kinetics in case of [PC] whereas were not satisfactory for [PMMA].

Key words: Thermodynamic parameters, Horowitz-Metzger and Coats-Redfern methods.

INTRODUCTION

The quality control and assessment in the industrial polymers have been found to be tedious and a series of experimental techniques were developed since past few decades¹⁻². Among such techniques, thermo analytical methods have emerged as a rapid and cost effective substitute over other analytical methods with reproducible results³⁻⁴. Most of the modern chemical and metallurgical industries employ process involving solid-state gas-solid interface reactions. A detailed knowledge of the thermodynamics, kinetic and reaction mechanisms of these thermally induced processes is of immense help to optimize and control the operating parameters leading to design of proper process equipment. Thermal analysis techniques like thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) etc, where the property of a substance measured, as a function of temperature is extremely useful in this context⁵. In addition, if

real time analysis of the product gases evolved during a thermally induced reaction will greatly enhance the possibility of correctly interpreting the kinetic data and arriving at most appropriate mechanism governing the process. Thus, knowledge of single particle kinetics becomes a pre-requisite for studying interface transport phenomena between moving gas stream and porous of solid materials⁶. Such single particle kinetics can be easily studied through simultaneous TG-DTA-DTG, evolved gas analysis EGA and thermo mechanical analysis TMA. Among such the technique of TG-DTA-DTG is frequently used as a means of assessing the thermal stability and conveniently provide valuable information about kinetics and thermodynamics of the solid state decompositions of polymers and related heat resistant materials⁵⁻⁶.

In the present research work, samples of polybisphenol-A carbonate [PC] with different viscosity average molecular masses [M_v]: $1.51 - 3.68 \times 10^4$] were prepared through their chemical

decomposition with hydrochloric acid. [PMMA] with viscosity average molecular mass (M_n): $1.55-3.52 \times 10^4$) was synthesized through benzoyl peroxide catalyzed free radical polymerization of freshly distilled monomer. The monomer and polymers were thermally characterized through simultaneous TG-DTA-DTG in nitrogen. Thermal data were used for calculations of thermodynamic parameters through Horowitz-Metzger⁷ and coats-Redfern methods⁸, kinetics and mechanism of degradations of each polymer at different molecular masses (Table 1)⁶.

MATERIALS AND METHODS

Starting materials

(a) Poly bisphenol-A-Carbonate [PC]:

[PC] was purchased with melt index 7 was purchased from Ms Sigma Aldrich Chemicals USA. It was decomposed with aqueous HCl solution (10-30% v/v) at $100 \pm 1^\circ\text{C}$ in the range of 0.5 to 1.0 h. This result a series of [PC] samples with different [PC] samples. Their molecular masses were deduced in tetrahydrofuran ($K = 38.9 \times 10^3 \text{ mL/g}$, $\alpha = 0.70$) through Mark Houwink equation using Oswald's capillary viscometer⁹ and was found in the range of $M_n = 1.51-3.68 \times 10^4$.

(b) Polymethyl methacrylate [PMMA]

PMMA solutions in benzene were prepared at a concentration of 10, 20 and 30% (VW). 50 ml of each solutions were separately polymerized in presence of benzoyl peroxide (0.1 M: 10 ml) for one hour at $100 \pm 1^\circ\text{C}$. PMMA of varying molecular masses were separately isolated from each of the solutions, by evaporating the solvent. Viscosity average molecular masses of each of PMMA specimens was separated investigated in benzene ($K = 5.5 \times 10^{-3} \text{ mL/g}$, $\alpha = 0.76$)⁹ and were found in the range of $1.55 - 3.52 \times 10^4$.

(c) Thermal Analysis

A simultaneous thermo gravimetric (TG) differential thermo-gravimetric (DTG) Differential thermal analysis (DTA) of each of the polymeric samples has been performed over NETZSCH-Geratebau GmbH Thermal Analyzer model STA 409C. The sample size was ranged from 13 to 19.8 mg. The samples were allowed to decomposed in nitrogen at heating rate of $25^\circ\text{C}/10.0 \text{ (K/min)}$ 1400°C using alumina as a reference. All such thermo analytical procedures were executed at RSIC, Indian Institute of Technology (IIT), Madras.

Non-isothermal kinetics of solid-state decompositions of samples has been calculated from TG data to ascertain the rate controlling process according to the procedure reported by Sestak and Berggen and Satava⁶. In this procedure evaluations were made from different integral forms of kinetic expressions and the declaring rate equation based on diffusion was studied in terms of parabolic law satisfied to one dimensional transport (D1), two dimensional diffusion (D2), three dimensional diffusion according to Jander equation (D3) and three dimensional diffusion according to Ginstling-Brounshtein equation (D4) and the rate laws at one dimensional, zero order (R_1), two dimensional; cylindrical symmetry (R_2) and three dimensional spherical symmetry (R_3) [Table I].

(d) Kinetics and Thermodynamics

Thermogravimetric (TG) data of each of the polymers were evaluated for their weight loss (%) with reference to their temperature, decomposition stages involved and kinetic parameters with reference to their order (n) and energy of activation of thermal degradation (E), Entropy change (As) through a series of calculation procedures such as Horowitz-Metzger method⁶ and Coate-Redfern method⁷. Thermal properties [Table II] and thermodynamic data of the solid-state decompositions [Table III] of polymers are summerized.

RESULTS AND DISCUSSION

Thermal properties of [PC] and [PMMA] at different molecular masses were deduced through simultaneous TG-DTA-DTG in nitrogen. In all the cases [PC] showed two-step decompositions with a pair of sharp endotherms at DTA-TG-DTA. At all the molecular masses, both type of polymers showed increasing values for their respective crystallization, oxidation, maximum decomposition and melting temperatures with molecular masses. [PC] at molecular mass 1.51×10^4 indicating two sharp decomposition with glass transition T_g 239.0 and indicated profiles for DTA at 453.8°C and 716.6°C with maximum decomposition at 600°C . At molecular mass 2.65×10^4 initially [PC] rendered weight loss at lower temperature and was rapidly increased at 400°C and with maximum decomposition at 800°C . For the same polymer, two sharp decomposition profiles were molecular mass 3.68×10^4 shows two sharp decomposition

Table-1: Non-isothermal integral forms of kinetic expressions for heterogeneous solid state reactions

D1	$\alpha^2 = Kt$	1- dimensional diffusion (Parabolic law)
D2	$(1-\alpha)[-1n(1-\alpha)] + \alpha = kt$	2- dimensional diffusion, cylinderal symmetry
D3	$[1-(1-\alpha)^{1/3}] = Kt$	3-dimensional diffusion, spherical symmetry (Jander equation)
D4	$(1-2-\alpha/3-(1/\alpha)^{2/3}) = kt$	3-dimensional diffusion, spherical symmetry (Giastiling Brownshtein equation)
F1	$-1n(1-\alpha) = kt$	Random nucleation; One nucleus on each particle (Mampel equation)
A2	$[-1n(1-\alpha)^{1/2}] = kt$	Random nucleation (Avrami equation I)
A3	$[-1n(1-\alpha)^{1/3}] = kt$	Random nucleation (Avrami equation II)
R2	$1-(1-\alpha)^{1/2} = kt$	Phase boundary reaction; cylinderal symmetry
R3	$1-(1-\alpha)^{1/3} = kt$	Phase boundary reaction; spherical symmetry

Table-2: Thermal properties of polybisphenol-A carbonate and polymethyl methacrylate [PMM A] at different molecular masses

Polymer	$M_n \times 10^4$	TG [Weight residue (%) at Temperature ("C)]			T_g	T_c	T_{ox}	T_d	T_m	
		20	40	60						
[PC]	1.51	632.0	466.6	455.5	433.3	239.0	388.8	570.9	695.0	524.8
	2.65	661.1	472.2	461.1	433.3	403.9	452.9	581.5	705.3	531.4
	3.68	666.6	483.3	466.6	450.0	503.3	535.9	573.9	654.5	654.5
[PMMA]	1.55	288.8	327.7	355.5	372.2	289.7	387.0	438.2	683.0	464.6
	2.50	305.5	333.3	355.5	372.2	341.5	386.5	499.8	639.2	476.6
	3.52	383.3	366.6	338.9	305.5	349.5	377.8	506.0	655.2	462.7
T_g	Glass transition temperature empirically according to the relation $T_g = 2/3 T_m^8$									
T_c	Crystallization temperature			T_{ox}	Oxidation temperature					
T_d	Decomposition temperature			T_m	Melting points					

profiles at 471.1 °C and 588.4 °C at DTA with T_g at 529.3 °C. Thermal decomposition of [PMMA] was progressed at the higher rates than [PC] with lower thermal stability, (Table 2).

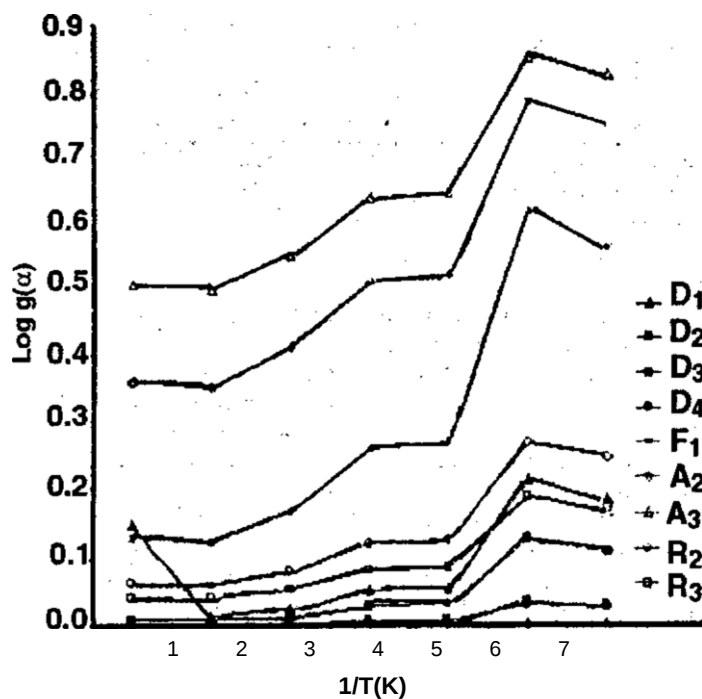
Kinetic and thermodynamic parameters of [PC] during thermal decomposition process were claculated for zero and first order kinetics in terms of energy of activation, frequency factors, and entropy changes according to Horwitz metzer (HM)⁷ and coats redfern (CR)⁸ methods. At molecular mass range $1.51 \times 2.65 \times 10^4$ the values calculated for energy of activation were observed at lower values for CR method than HM which was calculated in the reversed order at molecular mass 3.68×10^4 . At molecular mass 2.65×10^4 HM method showed negative values for entropy change than

other methods (Table 3).

Mechanism of thermal decomposition was studied under non-isothermal conditions at definite intervals of time (Table 1)⁶. This has been done by solving the thermo gram for a series of diffusion and phase boundary / and other related equations. A comparative account has beed made between [PMMA] and [PC] samples towards their thermal decomposition reaction, and related non-isothermal relative parameters studies conducted and indicated that the calculation involved, was found to be more suitable for [PC] than [PMMA]. These observations concluded that PBA like material can be more suitable studied in terms of their non-isothermal and other kinetic parameters than other thermoplastics like PMMA.

Table-3: Kinetic and thermodynamic parameters for [PC]

M_n	ΔT	DTA	Method	E	Z	ΔS
1.51×10^4	755-1055K	723K				
	n = 1		CR	2.768×10^4	1.547×10^5	1.486×10^5
			HM	3.28×10^5	1.447	2.795×10^5
	n = 0		CR	4.153×10^4	1.647×10^5	2.25×10^5
			HM	9.958×10^5	2.94	7.77×10^5
2.65×10^4	773-1123 K	734.1 K				
	n=1		CR	3.04×10^5	1.086×10^5	1.51×10^5
			HM	4.26×10^5	1.426	-36.029
	n = 0		CR	4.965×10^4	1.111×10^5	2.49×10^5
			HM	5.846×10^5	2.151	-47.559
3.68×10^4	773-1123K	734.1 K				
	n=1		CR	4.75×10^4	3.077×10^4	1.767×10^4
			HM	1.51×10^6	3.80	-11.45
	n=0		CR	7.134×10^4	4.134×10^4	2.865×10^4
			HM	2.07×10^6	4.97	15.18

 ΔT = Temperature RangeZ = Frequency Factor (Min⁻¹)E = Energy Of Activation For Decomposition (Kg mol⁻¹) ΔS = Entropy Change**Figure-1. Mechanism of thermal decomposition of PC at M_n 1.51×10^4**

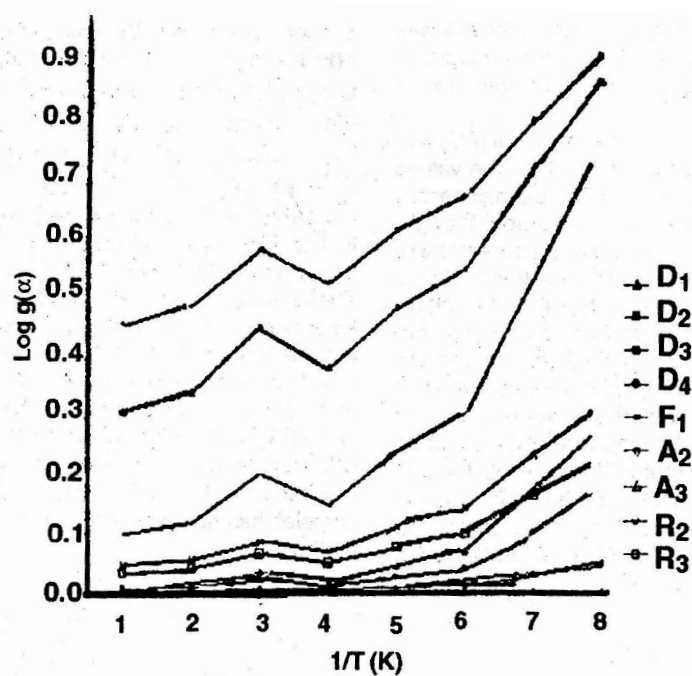


Figure-2. Mechanism of thermal decomposition of PC at $Mn\ 2.65 \times 10^4$

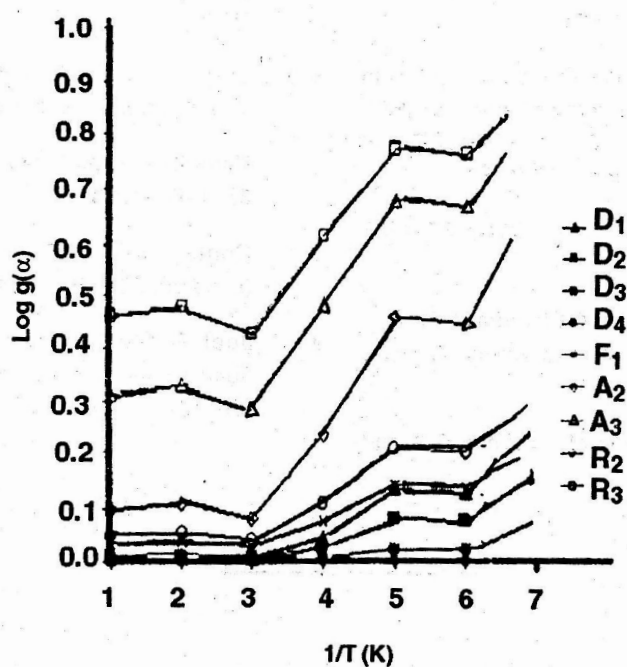


Figure-3. Mechanism of thermal decomposition of PC at $Mn\ 3.68 \times 10^4$

Thermodynamics of decomposition process was studied by the solution of resective thermograms using Horowitz-Metzger (HM)⁷ and Coats-redfern methods equation.

Various patterns of Mechanism of [PC] with $M_n = 1.51 \times 10^4$ was studied by plotting the values of $\log g(\alpha)$ against $T^{-1} (K) \times 10^3$ it has been observed that except D1 mechanism that is parabolic law for one dimensional transport all patterns were progressed almost according to same trends. These observations indicate that at higher temperature this compound indicated almost same behaviour towards various $\log g(\alpha)$ functions. Among all such mechanism, the most linear plot were observed at A_2 and A_3 indicating that mechanism of decomposition of this compound was satisfied according to Avrami-Erofeev Nuclei growth through either of two dimensional (A_2) or three dimensional (A_3) rate determinational with spherical symmetry. [PC] sample with $M_n = 2.65 \times 10^4$ indicated a

sudden increase in the value of $\log g(\alpha)$ at $T = 3 \times 10^{-3}$ K. Among all such variations the most linear plot of assign as Avrami-Erofeev three-dimensional nuclear growth A_3 [figure I].

Variation of $\log g(\alpha)$ against $T^{-1} (K)$ for [PC] sample with molecular mass 2.65×10^4 indicated a sudden increase in $\log(\alpha)$ at 3×10^{-3} K. For this case most linear plot was assigned to be according to Avrami-Erofeev nuclei growth A_3 . These observations indicated that non-isothermal kinetics of solid state decomposition of [PC] almost satisfied Avrami-Erofeev nuclei growth mechanism with three dimensional growth [Figure II] and the extend to three dimensional (spherical symmetry) R_3 for [PC] with molecular weight 3.68×10^4 [Figure III]. Due to the large rate of decompositions, mechanism of thermal of decomposition of [PMMA] samples has not been evaluated according to these methods.

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