

Synthesis and thermal characterization of polymethyl methacrylate

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ABSTRACT

PMMA with molecular mass (PMMA Mw: 1.2×10^5) was synthesized through AIBN initiated free radical polymerization methyl methacrylate at $100 \pm 1^\circ\text{C}$. The synthesized polymer was characterized through GPC coupled with RI detector in presence of THF as mobile phase at 1.0 mL/min and simultaneous TG-DTA-DTG in nitrogen. TG data were used to investigate the non-isothermal kinetics of solid-state decomposition of PMMA according to the method of Sestak, Berggren and Satava and thermodynamics through Horowitz-Metzger and coats-Redfern methods.

Key words: Polymethyl methacrylate, polymerization.

INTRODUCTION

The studies on kinetics and thermodynamics of solid state decomposition of polymers play integral role in their quality control and assessment¹⁻². Among a variety of thermoanalytical methods, the application of thermo gravimetric-differential thermal analysis and differential scanning calorimetry has recently 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, kinetics 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) 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, The technique 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 materials^{5,6}.

MATERIAL AND METHODS

PMMA with molecular mass (PMMA Mw: 1.2×10^5) was synthesized through AIBN initiated free radical polymerization of freshly distilled monomer at $100 \pm 1^\circ\text{C}$. The molecular mass of

synthesized PMMA was deduced over Varian Pro Star 230 HPLC/GPC system coupled with RI detector. THF was used as mobile phase at the flow rate of 1.0 mL/min.

Thermal characterization of PMMA was made through simultaneous TG-DTA-DTG over NETZSCH-Geratebau GmbH Thermal Analyzer model Perkin Elmer (Pyris Diamond) 1000°C. The sample size was 10.91 mg. The samples were allowed to decomposed in nitrogen at heating rate of 22°C/5.0 (Cel/min)/1000°C using alumina as a reference Table 1. Thermal data were used for calculations of thermodynamic parameters through Horowitz-Metzger (HM) ⁷ and coats-Redfern (CR) methods Table 2 ⁸. Non-isothermal kinetics of solid-state decomposition of samples has been calculated from TG data to ascertain the rate controlling process according to the procedure reported by

Sestak and Berggren and Satava⁹. 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

Table 1: Thermal Properties of PMMA

Thermal Properties	Temperature (°C)	Assignment
TG [Weight residue (%)/°C]	100	0.69
	200	4.83
	300	12.42
	400-500	41.40
DTA [ΔH (°C/ mJ/ mg)]	328	140
DTG [°C/ mg/ min]	143	0.2
	319	0.8

Table 2: Kinetic and thermodynamic data of solid state decomposition of PMMA

Reaction order (n)	Method	E (kg/mol.x 10 ³)	Z (min ⁻¹)	ΔS (JK ⁻¹ /min)
0	CR	54.64	2.54	-21.80
	HM	82.88	6.43	-12.56
1	CR	75.64	3.76	-18.75
	HM	99.78	7.67	-8.43
2	CR	87.89	5.38	-14.98
	HM	123.00	9.68	-4.97

Table 3: Mechanism of solid state decomposition verified for PMMA

D ₁	$\alpha^2 = kt$	1-dimensional diffusion (Parabolic law)
D ₂	$(1-\alpha)[- \ln(1-\alpha)] + \alpha = kt$	2-dimensional diffusion, cylindrical symmetry
D ₃	$[1-(1-\alpha)^{1/3}]^2 = kt$	3-dimensional diffusion, spherical symmetry (Jander equation)
D ₄	$(1-2\alpha/3-(1-\alpha)^{2/3}) = kt$	3-dimensional diffusion, spherical symmetry (Giastiling Brownshtein equation)
F ₁	$-\ln(1-\alpha) = kt$	Random nucleation; One nucleus on each particle (Mampel equation)
A ₂	$[-\ln(1-\alpha)]^{1/2} = kt$	Random nucleation (Avrami equation I)
A ₃	$[-\ln(1-\alpha)]^{1/3} = kt$	Random nucleation (Avrami equation II)
R ₂	$1-(1-\alpha)^{1/2} = kt$	Phase boundary reaction; cylindrical symmetry
R ₃	$1-(1-\alpha)^{1/3} = kt$	Phase boundary reaction; spherical symmetry

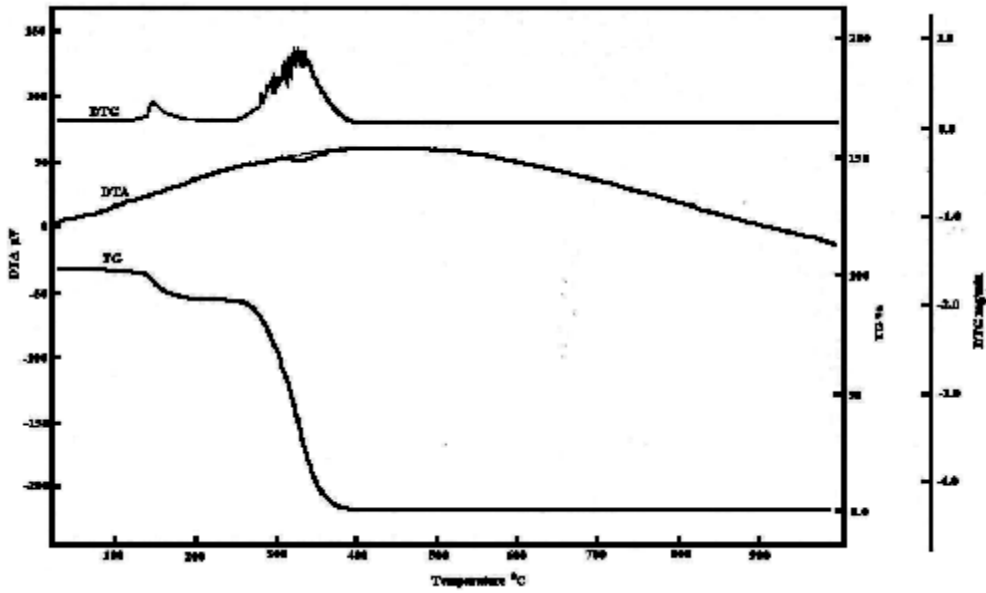


Fig. 1: TG-DTA-DTG Spectrum of PMMA

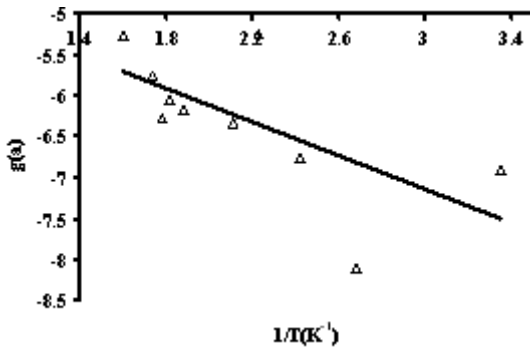


Fig. 2(a): CR plot of PMMA for n=0

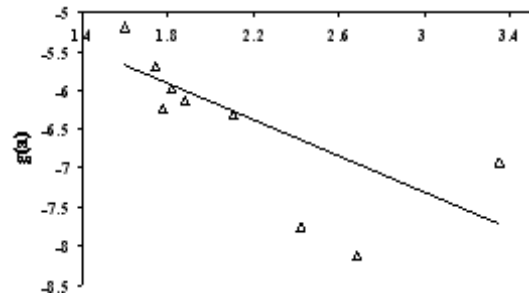


Fig. 2(b): CR plot of PMMA for n=1

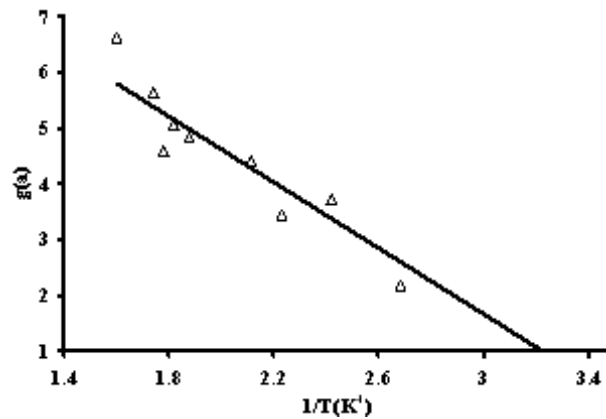


Fig. 2(c): CR plot of PMMA for n=2

of parabolic law satisfied to one dimensional transport (D_1), two dimensional diffusion (D_2), three dimensional diffusion according to Jander equation (D_3) and three dimensional diffusion according to Ginstling-Brounshtein equation (D_4) 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 1.

RESULTS AND DISCUSSION

Thermal decomposition of PMMA was investigated through simultaneous TG-DTA-DTG in nitrogen. PMMA showed two step decomposition Fig.1, with increasing order of weight loss at temperature ranging 100- 500°C. Within this temperature range, PMMA has shown maximum of 16% weight residue at 300°C. This was further supported with a DTA endotherm at 328°C associated with ΔH ($^{\circ}\text{C}/\text{mJ}/\text{mg}$) as 140. A three successive DTG profiles were shown by PMMA at

143 and 319°C respectively, corresponding to their respective rate of decompositions ranging 0.2-0.8 with maximum at 319°C Table 1.

The kinetic and thermodynamic data of solid state decomposition of PMMA deduced through CR [Figs. 2(a-c)] and HM [Figs. 3(a-c)] methods and are summarized in Table 2. It is evident that both of the methods have rendered a large discrepancy towards energy of activation, frequency factor and entropy change associated with solid state decomposition of PMMA at all the orders ranging 0.0-2.0. In general, HM method, has rendered higher values of the energy of activation and frequency factors over CR method. Both of the methods indicated negative entropy change indicating heat resistant characteristics of PMMA.

The mechanism of solid state decomposition of PMMA has been verified through investigation of various kinetic models. [Table III].

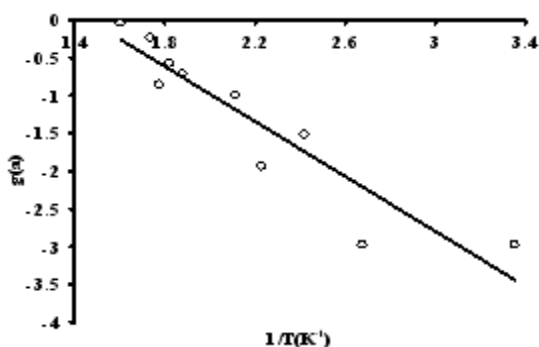


Fig. 3(a): HM plot of PMMA for $n=0$

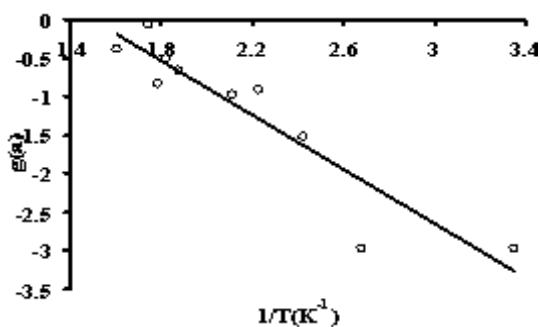


Fig. 3(b): HM plot of PMMA for $n=1$

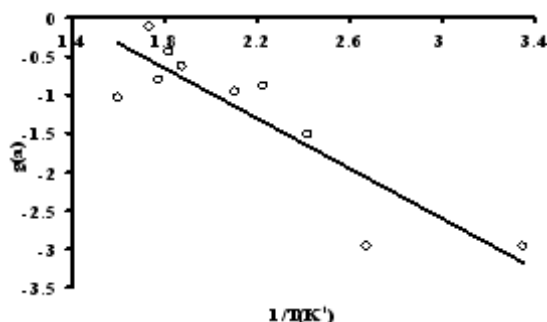


Fig. 3(c): HM plot of PMMA for $n=2$

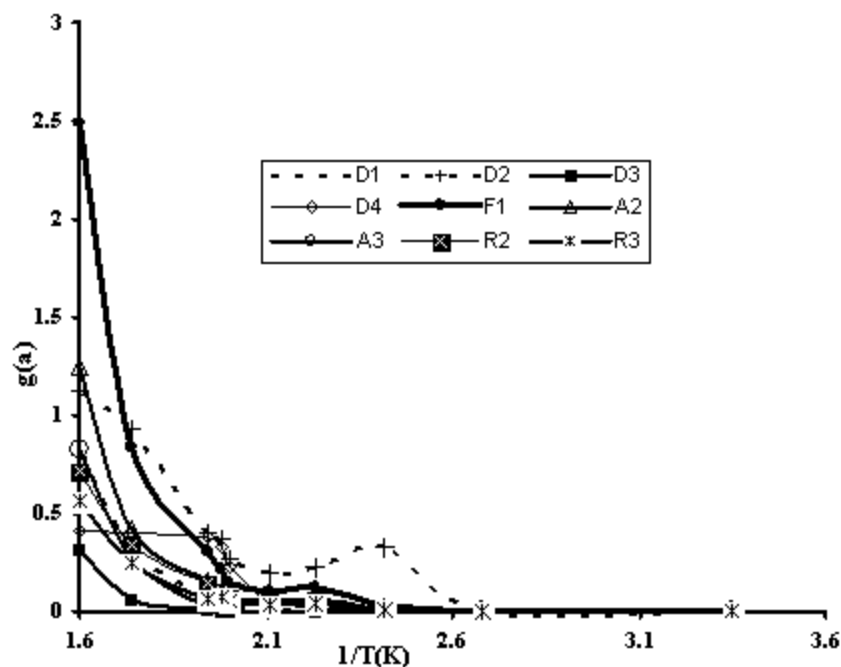


Fig. 4: Kinetic models of solid state decomposition of PMMA

This was studied in terms of variation $g(a)$ functions with $1/T$. The TG data indicated that the decomposition of PMMA was executed to higher $g(a)$ functions corresponding to various type of random nucleation models, followed by 1-dimensional diffusion, (parabolic law), phase boundary reaction(cylindrical symmetry)phase boundary reaction (spherical symmetry) and ,3-dimensional diffusion, spherical symmetry (Jander equation) respectively. The rules corresponding to 2-dimensional diffusion(cylindrical symmetry) and 3-dimensional diffusion, spherical symmetry (Giastiling Brownshtein equation) has not been followed by PMMA [Fig 4].

CONCLUSION

PMMA with molecular mass M_w : 1.2×10^5 was synthesized through free radical polymerization. The sample was characterized through HPLC/GPC and simultaneous TG-DTA-DTG in nitrogen. TG data were investigated for the evaluation of non isothermal kinetics and thermodynamics of the solid state decomposition of PMMA. The data indicated that the energy of activation, frequency factor and entropy change corresponding to decomposition of PMMA were higher for Horwetz Metzger over Coats & Redfern methods. In general, the decomposition of PMMA has satisfied possible kinetic models except to 2-dimensional diffusion(cylindrical symmetry) and 3-dimensional diffusion, spherical symmetry (Giastiling Brownshtein equation).

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